Real-time observation of ultrafast internal conversion in ethylbenzene by femtosecond time-resolved photoelectron imaging

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Abstract: The ultrafast dynamics of the second singlet electronically excited state (S2) in ethylbenzene has been studied by femtosecond time-resolved photoelectron imaging. The time evolution of the photoelectron signal can be well described by a biexponential decay: a rapid relaxation pathway with a time constant of 60 (± 9) fs and a longer-lived channel on a timescale of 2.58 (± 0.22) ps. The rapid relaxation is ascribed to the ultrafast internal conversion from the S2 state to the vibrationally hot S1 state. This internal conversion process has been observed in real time. The slow photoelectron signal reflects the depopulation of secondarily populated high vibronic S1 state.

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1. 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. With the advent of ultrafast laser pulses, electronic relaxation processes can be observed in real time. The initiation and subsequent control or the exploration of chemical transformations in real time has been the aim of femtochemistry [2,3].

As a prototypical aromatic molecule exhibiting the essential structure of numerous biologically important compounds in nature, benzene’s chemical properties and structure posted a challenge to scientists for decades [4–6]. Isolated benzene molecules have been the subject of a great number of investigations by femtosecond time-resolved techniques [7–10]. Recently, Suzuki et al. studied the ultrafast IC of benzene from the S2 state, at which a time constant of 48 fs was determined from the decay profile of the total photoelectron intensity [11]. More recently, Qiu et al. studied the S2 state of benzene [12]. A longer-lived channel with 1.06 ps was observed and attributed to ISC from S2 state to T1 state.

Despite their importance in atmospheric and petrol chemical processes, time resolved studies of mono-substituted alkyl-benzenes, e.g. ethylbenzene (EB), are rare. The reduced symmetry of the benzene derivatives results in a nondegeneracy of electronic states, which entails a higher density of vibrational levels and an increase of otherwise symmetry-forbidden interactions [13]. EB can have at most Cs symmetry [14]. Hence, higher rates for electronically nonadiabatic transitions are expected. Huang et al. have studied the photodissociation of jet-cooled EB in the S1 and S2 state using a vacuum ultraviolet (VUV) photoionization multi-mass ion imaging technique [15,16]. They conclude that EB in the S2 state, excited by a 193 nm photon reconverts to the electronic ground state (S0) prior to dissociation. A strong coupling between the S2 and S0 state has been found and an additional intermediate state that is involved in the relaxation mechanism has been suggested.

In this paper, we study the S2 state of EB by femtosecond time-resolved photoelectron imaging. The measured time-resolved photoelectron kinetic energy (PKE) and photoelectron angular distributions (PADs) are analyzed and discussed. The experimental data clearly confirm a fast relaxation time after a two-photon absorption (2 x 400 nm) that could be assigned to the S2→S1, IC.
2. Experiment

The experiments were performed with a home-built doubled-sided velocity map imaging setup. Figure 1 shows a sketch of the experimental apparatus. The apparatus consists of two chambers, a source chamber and a detection chamber with two velocity map imaging spectrometer on electron and ion sides. The detection chamber consists of two symmetrical, collinear 50 cm long time-of-flight (TOF) mass spectrometers sharing the same interaction region. Each spectrometer comprises a 7 element electrostatic optic providing a coincident longitudinal (Wiley-McLaren) and lateral VMI (Velocity Map Image) [17] 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). Though the setup allows simultaneous electron- and ion-VMI the mass spectra were acquired in this experiment integrally by directly recording the MCP signals of the ion side. The molecular beam was produced by seeding EB (Alfa Aesar, 99% purity without further purification) 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 intersects with a linearly polarized femtosecond laser pulse in the common interaction region of the two independent TOF mass spectrometers.

Fig. 1. Experimental apparatus. LB and MB stand for laser beam and molecular beam respectively.

The femtosecond laser system (Clark-MXR CPA-1000) has been described in detail previously [18]. The near infrared output of the laser system (at ~800 nm) was split into two beams with equal intensity. One part was frequency doubled to ~400 nm in a beta barium borate crystal (BBO type I) and used as ‘pump’ beam, while the other part passed an optical delay stage (PI, M-403.4PD) and acts as ‘probe’. Utilizing half wave plates and thin film polarizers, both, pump and probe pulses were vertically polarized, merged with a dichroic mirror. Before focusing with a f = 400 mm into the interaction the laser beam diameters were reduced to 3 mm with a telescope. The divergency of the beam is kept as small as possible. Typical energies for pump and probe pulses are ~2 uJ and ~17 uJ, respectively.

3. Results

The energy of the S2 state of EB is estimated to be at Tc = 5.90 eV [15,16]. Thus, a two-photon absorption process at 400 nm (3.10 eV) can be used to populate the S2 state of EB with excess vibrational energy of 0.3 eV. The polarization of pump and probe pulses are perpendicular to the direction of the molecular beam. The EB time of flight mass spectra displays two major peaks, with an intensity ratio of 16:1, corresponding to the C6H5C2H5+ parent and the C6H5CH2+ fragment ion, respectively. Within the sensitivity of the detector, the
other expected fragments CH$_3^+$ and H$^+$ have not been observed. Most of the C$_6$H$_5$CH$_2^+$ ions arise from the dissociation of the C$_6$H$_5$C$_2$H$_5^+$ parent and hence overall contributions to the photoelectron signal from the C$_6$H$_5$CH$_2^+$ ions are assumed to be negligible.

![Graph showing the time-resolved total photoelectron intensity as a function of delay time between the pump pulse at 400 nm and the probe pulse at 800 nm. The circles are the experimental results, and solid lines are obtained by a bi-exponential least-squares fit to the spectrum.]

Fig. 2. Time-resolved total photoelectron intensity as a function of delay time between the pump pulse at 400 nm and the probe pulse at 800 nm. The circles are the experimental results, and solid lines are obtained by a bi-exponential least-squares fit to the spectrum.

Figure 2 shows the time-resolved total photoelectron intensity upon two-photon excitation of the S$_2$ state as a function of the pump-probe time delay. The temporal behavior can be fitted to a biexponential decay, convoluted with a 100 fs wide Gaussian instrument response function. Two distinct lifetimes of 60 (± 9) fs (Stdv) and 2.58 (± 0.22) ps have been determined from the least square fit. A more detailed insight of the ultrafast relaxation dynamics from this state can be obtained by time-resolved photoelectron imaging.

Figure 3 shows time-resolved photoelectron images and corresponding 3D photoelectron scattering distributions inverted by using Basex [19]. Adopting Koopman’s model, ionization maps the state distribution from where ionization occurs to approximately the same distribution in the ionized state manifold [20]. Accordingly, the observed PKE is a function of the difference between the excitation energy in the related intermediate states and the energy of the finally reached state. Under this assumption, time series of photoelectron imaging allow for simultaneous monitoring of the electronic and vibrational excited-state dynamics [21].
The electron image displays photoelectrons in several bands with different kinetic energy. A typical PKE distribution inferred from the image in Fig. 3 at t = 40 fs is shown in Fig. 4. The red arrow at 0.53 eV indicates the maximum possible electron energy after two-photon ionization from S₂ using an 800 nm probe beam, according to the EB ionization energy of 8.77 eV reported in [22]. The ethyl substituent lifts the degeneracy of benzene orbital upon ionization, which leads to an electronic splitting of cationic states. The energy difference between the D₁ and D₀ levels has been determined to 0.53 eV [23]. However, a two-photon ionization with 800 nm pulses to D₁ is not possible. The two strongest well-resolved bands centered at 0.13 eV and 0.36 eV, named I and II below are thus due to two-photon ionization from the vibrationally excited S₂ state. The energy difference of Δ = 0.36 - 0.13 = 0.23 eV between bands I and II compares well to the 0.19 eV vibrational splitting in the EB cation observed by Klasinc, et al [23] with He I ultraviolet photoelectron spectroscopy. The faint features beyond 0.53 eV PKE in Fig. 4 presumably result from three-probe-photon ionization.

An energy excitation scheme including the ground, excited and ionic states of EB is sketched in Fig. 5. EB can have at most Cₛ symmetry. Under the assumption of Cₛ symmetry, the electronic states of EB are either A' or A''. Out of the 48 vibrational modes, 27 are of A' and 21 are related to A'' symmetry [14]. Within the bandwidth of our excitation pulses, there exist single- and multi-photon transitions between the all considered electronic singlet (S₁,2) and ionic (D₁,2) states. For the interpretation of our experimental findings, we neglect in a first approach differences in excitation or ionization efficiencies. According to the scheme of Fig. 5, bands I and II derive from the ionization of the initially excited state (S₂ state) to ion D₀ state. Upon two-photon excitation at 400 nm, the vibrational energy in S₂ state amounts to about Eᵥ = 0.30 eV. With the assumption that the vibrational energy Eᵥ persist in the ion state after ionization, a PKE band with kinetic energies in a range of ∆' = 2hν_pump + 2hν_probe - Eᵥ - D₀
$0.23 \text{ eV}$ is thus expected. The value of $D_0 = 8.77 \text{ eV}$ has been adopted from [22]. The discrepancy of 0.1 eV is explicable by uncertainties in determination of the $S_2$ state energies [15,16].

![Diagram](image1)

Fig. 4. PKE distributions extracted from the image at $t = 40 \text{ fs}$. I and II are the names for the peaks assigned for discussion. The red arrow (0.53 eV) indicates the maximum electron energy by two-photon absorption of probe beam at 800 nm after two-photon excitation of the $S_2$ state at 400 nm.

![Diagram](image2)

Fig. 5. Energy excitation scheme of the ground, excited and ionic states of EB. The pump beam (400 nm) prepares the $S_2$ state. Due to ultrafast IC, this state converts to the lower-lying state $S_1$ with increased vibrational energy. The transitions corresponding to PKE bands are named arbitrarily I-IV.

By monitoring the PKE distribution as a function of pump-probe delay time we observed a rapid decay of bands I and II within the first 320 fs (Fig. 6). The findings are rationalized by a quick depopulation of the initially excited $S_2$ state. The fitted time constant of $\tau_1 = 60 \text{ fs}$, as inferred in Fig. 2, is close to the lifetime of the $S_2$ state for EB’s analogues, e.g. benzene with 40-50 fs [7,11,12], toluene with ~65 fs [11,13] and o-xylene with 60 fs [24]. Moreover, it seems that the weak features above 0.53 eV follow the same trend as the strong bands I and II (Fig. 6). From this behavior we infer that three-photon ionization processes from $S_2$ are the dominant contributions to the PKE at energies above 0.53 eV. In any case, some PKE contributions above 0.53 eV persist for longer delays.
Fig. 6. Photoelectron kinetic energy distributions extracted from the images of Fig. 3.

Considering the short lifetime of S2 the ionization features associated with an intermediate S2 state population are expected to vanish at pump-probe delays above a few hundreds femtoseconds. The temporal profiles of the two dominant bands I and II are fitted on the specific kinetic energy windows. The decay profile of band I fits a sub-100 time scale corresponding to $\tau_1$ inferred from fitting the total photoelectron signal shown in Fig. 2. The band II has a similar sub-100 component but comprises a small tail with longer time scale. As shown in Fig. 6, this small tail derives from the contribution of band III which overlaps with band II. At longer time delays (after 320 fs) the two weak and broad bands III and IV centered at 0.40 and 0.95 eV, become visible. Their decay is much slower compared to bands I and II and it is reasonable to relate these two weak bands to the ‘slower’ component with $\tau_2 = 2.58$ ps as shown in Fig. 2.

Bands III and IV arise from a three probe-photon ionization starting from a secondarily populated ensemble of highly excited vibrations in S1 (Fig. 5). The origin of the S1 state has been measured to be at 4.66 eV by REMPI [22]. After IC from the S2 state to the S1 state, an excess energy of 1.54 eV is available as vibrational energy. Therefore, it is most unlikely to probe the secondary population of the S1 state by two-photon absorption of the probe beam due to the extremely low Franck-Condon factors and ionization by at least three probe photons prevails. To disentangle two- and three-photon contributions, power-dependent measurements have been performed (Fig. 7). To compare the power-dependence of bands III + IV (added signals) and bands I + II, the maximum of both signals were normalized to 1. The intensity of the slow contribution from bands III and IV drops more with decreasing probe power than the fast contribution from bands I and III indicating the predominance of more than a two-photon ionization processes. The difference of 0.55 eV between the peaks of band III and IV matches the energy difference between the D0 and D1 state of 0.53 eV as determined in [23]. Compared to bands I and II, the bands III and IV are energetically broadened, most probably caused by fast intramolecular vibrational redistribution (IVR) processes of highly excited vibrations within the S1 potential surface. Unfortunately, the intensity of bands III and IV is too weak to resolve distinct vibrational states.
In addition to intensity dependencies and energy consideration, temporally resolved photoelectron angular distributions (PADs) are a powerful tool for real-time observation of dynamics, especially in the analysis of overlapping bands [25]. It can be inferred from Fig. 5 that band III attributed to ionization from the S1 state overlaps band II originating from the S2 state. For a more detailed analysis the time evolution of PADs with distributions of PKE in the region from 0.2 to 0.44 eV where the two bands overlap is explored. The laboratory frame PADs resulting from ionization with linear and parallel polarized pump and probe laser beams, can be described [26] by:

\[
I(\theta; t) = \sigma(t)[1 + \beta_2(t)P_2(\cos \theta) + \beta_4(t)P_4(\cos \theta) + \beta_6(t)P_6(\cos \theta) + \beta_8(t)P_8(\cos \theta)],
\]

where \(\sigma(t)\) is the integral cross section, \(\beta_n(t)\) are the anisotropy parameters, \(P_n(\cos \theta)\) are Legendre polynomials, and \(\theta\) the angle between the laser polarization direction and the direction of the ejected electron. The anisotropy coefficients from 0.2 to 0.44 eV PKE were obtained by using the recently developed lin-Basex algorithm [27]. Considering the statistical error according to lin-Basex evaluation, \(\beta_8\) can be neglected with values close to 0. The remaining anisotropy coefficients derived are shown in Table 1.

### Table 1. The anisotropy coefficients of PKE of the region from 0.2 to 0.44 eV of the second band overlapping the third one at different time delay.

| Delay (fs) | \(\beta_2\) | \(\beta_4\) | \(\beta_6\) |
|-----------|-------------|-------------|-------------|
| 40 fs     | 1.21        | 0.66        | 0.62        |
| 80 fs     | 1.22        | 0.63        | 0.54        |
| 120 fs    | 1.20        | 0.60        | 0.50        |
| 160 fs    | 1.14        | 0.58        | 0.54        |
| 200 fs    | 1.10        | 0.48        | 0.47        |
| 240 fs    | 0.95        | 0.40        | 0.37        |
| 280 fs    | 0.81        | 0.32        | 0.24        |
| 320 fs    | 0.73        | 0.31        | 0.35        |

A full discussion of the observed anisotropies will undoubtedly require high-level theoretical studies in the future. Nevertheless, it is instructive to look at the time-evolution on specific energy region to gain qualitative insights into the main findings. The anisotropy coefficients remain almost constant at small pump-probe delays (40-160 fs) and decrease gradually at longer delays (200-320 fs). This observation can be interpreted as follows:
Initially, band II from the S$_2$ state is dominant, while band III from S$_1$ state is too weak to play a role in the PADs of this region. However, for longer delays (200-320 fs), the population of the S$_2$ state vanishes while band III related to the S$_1$ intermediate state with longer lifetime becomes the exclusive contributor to the PKE in range 0.2-0.44 eV. Due to a ‘coherent’ multiphoton ionization from S$_2$ within the first 100 fs the induced anisotropy is maintained, whereas it diminishes after relaxation to the manifold of highly excited ro-vibrationally states in S$_1$. In this respect the temporal evolution of the induced anisotropy compares to the ultrafast IC from the S$_2$ to S$_1$ state and supports the interpretation inferred from time-resolved PKE distributions above.

4. Conclusion

We have used femtosecond time-resolved pump–probe photoelectron imaging to observe ultrafast processes arising from the optically excited S$_2$ state of EB in real time. The lifetime of the S$_2$ state is determined to be 60 fs according to the decay of the measured photoelectron intensities. A fast conversion from the S$_2$ to S$_1$ state is evidenced by time-resolved PKE and PADs. The slower decay time of 2.58 ps has been related to relaxation dynamics of the vibrationally excited states within or from S$_1$.

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