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Ultrafast Imaging of Electronic Relaxation in Ortho-xylene: New Features from Fragmentation-Ion Spectroscopy

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As a continuous work of tracking electronic relaxation of the S₄ state in o-xylene by photoelectron imaging [Y. Liu et al., Phys. Chem. Chem. Phys. 15 (2013) 18101], we report another contribution from the view of fragmentation-ion spectroscopy. Three components with time constants of τ₁ ≃ 60 fs, τ₂ = 55(±20) fs and τ₃ = 6.39(±0.25) ps are observed for the only fragment-ion C₆H₄CH₃⁺. The velocity map image of the fragment-ion against the delay time are analyzed and discussed. New features for competing ultrafast internal conversion and intersystem crossing are obtained.

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After light absorption, a molecule can undergo radiationless processes, and photophysics is one of the important general types.[1] The photophysical processes involve internal conversion (IC) due to electronic nonadiabaticity and intersystem crossing (ISC) induced by spin-orbit coupling.[2][3] 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 femtosecond ultrashort pulse, tracking[4] and controlling[5] the ultrafast photophysical processes become realizable.

Due to the fact that ISC requires a change in the spin of an electron, it is usually a slower process than IC.[6] However, extensive reports show that ultrafast competing ISC exists in a number of systems.[7][8] Recently, Richter et al. reported femtosecond ISC in cytosine.[9] Martinez-Fernandez et al. simulated the deactivation dynamics of photo-excited 6-thioguanine using a direct surface hopping dynamics approach.[10] Their simulations show that 6-thioguanine is another example of a system showing ultrafast ISC that can compete with IC in the same time scale. Both the spin-orbit and the dynamic couplings are important to describe realistically the excited state dynamics of 6-thioguanine. A similar phenomenon has also been evidenced in the S₁ state of benzene.[11] The experimental results show that the ultrafast decay of the S₁ state is due to competing IC and ISC processes and both processes occur on a femtosecond timescale. Spin-orbit coupling is highly effective when the involved states are nearly isoenergetic.

In the previous work,[12] we reported an ultrafast competing ISC process observed in o-xylene, one of substituted benzenes, via photoelectron imaging. To gain more convincing evidence and features for such a challenging interpretation, we investigate its relaxation dynamics from the view of fragmentation spectroscopy as a complementary understanding.

The experiments were performed with a homemade double-sided velocity map imaging spectrometer. Each spectrometer comprises a 7-element electrostatic optic providing a coincident longitudinal (Wiley-McLaren) and lateral velocity map image (VMI)[13] focus at the image plane. The details were introduced in our recent work.[14] All the experimental conditions including the femtosecond laser system[14] and molecular beam are the same as in the previous report.[12] Here we just introduce the data acquisition technique for ion signals and ion images. The time-of-flight (TOF) mass spectra of the ions are obtained by directly recording the MCP signals of the ion side. Transient signals for all ions are measured by a Labview program integrating signal intensity of the different ions of the TOF mass spectra against the delay time simultaneously. To track the ion image of the certain fragment ion, a high voltage pulse with 100 ns duration forming a ‘mass gate’ is applied to the MCP to separate it from the parent ions or other fragment ions with different masses. The images were accumulated over 60000 shots or more. The backgrounds were removed by subtracting the images collected under the negative delay. The velocity ion imaging spectrometer was calibrated by means of an experiment on CH₃I photolysis and photoinization.

A two-photon absorption process with 3.10 eV photons (400 nm) is used to populate the S₂ state of o-xylene with an excess ro-vibrational energy of...
The fundamental beam at 800 nm for multiphoton ionization is used to act as the probe beam. The power of the pump and the probe beams was optimized to minimize the single color ionization process from the pump or probe pulse. The time-resolved TOF mass spectra upon pump and probe ionization starting from the S₂ and possibly secondary populated states are acquired at different delays between the pump and probe. A typical mass spectrum at delay of 50 fs is displayed in Fig. 1.

Three peaks are observed, corresponding to one fragment ion of C₆H₄CH⁺ at 91 amu and two parent ions of C₆H₄(CH₃)⁺ at 106 amu and 107 amu, respectively. The parent ion at 107 amu is due to the ¹³C isotopic component. This (¹³C¹²C₂H₁₀) takes up 6% of the whole parent ion signal. In the spectrum, only one fragment ion C₆H₄CH⁺ with CH₃ loss by fragmentation is observed. The signal intensity is low, and the ratio of the fragment ion to the parent ion is roughly 7%. The power of the probe beam in the measurements is too weak to probe the neutral fragment. The appearance of fragment ion C₆H₄CH⁺ is due to the dissociation of the parent ions after pump-probe ionization, which is displayed as the following processes:

\[
\text{C}_6\text{H}_4(\text{CH}_3)_2 + 2h\nu_{\text{pump}} + n h\nu_{\text{probe}} \rightarrow \text{C}_6\text{H}_4(\text{CH}_3)⁺ + \text{CH}_3. \tag{1}
\]

The transient signal of the fragment ions C₆H₄CH⁺ due to CH₃ loss and the parent ion C₆H₄(CH₃)⁺ are shown in Figs. 2(a) and 2(b), respectively. For the fragment ion C₆H₄CH⁺, three components with time constants of \(\tau_1 \approx 60\) fs, \(\tau_2 = 554(\pm 20)\) fs and \(\tau_3 = 6.99(\pm 0.25)\) ps are observed (Fig. 2(a)). However, only two corresponding components appear for the parent ion (Fig. 2(b)). The fitted time constants for these two components are \(\tau_1 \approx 60\) fs and \(\tau_3 = 6.89(\pm 0.35)\) ps, respectively. The differences on time constants \(\tau_1\) and \(\tau_3\) between the parent ion and the fragment ion are in the order of the fitting error. For clarity, transient signals of the fragment ion and parent ion are plotted together, as shown in Fig. 2(c). The fragment ions are from the dissociation of the parent ion. Thus they are expected to have a similar trend. Interestingly, it is found that the second component of \(\tau_2\) is missing for parent ions compared with the fragment ions.

![Fig. 1. TOF mass spectrum of pump-probe ionization acquired at the delay of 50 fs.](image)

![Fig. 2. Transient signals of (a) the fragment ion C₆H₄CH⁺, (b) the parent ion C₆H₄(CH₃)⁺; (c) comparison of the parent ion and the fragment ion, and (d) transient total electron signal for reference.](image)

For reference, transient signals for electrons are also shown in Fig. 2(d). The results for electrons are very similar to the fragment ions. Three fitted constants are \(\tau_1 \approx 60\) fs, \(\tau_2 = 540(\pm 17)\) fs and \(\tau_3 = 7.23(\pm 0.21)\) ps, respectively, which are very similar to the fragment ions with a small difference within the fitting error. Without secondary dissociation after ionization, the transient signals of the electrons
and the parent ions are expected to be exactly the same. Our measurements show that the fragment ions are the same as the electrons while one component is missing for the parent ions. The only reasonable explanation for the findings is that the parent ions from this component have dissociated during the flight before they are detected by the MCP. In the previous report,[12] we have given attributions to these three components by considering the energy of the ejected photoelectrons. The component with a time constant of $\tau_1 \approx 60 \text{fs}$ is from the ionization of the initial populated $S_2$ state. The second one with $\tau_2 = 540(\pm 17) \text{fs}$ and the third one with $\tau_3 = 7.23(\pm 0.21) \text{ps}$ are due to the ionization from the secondary populated $S_1$ state and $T_3$ state, respectively. Due to the energy conversion, the secondary populated $S_1$ state is highly vibrational excited with the vibrational excitation energy of $\sim 1.57 \text{eV}$.[10] With the assumption that the vibrational energy remains conserved in ionization, the parent ions from this second component are also expected to have high vibrational excitation in the order of $\sim 1.57 \text{eV}$. While for the first component from the $S_2$ state and the $T_3$ state, the vibrational energies are much lower.

The current transient ions’ measurement indicates that the second component ascribed from the vibrational hot $S_1$ state is missing in the parent ions displayed in Fig. 2(b). This is ‘missing’ due to the dissociation of the parent ions prior to being detected. Why do the parent ions from this channel dissociate? It is due to the high vibrational excitation. The flight time for the parent ions is determined to be 10.6 $\mu$s by the TOF mass spectrum. The time scale for vibrational dissociation is roughly from ns to $\mu$s. The dissociation due to the high vibrational could occur during the flight to the detector. Such phenomena from transient ions measurement strongly support the previous attribution from the view of the photoelectrons. (as shown in Fig. 3) can be inferred with the lin-Basex algorithm.[17] For the ease of comparison, all the kinetic energy distributions for different delay times are normalized to the strongest signal.

The transient kinetic energy distributions shown in Fig. 3 clearly visualize two trends as the delay time.

Firstly, the peak energy of the kinetic energy distribution decreases with the delay time. After absorption of the pump photons, two competing relaxation channels of the $S_2$ state were observed and assigned to the $S_1 \leftrightarrow S_2$ IC and $T_3 \leftrightarrow S_2$ ISC, respectively.[12] After radiationless electronic relaxation from the upper electronic $S_2$ state to lower $S_1$ and $T_3$ states, more vibrational energies are obtained. Under the assumption that vibrational energy is conserved after ionization by the probe beam, the cations prior to the dissociation are expected to have higher vibrational energy for the lower secondary populated states. Thus as the time delay, the kinetic energy decreases since more energies are distributed to the vibrational states.

Secondly, the energy distribution becomes narrower. Here the full width at half maximum decreases from $\sim 0.10 \text{eV}$ at 50 fs to $\sim 0.05 \text{eV}$ at 2.4 ps, gradually. The previous work[12] has shown that $S_1 \leftrightarrow S_2$ IC and $T_3 \leftrightarrow S_2$ ISC occur on tens of a femtosecond. At 50 fs, the initial $S_2$ state, the secondary populated $S_1$ state by IC and the secondary populated $T_3$ state by ISC are populated. With the time delay, the initial $S_2$ state depopulated completely with a lifetime of $\tau_1 \approx 60 \text{fs}$. The secondary populated $S_1$ and $T_3$ states also decay with lifetimes of $\sim 540 \text{fs}$ and $\sim 7.23 \text{ps}$, respectively. Thus with the time delay from 50 fs to 2.4 ps, the populated states become purer and purer, which can explain the phenomenon of the transient trend of the energy distribution becoming narrower.

Additional information is preserved from the angular distribution of the detected fragment ions. The angular distributions are derived from the images by fitting the lin-Basex result[17] to an expansion in Legendre polynomials. The laboratory frame PADS resulting from ionization with linear and parallel polarized pump and probe laser beams can be expressed by[18]

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

(3)

where $\sigma(t)$ is the integral scattering cross section, $\beta_n(t)$’s are the anisotropy parameters, $P_n(\cos \theta)$ are Legendre polynomials, and $\theta$ is the angle between the laser polarization direction and the direction of the ejected electron, $\beta_2$ is between $1 \leq \beta_2 \leq 2$ and for a single photon transition $\beta_{\perp} = 0$, $\beta_2 = 2$ relates to transitions with maximum intensity along the polarization axis while $\beta_2 = 1$ corresponds to perpendicular transitions, and $\beta_2 = 0$ reflects an isotropic electron distribution. Multiphoton transitions also su-

![Fig. 3. Time-resolved kinetic energy distributions for the fragmentation $C_6H_4CH_3^+$ at different delay times.](image-url)
cessively contribute to the higher order Legendre polynomials in Eq. (3). The fitted anisotropy coefficients are obtained. It is found that with the time delay, the main anisotropy coefficient $\beta_2$ decreases from 0.72 at 50 fs to 0.48 at 2.4 ps, gradually. Here the angular distribution and the fitting for two typical delay times are shown in Fig. 4. The anisotropy coefficients $\beta_2$, $\beta_4$ are also given and $\beta_6$ with higher order is so small that it can be neglected.

$$
\beta_2 = 0.72 \\
\beta_4 = 0.48 \\
\beta_2 = 0.59 \\
\beta_4 = 0.35
$$

Fig. 4. Time-resolved angular distributions for the fragmentation $C_6H_4CH_3^+$ at 50 fs and 550 fs. The dot is the raw data, and the line is the fit. The linear polarization of the ionization laser is aligned to be vertical in the plane of the figure.

Fragment ions dissociated from different cation states or with different middle resonance states are expected to show differences in the $\beta$ values. The investigation via time-resolved photoelectron image shows that the value of $\beta_2$ for $S_2$ state ionization is around 1.6–1.8, while for $S_1$ and $T_3$ states, the ionization $\beta_2$ is reduced to $\sim$0.8–1.0 and $\sim$0.1–0.3, respectively. The anisotropy is reduced upon crossing the potential energy surfaces. The similar trend for decreasing the anisotropy as the time delay for the fragment ions is also verified. Nevertheless, the anisotropy characteristics observed for the fragment ions offers new features for an interpretation based on photoelectron imaging.

In conclusion, we have investigated ultrafast relaxation dynamics of the $S_2$ state in o-xylene from the view of fragment ion spectroscopy. Three components with time constants of $\tau_1 \approx 60$ fs, $\tau_2 = 55(\pm 20)$ fs and $\tau_3 = 6.99(\pm 0.25)$ ps are observed and assigned. The energetic and angular analyses on the time-resolved velocity map image of the fragment ion verify three transient characters. First, the peak energy of the kinetic energy distribution decreases with the time delay. Secondly, the kinetic energy distribution becomes narrow with the relaxation process. Thirdly, the angular distributions of the ejected fragment-ions become more isotropic with the time delay. All these new features from the fragment-ions greatly support the previous interpretation based on the discussion of photoelectron images. The present study also verifies the importance for the measurements of fragment ion in tracking molecular ultrafast relaxation dynamics.

References

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