

Mapping the fragmentation of acetylene with femtosecond resolution pump probe at LCLS using 2, 3, and 4 particle coincidences

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Abstract: A three-layer delay line anode detector has been used in x-ray pump x-ray probe time-resolved measurement at LCLS. We used ~10 fs long pulses to initiate and probe ultrafast dynamics in the dication of acetylene. The dynamics are discerned from the temporal evolution of multi-particle coincidences.

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1. Introduction

The dissociative ionization of the acetylene dication has been the subject of this study in order to understand how the relaxation upon core ionization of a prototypical hydrocarbon occurs. There are four two-particle fragmentation pathways in the dication, two that involve deprotonation (P1) and (P2), a symmetric pathway that involves first breaking the bond between the two carbons (A), and a pathway through which acetylene first isomerizes to vinylidene (V). The (V) pathway is of particular interest because it involves proton migration.

The states associated with each of these pathways have been identified by T Osipov et. al. [2]. Synchrotron measurements put an upper bound of 60 fs on the time in which proton migration occurs [3]. However, the theoretically predicted ~50 kcal/mol isomerization barrier between acetylene and vinylidene in the ground state of the dication predicts a longer isomerization time [4,5].

To probe this process further, we have conducted a time-resolved x-ray pump x-ray probe experiment at LCLS. We can completely resolve the energy and momentum of the ion fragments generated, and can therefore identify different decay channels. By monitoring how the different decay channels evolve in time, we have the opportunity to better understand each of the pathways.

2. Experimental details

We performed an x-ray pump x-ray probe experiment on both acetylene and deuterated acetylene (C₂D₂) using 400eV (just above the K-edge of carbon) x-ray pulses with duration of ~10 fs. The pump pulse core-ionizes the sample. The Auger decay that follows impulsively excites states within the energy range that corresponds to the inverse of the core-hole lifetime (~6 fs in carbon) [2]. The ensuing dynamics are probed by the second x-ray pulse that, after subsequent core ionization and Auger process, initiates Coulomb explosion in the tetracation. The delay between the pump and probe x-ray pulses was varied between 0 and 100 fs. Two methods were used to produce two nearly-identical x-ray pulses: the slotted spoiler method and the newly installed split and delay apparatus [6,7].

The measurement was done in a molecular beam under the conditions where on average one molecule fragments per event. The ion fragments are detected using a newly commissioned delay line anode detector. This detector allows us to resolve both the position and arrival time of each ion fragment, yielding all three components of the momentum. In addition, this detector has 3 layers of delay lines, which increases the number of individual ions that can be resolved when they arrive at similar times and position, permitting us to detect multi-particle coincidences. Figure 1 illustrates the benefits of the three-layer detector compared to a two-layer one.

3. Analysis

The process of analyzing the data relies on the ability to identify “real” coincidences, i.e. combinations of ion fragments that result from the decomposition of the same acetylene molecule. This is achieved by applying constraints on each potential coincidence based on conservation of momentum and energy. A visualization of this is shown in Fig. 2 for the case of the (V) decay pathway after a single photon absorption. In addition to being able to observe 2 particle coincidences as shown in Fig. 2, initial results have shown that we can in fact resolve 3 and 4 particle coincidences. This permits probing the x-ray initiated ultrafast dynamics in great detail.

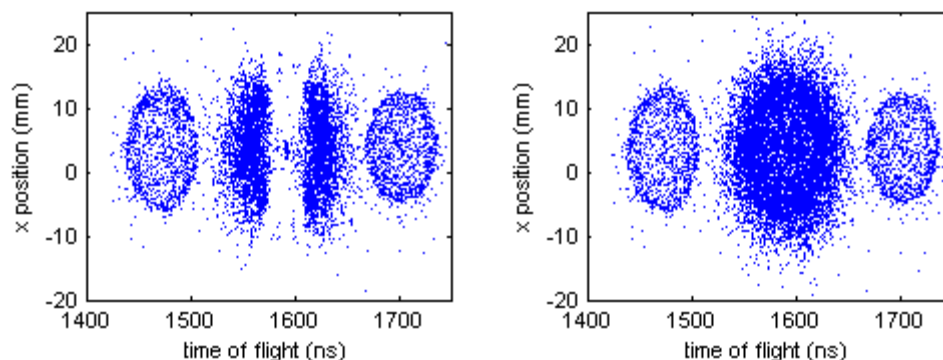


Fig. 1. To demonstrate the benefits of the three layer delay line anode detector (right) compared to a two layer one (left) for resolving ion fragments with similar arrival time and position, we plot the x position vs. time of flight for a subset of ions in two particle coincidences. The CD^+/CD^+ pairs can be seen as the feature at ~ 1600 ns (the features at ~ 1470 and ~ 1700 ns are due to C^+/CD_2^+ coincidences). The events that are discarded due to the inability of the two-layer detector to resolve them result in a missing portion of the data on the left while the same portion of the data can be resolved with the redundancy provided by the three-layer detector on the right.

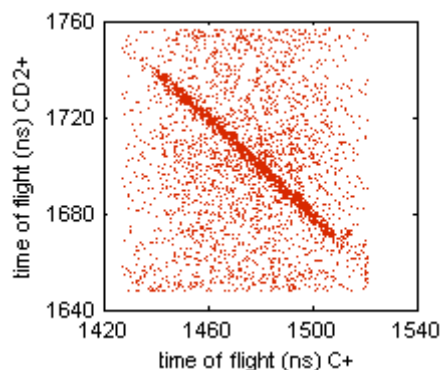


Fig. 2. To find coincidences corresponding to the isomerization pathway (V) after the x-ray photon absorption, coincidences of C^+ and CD_2^+ are found. For true coincidences the conservation of the momentum (along the time of flight axis in this case) results in the data lying on a line as shown above. Analysis of the temporal evolution of the multi-particle coincidences will provide the necessary information about the x-ray initiated change of the molecular geometry associated with this pathway.

4. References

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