

Femtosecond Time-Resolved X-ray-Induced Isomerization

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Abstract: We investigated rapid proton migration in acetylene induced by 10 fs 400 eV x-rays, and probed with a second delayed x-ray pulse. Dynamics are revealed through delay-dependent fragmentation momenta.

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We have studied the time scale for x-ray induced proton migration in acetylene from the linear HCCH isomer to the vinylidene CCH₂ form. We have used 10 fs x-ray pulses from the LCLS x-ray free electron laser during the AMO75113* experimental run of 2013. Our preliminary conclusion is that the time scale for isomerization is far more rapid than previous estimates. We find substantial proton migration on the order of 20 fs.

The acetylene isomerization transition has been studied extensively, as a model of hydrogen migration in organic molecules. Usually proton migration is initiated by photoexcitation or photoionization within the valence shell of the molecule. Relatively little is known about isomerization induced by photoionization of the 1s shell. X rays above the carbon K-edge generally induce core shell ionization followed by Auger relaxation, leading to the production of a molecular dication. Previous experiments conducted at x-ray synchrotrons have shown strong evidence that in some cases x-ray dication formation is accompanied by proton migration from the initial HCCH²⁺ configuration to the CCH₂²⁺ vinylidene metastable isomer [1]. These studies analyze the charged dissociation fragment momenta following decay of the dication, and so they cannot resolve the motion of the protons within the molecule prior to dissociation. Photoelectron-photoion coincidence measurements at synchrotrons have been used to clock proton migration times, and have concluded that they are faster than 60 fs [2]. This is at odds with the ~2 eV isomerization barrier between acetylene and vinylidene in the ground state of the dication, which suggests a longer isomerization time [3, 4].

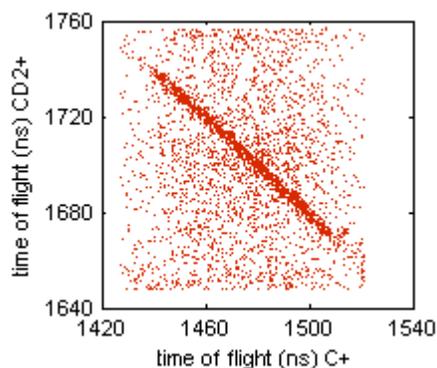


Fig. 1. Momentum correlation may be used to find coincidences corresponding to the isomerization pathway after the x-ray photon absorption. Here, coincidences of C⁺ and CD₂⁺ are found. For true coincidences the conservation of the momentum (along the time of flight axis in this case) results in the data lying on a line as shown above. In the study reported here, similar constraints were placed on four-particle coincidences that correspond to full dissociation of acetylene.

Experiments were carried out by the AMO75113 collaboration* using the newly commissioned x-ray split and delay capabilities at the Atomic Physics Hutch at LCLS, and a target gas of either acetylene (HCCH) or deuterated acetylene (DCCD). The x-ray source was tuned to an energy of 400 eV. This is approximately 100 eV above the K-shell ionization edge. The pulses had a width of ~10 fs. The first x-ray pulse initiated the dynamics through photoionization. The cation was then further ionized to a dication through the Auger process, which is calculated to take approximately 6 fs in carbon [5]. Proton migration dynamics proceed following excitation, but this process is stopped by the arrival of a second x-ray pulse, which ionizes another 1s electron, and results in a second Auger relaxation. The four charges on the molecule – a tetracation – now render it unstable, and result in a coulomb like explosion. It dissociates into two, three, or four fragments which are detected by a three-layer Roentdek delay-line anode detector that is mounted in a flat-field momentum imaging apparatus. The detector can sort and resolve the position and arrival time of each ion fragment for up to sixteen independent ions, therefore measuring the full momentum vectors. The pump and probe x-ray pulses could be delayed by from 0 to 100 fs. The target gas was delivered in a molecular beam, and the conditions were kept to a level where on the order of one molecule fragmented per x-ray shot.

Data in this study include events where four charged dissociation products were produced from the same molecule. We found that an effective filter to eliminate backgrounds with false coincidences was to require that the four particles be singly charged, two protons and two carbon ions, and that the total vector sum of the momenta of all fragments was approximately zero, to within 10% of the peak momentum. Figure 2 shows how this works in the case of only two fragments, where the display is simpler. We applied this to the four-dimensional product space of four particle coincidences. This is quite challenging at LCLS because the x-ray laser repetition rate is only 120 Hz.

The process of proton migration towards the vinylidene form of the molecule can be detected by analyzing the individual ion momenta. For example, in preliminary data analysis we have used the following protocol: The four momentum vectors are \mathbf{p}_{C1} , \mathbf{p}_{C2} , \mathbf{p}_{H1} , and \mathbf{p}_{H2} . Our event selection filter ensures that the vector sum of all momenta is zero: $\mathbf{p}_{C1} + \mathbf{p}_{C2} + \mathbf{p}_{H1} + \mathbf{p}_{H2} = 0$. We then define the molecular axis in the lab frame as the unit vector $\hat{\mathbf{A}} = (\mathbf{p}_{C1} - \mathbf{p}_{C2}) / |\mathbf{p}_{C1} - \mathbf{p}_{C2}|$. Finally, we look at the projection of the proton momenta on $\hat{\mathbf{A}}$. If the dot products $\hat{\mathbf{A}} \cdot \mathbf{p}_{H1}$ and $\hat{\mathbf{A}} \cdot \mathbf{p}_{H2}$ have different signs, then we identify that detected event as a molecule that has not undergone isomerization (the acetylene channel “A” or deprotonation channel “P”). If, on the other hand, $\hat{\mathbf{A}} \cdot \mathbf{p}_{H1}$ and $\hat{\mathbf{A}} \cdot \mathbf{p}_{H2}$ have the same sign, then one proton has migrated to the other side of the molecule. This is the “V” channel.

We find some striking physical features of the data sorted in this way. First the collection of A- and P-channel events have a total kinetic energy (TKE) release distribution that is approximately 10 eV larger than V-channel events. This difference is so large that TKE may be used as a method to separate non-isomerizing events from V-type events.

Second, we find that the ratio of V-type to non-isomerizing events is a strong function of the time delay between the pulses. The time-dependence is consistent with the LCLS x-ray autocorrelation time, and suggests that proton migration occurs on a time scale of approximately 20 fs or less following x-ray ionization.

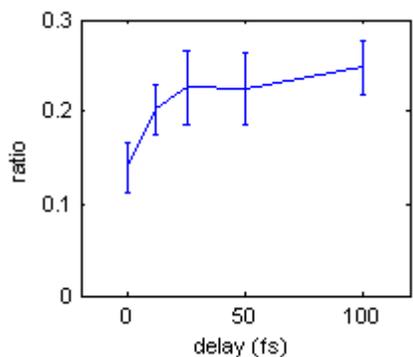


Figure 2: This shows the ratio of the isomerized (V-type) to non-isomerized molecules following x-ray induced core ionization and Auger relaxation in acetylene. Isomerization is detected by examining the 4-fragment channel of a coulomb explosion induced by a second 10 fs x-ray pulse after a time delay shown on the x-axis in the plot. Events are identified as V-type if the two detected protons have fragment momenta on the same side of the plane that bisects the C-C bond (see text).

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