

Tabletop Imaging of structural Evolutions in chemical Reactions

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Abstract: The first high-resolution molecular movie of proton migration in the acetylene cation is obtained using a tabletop multiphoton pump-probe approach – an alternative to demanding free-electron-lasers and other VUV light sources when ionizing from the HOMO-1.

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Introduction

Since the introduction of femto-chemistry, electron or X-ray diffraction have been the most commonly employed techniques to track nuclear rearrangement in molecules. Unfortunately, these techniques are largely insensitive to the more subtle and irregular structural changes that can occur within a single small molecule undergoing a chemical reaction. Pump-probe Coulomb Explosion Imaging (CEI) allows observation of these changes on a femtosecond (fs) timescale with atomic resolution, so *e.g.* proton migration on the acetylene dication [1,2].

Since laser driven tunnel ionization preferentially ionizes the highest occupied molecular orbital (HOMO) compared to lower lying orbitals, the dynamics within the cation typically involves mostly the electronic ground state – where a potential energy barrier of 2 eV prevents isomerization. To overcome this barrier it is thus necessary to populate the first electronically excited state which requires ionization from the HOMO-1 orbital. We present a table top approach to efficiently launch dynamics from ionization of the HOMO-1 of small organic molecules [3], which so far required VUV sources like free electron lasers (FEL) or high harmonics [4,5]. Once on the first excited state of the acetylene cation, a proton can migrate from the linear acetylene cation ($[\text{HC}=\text{CH}]^+$) to the vinylidene cation ($[\text{C}=\text{CH}_2]^+$).

While FELs are limited by repetition rate and fluctuations, our approach provides tremendous benefits in terms of statistics, accessibility and temporal resolution. Here we show that 266 nm ultrashort laser pulses are capable of initiating rich dynamics on excited states through multiphoton ionization. With our generally applicable tabletop approach that can be transferred to other small organic molecules, we have investigated two basic chemical reactions simultaneously: proton migration (shown in the first high resolution molecular movie) and C=C bond-breaking, triggered by multiphoton ionization. The experimental results are in excellent agreement with the timescales and relaxation pathways predicted by new and definitively quantitative *ab initio* trajectory simulations [3].

2. Results and Discussion

A pump pulse (266 nm, 32 fs, four photon absorption) ionizes the system to the acetylene cation and launches proton migration dynamics. A time delayed probe pulse (800 nm, 40 fs) further ionizes it to higher charged states. Its electric field stripes off electrons almost immediately, leaving positively charged fragments behind which undergo Coulomb explosion. They represent the molecule's geometric configuration at the arrival time of the probe pulse.

Newton plots of three correlated fragments (H^+ , C^+ and CH^+) provide frames of the molecular movie of isomerization (Fig. 1) – starting from the linear geometrical shape of acetylene (\cdot) on the left, via a transition state (+) to vinylidene (x) on the right hand side. The trans-configuration is reached after 20 fs, which matches a half-period of the trans-bent vibrational mode. At 40 fs the centre of mass reaches the classically calculated transition state, which agrees with timescales predicted by our semi-classical simulations for a population transfer to the ground state mediated by the conical intersection between ground and first excited state. A maximum in vinylidene is observed around 100 fs, after which the population maximum swings back to the acetylene side (with a vinylidene population minimum around 150 fs). This oscillation on the ground state continues, with the next vinylidene population maximum observed at 180 fs.

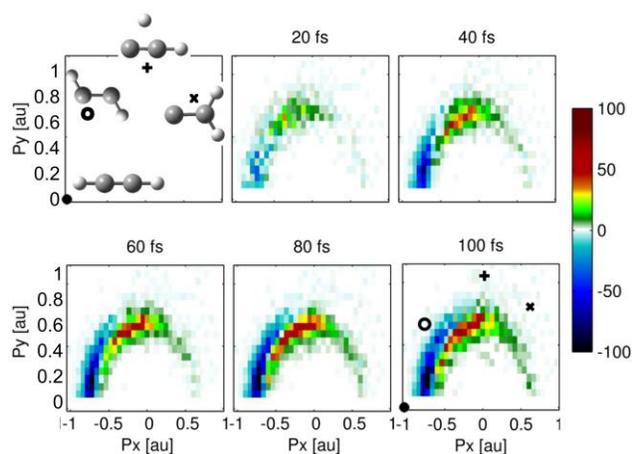


Figure 1: The molecular movie of proton migration in the acetylene cation: Newton plots filtered for KER > 13 eV. Symbols show classical calculations assuming Coulomb potentials for linear (•) and trans configuration (◦), transition state (+) and vinylidene (x), as given in the upper left corner. The plots show the evolution of H^+ momenta (after subtracting the distribution at $\Delta t=0$) from acetylene to vinylidene with increasing time delay from 0 to 100 fs, normalized to the integral. The distribution appears localized at 20 fs (dark green data points) and later spreads out. White corresponds to zero, blue to negative contributions (*i.e.* where the population originates) and other colours to positive contributions (*i.e.* where the population is going).

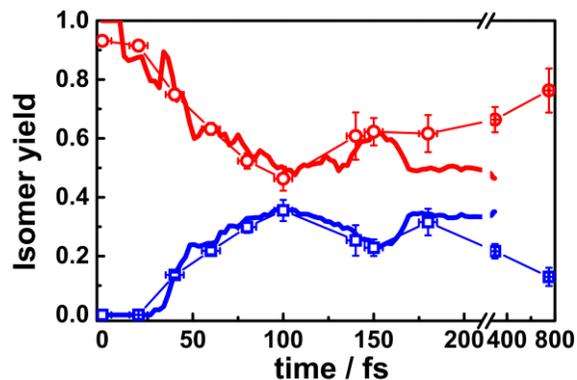


Figure 2: Comparison of theory (thick lines) and experiment (open symbols) for acetylene (red) and vinylidene (blue) yield: Theoretical curves show the superposition of acetylene and vinylidene yield in both the ground state and excited states of the cation as a function of time. Experimental values are obtained by integrating the Newton plots of Fig. 1. **Error! Reference source not found.** for negative P_x (acetylene, circles) or positive P_x (vinylidene, squares). Note the broken axis for long time delays. Experimental data are corrected by offset and scaling factor to fit the theoretical points.

As shown in Fig. 2, the observed to and fro isomerization between acetylene (red) and vinylidene (blue) is in excellent agreement with the theoretical computations presented as solid lines. Due to careful investigation we are able to uniquely assign the involved electronic and charged states.

Additionally, new dissociation channels involving subsequent photon absorption on the cation have been observed from two fragment correlation ($CH^+ + CH^+$ and $C^+ + CH_2^+$). They show up in both, the acetylene and vinylidene molecule and are thus assigned to a C=C bond cleavage.

Merging the information from 1, 2, and 3 fragment correlations with theoretical simulations, our results present the most complete picture of population transfer on the excited state of the acetylene cation. If one aims to populate the excited states of charged molecules whose difference in ionization potentials is too large to be overcome by 800 nm photons, our experimentally rather simple approach provides an alternative to demanding VUV sources. It allows studying of excited states dynamics of *e.g.* the acetylene or ethylene cation and should be applicable to a great many of other small organic molecules.

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