EUV-driven femtosecond dynamics in ethylene

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Abstract. We studied ion fragment yields from EUV-pump NIR-probe experiments performed on ethylene molecules (C\(_2\)H\(_4\)). Through study of the ion yields as a function of pump-probe delay we resolve molecular dynamics on the excited electronic states of the ion. The breakup channel yielding CH\(^+\) and CH\(_2^+\) indicated photo-isomerization to the ethylidene configuration (HC\(^-\)CH\(_3^+\)) on an ultrafast timescale. This configuration is predicted to be a transient configuration for electronic relaxation. We observed this channel, and found that it takes the excited cation (C\(_2\)H\(_4^+\))\(^\ast\) 50 ± 25 fs to reach the ethylidene configuration. The transient ion yield of C\(_2\)H\(_2^+\) at zero delay (in combination with independent synchrotron experiments) indicates other ultra-fast dynamics in short-lived intermediate states are present.

Photo-excitation of hydrocarbons is of fundamental interest to many subject areas, such as astrophysics, medicine, biology, and atmospheric science [1, 2, 3]. Population transfer to an excited electronic state, whether in the neutral or ion, often leads to molecular dynamics on the excited electronic potential energy surface (PES). Such dynamics could include isomerization and/or internal relaxation, in which the excited electronic energy is converted to nuclear motion. Often the complexity of photo-induced molecular dynamics can be reduced to the motion about a single carbon double bond. For example, the photo-isomerization of retinal in rhodopsin can be effectively modeled using the reduced reaction coordinate set of the twist and stretch of the C\(_{11}\) = C\(_{12}\) double bond [3]. For this reason, we studied the interaction of photons with the simplest molecule that contains a carbon double bond, ethylene (C\(_2\)H\(_4\), also referred to as ethene).

Theoretical insight into ethylene has improved over the years due to the availability of more advanced tools. These studies [4, 5, 6, 7, 8, 9, 10] have shown that twisting, pyramidalization, hydrogen migration, and isomerization to ethylidene (HCCH\(_3\)) are dynamics leading to molecular configurations where the excited state PES’s connect to the vibrationally hot ground state. Experimental efforts have been largely limited to time-independent studies [11, 12] while time-dependent work was performed mainly on excitations on the neutral molecule [13, 14, 15]. We however will target femtosecond dynamics in the excited ionic states of ethylene, such as states A to D in Fig. 1. These states already have one electron missing and thus have a variety of fragmentation pathways [11]. Note that one cannot simply use an intense NIR field to excite such dynamics, since strong field ionization will predominantly produce the lowest energy state of the ion.

In order to study the dynamics following photo-excitation to the excited cation (C\(_2\)H\(_4^+\))\(^\ast\), we have constructed an intense high-harmonic generation (HHG) system. This experimental system
Figure 1. Schematic representation of the energy levels for ethylene (C2H4). A minimum photon energy of 11 eV is required to ionize ethylene, versus 30 eV for double ionization. On right several cartoons of relevant ethylene configurations are depicted. Note that hydrogen migration can lead to the ethylidene isomer.

has been more extensively described elsewhere [16, 17], but the essentials will be reiterated here. The HHG source delivers per shot both intense NIR probe laser pulses and ~ 10^9 EUV pump photons (20-25 eV range) on an ethylene gas target. The experimental setup used for our studies is depicted in Fig. 2. After pulse compression to 35 fs, a 90/10 beam splitter (see Fig. 2) delivers 10% of the energy to a laser probe arm, with the remaining 90% used for the production of higher order harmonics. The HHG-production laser beam enters the vacuum system and focuses onto a 5-cm-long gas cell filled with xenon (Xe) gas where the harmonics are produced. Both the HHG beam (also labeled as EUV pump beam) and remnant NIR laser light exit the cell. Two silicon (Si) plates at the NIR Brewster angle reflect only the EUV pulse.

The transmitted beam through the 90/10 beam splitter (see Fig. 2) was propagated through a delay stage, a half-wave plate & polarizer combination (used for intensity control), another half-wave plate (for polarization control), window W2, and onto the mirror-with-hole. The effects of the optical components were calculated to have stretched the probe pulse to 100 fs [full-width-at-half-max (FWHM)] inside the vacuum chamber. The time resolution of the apparatus is dominated by the stretched probe pulse duration. The high order harmonics and NIR probe pulse are recombined at a turning mirror with a 2 mm diameter hole drilled 45 degrees to the surface normal. The harmonics go through the hole and the NIR probe beam is reflected with the center portion of the beam missing. Both beams are focused by a 20 cm radius of curvature mirror (labeled CM2) with a multi-layer coating designed to reflect EUV radiation with energies between 20 and 25 eV. The coating was designed and produced by the Center for X-Ray Optics (CXRO) at LBNL. The curved mirror CM2 has a non-zero reflectivity for low energy photons in the 1-10 eV range due to metallic elements in the multi-layer coating. Therefore, both NIR and EUV beams were reflected and focused onto the same focal volume. A super-sonic gas flow of ethylene molecules was directed to overlap at focus (background pressure in the chamber, mainly water, was ≃ 4 × 10^-8 mbar). Ions produced in the focal region were selected by a 2 mm aperture and directed to a time of flight mass spectrometer.

The red curve in the inset of Fig. 2 shows the EUV spectrum incident on CM2, measured
with a scanning monochromator. The monochromator was calibrated to yield absolute photon numbers. The blue area curve in the inset of Fig. 2 shows the expected spectrum after reflection off CM2. One can see that the reflected spectrum mainly consists of the 13th and 15th harmonic (20-25 eV photons), with close to $10^9$ photons per harmonic. Note that the insertion of the mirror-with-hole (see Fig. 2) further reduces the EUV flux by about a factor of 2–3.

Ion fragment yields vs. time delay (delay between EUV pump and NIR probe pulses) are plotted in Fig. 3. The delay stage position for time zero $t_0$ ($\tau = 0$, the delay where both EUV and NIR pulses overlap in time) was verified independently with an NIR/NIR cross-correlation by leaking in NIR photons in the otherwise EUV-dominated pump arm. Several transient ion yields occur at time zero, when the EUV and IR pulses are overlapped. We define a transient configuration as a configuration with a life-time short compared to the instrument response function. $\text{H}_2\text{O}^+$ (from the chamber background), $\text{C}_2\text{H}_5^{2+}$ and the mass-29-isotope $\text{C}_2\text{H}_5^{3+}$ are plotted in Fig. 3(a). The solid curves are Gaussian fits centered around $\tau = 0$ fs. These transients allow the time zero position to be acquired simultaneously with the rest of the data-set.

We collected ions during 800 laser shots (two identical scans of 400 shots in opposite direction) at a laser intensity of $8 \times 10^{13}$ W/cm$^2$. We will focus our attention to the isomerization to ethylidene (see cartoon in Fig. 1). As mentioned in the introduction, ethylidene is a excited-state configuration believed to play a role in internal relaxation. The ion yields for $\text{CH}_3^+$ and $\text{CH}^+$, reflecting the break-up of the transient ethylidene configuration (HC-CH$_3$)$^+$ by the NIR probe, are plotted in Fig. 3(b). While both CH$_3^+$ and CH$^+$ yields have a strong transient component, the CH$^+$ curve does have a more prominent background. The background is attributed to alternative pump-probe channels such as EUV-only contributions, NIR-only contributions, NIR-pump EUV-probe contributions, and non-transient EUV-pump NIR-probe channels, and will be ignored in
Figure 3. (a) Transient ion yields centered around $\tau = 0$. The transient nature of $\text{C}_2\text{H}_2^{+}$, in combination with synchrotron data, indicate the existence of a short-lived intermediate state. (b) Ion yields for the ethylidene fragments $\text{CH}_3^{+}$ (multiplied by 3) and $\text{CH}^{+}$ (shifted up by 0.15). Maximum yield occurs at $\tau = 80$ fs. (c) Ion yield for the fragment $\text{H}_2^{+}$ (maximum at $\tau = 110$ fs), believed to represent fragmentation from a transient configuration succeeding ethylidene. The solid black curves in (b) and (c) represent modeled curves, consisting of a background (black dotted curves) and a transient signal $S(\tau)$ (solid blue curves). Data-to-model comparison yields an isomerization time for ethylidene of $50 \pm 25$ fs, and the data is found consistent with a $(50 \text{ fs})^{-1}$ ethylidene decay rate into the transient configuration yielding $\text{H}_2^{+}$. The error bars are based on Poisson statistics.

this discussion. The transient profile that we consistently measure for $\text{CH}_3^{+}$ and $\text{CH}^{+}$ peaks at $\tau \simeq 80$ fs. We have verified that the yields are not a result of multi-photon ionization involving remnant lower orders (photons $< 10$ eV) in the pump beam by inserting a MgF$_2$ window [17] which transmits only the lower orders ($\leq 5$). The modeled curves in Fig. 3 are based on a delayed exponential decay model. This model was described by van Tilborg et al. [16]. It involves the delayed population $N(t)$ of a probe-accessible state, which in turn has a decay time $\tau_1$ following $\partial N(t)/\partial t = -N(t)/\tau_1$. So in the model the population following excitation at $t = 0$ is given by $N(t) = 0$ for $t < t_{\text{isom}}$, and $N(t) = \exp \left[ -(t - t_{\text{isom}})/\tau_1 \right]$ otherwise, with $t_{\text{isom}}$, the isomerization delay. Further details of the model are in [16]. Fitting the $\text{CH}^{+}$ and $\text{CH}_3^{+}$ fragment data to this model gives $t_{\text{isom}} = 50 \pm 25$ fs. We interpret this as the time required for the molecule to undergo isomerization to the ethylidene configuration. The confidence interval is based on variation of $\chi^2$ by 68%. $\tau_1$ can only be confirmed to be smaller than the instrument response. Attempts to model the data with only experimental decays ($t_{\text{isom}} = 0$) give poor agreement.

Whether the molecule undergoes electronic relaxation (through a conical intersection) or further isomerization along the same PES is beyond the scope of our analysis. However, as
noted in several publications (for example Sannen et al. [5] and Kosma et al. [15]) the ethylidene configuration is potentially followed up by an H₂ stretch (two hydrogen atoms moving closer to one other and away from the rest of the molecule) leading to H₂ elimination, see cartoon on the left of Fig. 3(c). It is therefore conceivable that at a specific H₂ distance the NIR probe is able to isolate and ionize H₂. The data for H₂⁺ is plotted in Fig. 3(c). The strong transient signal is consistent with the interpretation that the H₂⁺-yielding configuration is depopulating at rate 1/τ₂ but populated at the same rate 1/τ₁ that the ethylidene configuration is depleting. The solid black curve in Fig. 3(c) reflects this match, with model parameters of t_isom.=50 fs and τ₁=50 fs for ethylidene, and a transient lifetime (τ₂ < σ) for the H₂⁺-yielding configuration. Note that for the H₂⁺ fit we had to use a shorter instrument response function (70 fs FWHM), which could be due to a higher degree of non-linearity for the probe beam.

![Figure 4. Ion yield for H₂⁺ using a higher NIR intensity than for the experiment yielding Fig. 3(c). One can see that the transient features have diminished compared to the overall background and long-decay-time ion yield.](image)

We also want to note the critical choice of NIR probe intensity. If too low, the pump-probe count rates will drop dramatically, and if too high several other non-transient channels open up, complicating the analysis. For example, if the NIR intensity is increased the dominant transient features diminish with respect to the background and long-decay time features. This is obvious if one compares the H₂⁺-data in Fig. 3(c), taken at 8 × 10¹³ W/cm², with the more intense NIR data in Fig. 4, taken at 1 – 2 × 10¹³ W/cm². All other parameters are identical. The ratio of the transient feature in Fig. 4 to background is severely suppressed.

One can see that all three curves in Fig. 3(a) display strong transients on top of their respective backgrounds. While H₂O⁺ and C₂H₂⁺ are beyond the scope of this paper, the transient nature of C₂H₂⁺ will be addressed now. Besides the fact that the transient yields in Fig. 3(a) provide alternative indication of t₀ (in addition to the NIR/NIR cross-correlation), the C₂H₂⁺ curve also hints to ultrafast molecular dynamics. Unpublished experiments at the Advanced Light Source at LBNL, Berkeley, where a weak photon beam interacted with an ethylene gas target, have indicated that a 40 eV photon beam cannot produce the stable dication, although this is energetically allowed as Fig. 1 indicates. The same results were acquired for a 80 eV photon beam. Either insufficient electron-electron correlation for the two HOMO π orbitals or an insignificant Frank-Condon overlap between the planar neutral ground state and the twisted di-cation states (see also cartoon in Fig. 1) disallow the reaction hν+C₂H₄→C₂H₂⁺ (stable). However, similar experiments showed that a 310 eV photon beam (which removes a carbon 1s electron leading to Auger emission of a secondary electron) can produce the stable di-cation. It is believed that the intermediate process of Auger decay provides sufficient time for the molecular intermediate state to undergo dynamics such that the stable di-cation channel is accessible. This observation highlights the importance of an intermediate state. In the present work, we observe the stable C₂H₂⁺ through multiphoton ionization. We do not observe C₂H₄⁺ as a step-function in yield versus pump-probe delay or through a long-lived intermediate state. The C₂H₄⁺ transient is dominated by the time resolution of our apparatus, indicating that the
multiphoton ionization proceeds through a short lived excited states. It is not clear at this moment which intermediate states are involved (either excited states in the neutral or ion). These results just provide a hint of excited state dynamics, and future experiments will be tailored towards understanding such dynamics.

In summary, we have studied the dynamics in the EUV-pumped excited ethylene cation \((\text{C}_2\text{H}_4^+)^*\), leading to formation of the transient stable ethylidene configuration \((\text{HC-CH}_3^+)^*\). Application of an NIR probe resulted in ethylidene fragmentation to \(\text{CH}_3^+\) and \(\text{CH}^+\), which occurred favorably at a 80-fs probe delay. Comparison to a model was performed yielding an isomerization time of \(50 \pm 25\) fs. The fragment \(\text{H}_2^+\) was measured predominantly at an 110-fs probe delay, consistent with an \(\text{H}_2\) stretch motion following from this ethylidene configuration. In addition to ethylidene-related ion yields, we also saw the transient production of the stable di-cation \((\text{C}_2\text{H}_4^2)^+\), believed to be produced through a short-lived intermediate state.

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