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FAST TRACK COMMUNICATION

Femtosecond isomerization dynamics in the ethylene cation measured in an EUV-pump NIR-probe configuration

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Abstract

Dynamics in the excited ethylene cation $C_2H_4^+$ lead to isomerization to the ethylidene configuration $(HC-CH_3)^+$, which is predicted to be a transient configuration for electronic relaxation. With an intense femtosecond extreme ultraviolet pump pulse to populate the excited state, and a near infrared probe pulse to produce the fragments CH^+ and CH_3^+ (which provides a direct signature of ethylidene), we measure optimum fragment yields at a probe delay of 80 fs. Also, an H_2 -stretch transient configuration, yielding H_2^+ upon probing, is found to succeed the ethylidene configuration. We find that a simple single- or double-decay model does not match the data, and we present a modified model (introduction of an isomerization delay of 50 ± 25 fs) that does provide agreement.

(Some figures in this article are in colour only in the electronic version)

Photochemical reactions can be described in terms of photoinduced vibrational wave packets evolving on one or several adiabatic potential energy surfaces (PES). Quantum-mechanical studies have established that numerous ultrafast reactions are intimately connected with the internal conversion of electronic energy to nuclear motion via so-called conical intersections (CI) [1]. In this highly non-adiabatic region, electronic and molecular dynamics are strongly coupled. Even if the dynamics of large systems such as proteins and chromophores are quite complicated, the initial steps of internal conversion can often be traced back to the excitation of a specific small hydrocarbon unit. For example, the photoisomerization of retinal in rhodopsin can be effectively modelled using the reduced reaction coordinate set of the twist and stretch of the $C_{11} = C_{12}$ double bond [2].

The simplest molecule containing a carbon double bond is ethylene (C_2H_4 , also referred to as ethene), which has been a model molecule for theoretical and experimental studies for

decades. Theoretical insight into ethylene has improved over the years due to the availability of more advanced tools. These studies [3–9] have shown that in neutral ethylene excited to the V-state ($\pi\pi^*$ state), twisting and pyramidalization, hydrogen migration, and isomerization to ethylidene ($HC-CH_3$) are important configurations that connect the excited state to a vibrationally hot ground state. Experimental efforts have been largely limited to time-independent studies; following absorption of photons over a wide range of energies, groups have studied the yield of ion fragments [10, 11], photoelectrons [12, 13] and fluorescence photons [14] (see also references therein). Time-dependent work was performed only on excitations in the neutral state through pumping with 6–8 eV photons and probing with a near infrared (NIR) laser [15–17].

Here we apply a pump pulse at extreme ultraviolet (EUV) photon energies, several eV above the ethylene ionization potential. Theory predicts [3, 4] that several CIs will be crossed

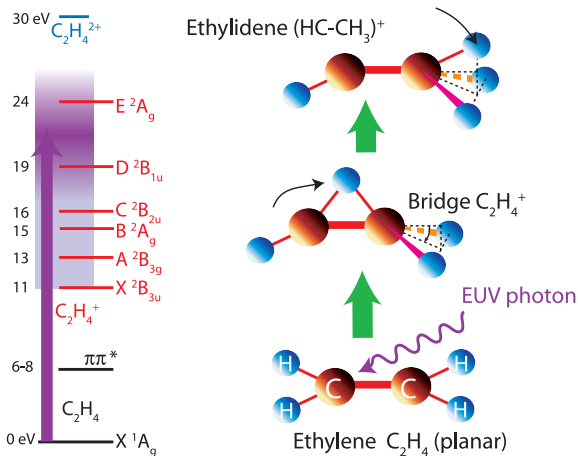


Figure 1. The left diagram shows the energy levels of the ground and excited states of neutral ethylene, the cation and the dication. On the right is a sketch of a predicted [3, 4, 17] isomerization sequence following EUV-driven population of the excited states of the cation. Note the ethylidene configuration, which is believed to be followed by a H_2 stretching configuration.

after population of the excited cationic states (A^2B_{3g} , B^2A_g , C^2B_{2u} , D^2B_{1u} and E^2A_g , see energy diagram in figure 1). The isomerization sequence [4, 17] is depicted as a cartoon on the right of figure 1. Just as for excited neutral ethylene [5–9], and references therein, the isomerization to ethylidene in the cation is found to play a major role in photodissociation and -excitation dynamics. Therefore, the ethylidene configuration was chosen as the focus of our study. The EUV-induced isomerization to $(HC-CH_3)^+$ can be directly observed through probing by an NIR pulse intense enough to break the C–C bond, leaving the fragments CH^+ and CH_3^+ to be detected. The fs EUV source has to be intense enough to pump a substantial fraction of the C_2H_4 target to the excited states of the cation.

We report here on a direct measurement of ethylidene isomerization, which, as we found, develops in a transient matter several tens of femtoseconds after pumping. To achieve this measurement, we developed a unique intense synchronized EUV-pump NIR-probe source. Our results, and the applicability of our setup in general, provide new insight and demonstrate experimental opportunity in the timescales involved in isomerization and electronic relaxation in ethylene and other model molecules.

We have constructed an intense high-harmonic generation (HHG) system delivering per shot both an NIR probe laser and $\sim 10^9$ EUV pump photons (20–25 eV range) on an ethylene gas target. The experimental setup used for our studies, constructed at the Lawrence Berkeley National Laboratory (LBNL) in Berkeley, CA, is depicted in figure 2. The setup (similar to [18]) is based on a home-built 10 Hz laser system delivering 25 mJ 35 fs laser pulses at 800 nm central wavelength. After the pulse compressor, a 90/10 beam splitter (see figure 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 beam enters the vacuum system, is incident on the curved mirror CM1 (focal length of 4.5 m) and focuses onto a 5 cm long gas cell (laser-drilled

entrance holes) filled with xenon (Xe) gas. The gas cell position, gas pressure and laser focal parameters were varied to yield optimum phase matching and HHG yield. Both the HHG beam (also labelled as EUV pump beam) and remnant NIR laser light exit the cell. Two silicon (Si) plates (rotated to the laser's Brewster angle) reflect only the EUV pulse (efficiency $\sim 60\%$ per plate). The EUV pulse is then propagated through a 45° mirror with a 2 mm diameter hole in the middle (located 4 m from the gas cell). A curved mirror (labelled CM2) with a focal length of 10 cm was coated with a multi-layer to reflect EUV radiation with energies around 20–25 eV. The coating was performed by the Center for X-Ray Optics (CXRO) at LBNL. CM2 was slightly tilted to guarantee that the focus did not overlap with the incoming EUV beam.

The transmitted beam through the 90/10 beam splitter (see figure 2) was propagated through a delay stage, a half-wave plate and 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 pulse to 100 fs (full width at half-maximum, FWHM) inside the vacuum chamber. A large fraction of the beam was reflected (with the central part missing due to the hole) and co-propagated with the EUV beam. 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 supersonic gas flow of ethylene molecules was directed to overlap at focus (background pressure in the chamber, mainly water, was $\simeq 4 \times 10^{-8}$ 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 figure 2 shows the EUV spectrum incident on CM2, measured by removing it and allowing the beam to be incident on a Rowland circle monochromator (Acton GIMS-551.5-M). The monochromator was calibrated to give absolute photon numbers. The blue area curve in the inset of figure 2 shows the expected spectrum after reflection off CM2 (the mirror reflectivity was modelled and measured by CXRO). One can see that the reflected spectrum mainly consists of the 13th and 15th harmonics (20–25 eV photons), with close to 10^9 photons per harmonic. Note that the insertion of the mirror-with-hole (see figure 2) further reduces the EUV flux by about a factor of 2–3.

At each temporal delay between the EUV pump and NIR probe pulses (same polarization) we collected ions during 800 laser shots (two identical scans of 400 shots in opposite direction), yielding an average count rate. The error bars are derived from the square root of the total ion count, assuming Poisson statistics. The laser intensity was estimated to be $8 \times 10^{13} \text{ W cm}^{-2}$ based on observing the ratio of Ar^{2+} to Ar^+ produced at focus with only the NIR beam [19]. For determination of time zero t_0 (the delay at which both beams are overlapped in time) we followed two approaches: (1) by leaking laser light of opposite polarization in the EUV arm, we performed an NIR-pump NIR-probe scan observing $C_2H_4^+$ through multi-photon ionization. Also (2) the EUV-pump NIR-probe dataset already includes a transient ion yield

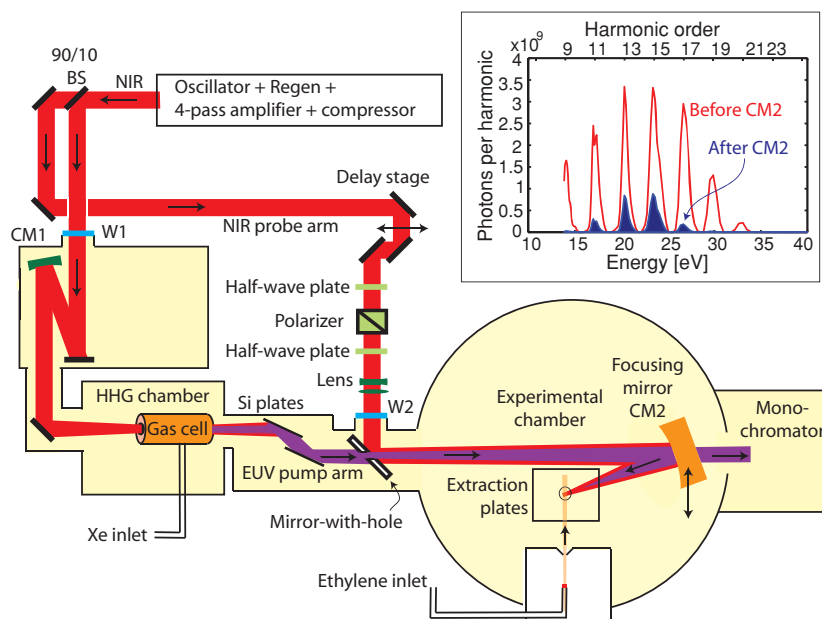


Figure 2. Figure of the experimental setup. Through use of the mirror-with-hole, both an NIR probe beam and an intense EUV pump beam are co-propagating to curved mirror CM2, which focuses both beams over an ethylene (C_2H_4) gas target. The inset shows the spectrum of the reflected EUV spectrum.

peaked at t_0 , namely H_2O^+ (from chamber background), see figure 3(a). As was extensively studied, the two methods agreed on the t_0 timing. The t_0 curve was fitted with a Gaussian profile (see black curve). The fit provided us with the value of $\sigma = 105$ fs (FWHM) for the Gaussian instrument response function (the temporal convolution of pump and probe pulses), see figure 4.

The ion yields for CH_3^+ and CH^+ , reflecting the break-up of the transient ethylidene configuration $(HC-CH_3)^+$ by the NIR probe, are plotted in figure 3(b). While both CH_3^+ and CH^+ yields have a strong transient component, the CH^+ curve does have a more prominent background. In this work we will focus our analysis on the transient profile that we consistently measure, which peaks at $\tau \simeq 80$ fs for both CH_3^+ and CH^+ . The measurement is consistent with the NIR probe breaking the C–C bond of the ethylidene cation. The NIR beam is sufficiently intense to remove a second electron. We have verified that the results are not related to multi-photon ionization with remnant lower orders (photons < 10 eV) in the pump beam since insertion of a MgF_2 window [20] (transmission < 10 eV) did not show any contribution to ion transient signals reported here.

In order to get a better understanding of the isomerization dynamics, we fit the data with a model (see also figure 4), which is based on an extension of the simple single- or double-decay model [15, 17]. After EUV excitation to the excited cationic states, the molecule will undergo nuclear rearrangement. As the nuclear wave packet spreads over the PES, a specific region L with a unique probe channel (such as the ethylidene configuration) is reached after time t_{isom} . The population probability $N(t)$ in L has a decay rate of $1/\tau_1$. The modelled probe signal $S(\tau)$, see the blue dashed curve in figure 4, is constructed by convolving $N(t)$ with the instrument response function. Note that the maximum for $S(\tau)$ does occur

at a time later than t_{isom} , which is due to the convolution of the Gaussian instrument response function with the asymmetric exponential function $N(t)$. The background to the data (see black dotted curves in figures 3(b) and (c)) was modelled based on a secondary weaker probe channel with slower decay rate. Also, for CH^+ in figure 3(b), we found a nonzero background contribution at negative delays based on an NIR-pump EUV-probe time ordering. Note that the background was found to have negligible impact on the analysis of the stronger transient signals. Also, we checked that the temporal location of the transients was not affected by an increase of NIR probe energy.

The transient yields for CH^+ and CH_3^+ are both best modelled based on the parameters $t_{isom} = 50 \pm 25$ fs and $\tau_1 < \sigma$ (transient limit). The confidence interval for t_{isom} is based on variation of χ^2 by 68%, with t_{isom} and τ_1 as free fitting parameters while keeping the background curves constant. The transient curves are plotted as blue curves in figure 3(b), using $\tau_1 = 50$ fs, while the full fits (including background) are the solid black curves. Based on the data, and within the framework of our proposed model, we can therefore state that upon EUV excitation it takes about 50 fs for the molecule to undergo isomerization to the ethylidene configuration. Whether the molecule undergoes electronic relaxation (through a CI) or further isomerization along the same PES is beyond the scope of our analysis. However, as noted in several publications (for example [4, 17]) the ethylidene configuration is potentially followed up by an H_2 stretch leading to H_2 elimination, see cartoon on the left of figure 3(c). It is therefore conceivable that at a specific H_2 distance the NIR probe is able to isolate and ionize H_2 . The data for H_2^+ are plotted in figure 3(c). The strong transient signal is consistent with the interpretation that the H_2^+ -yielding configuration is populated at the same rate ($1/\tau_1$) that the ethylidene configuration is depleting. The solid black curve

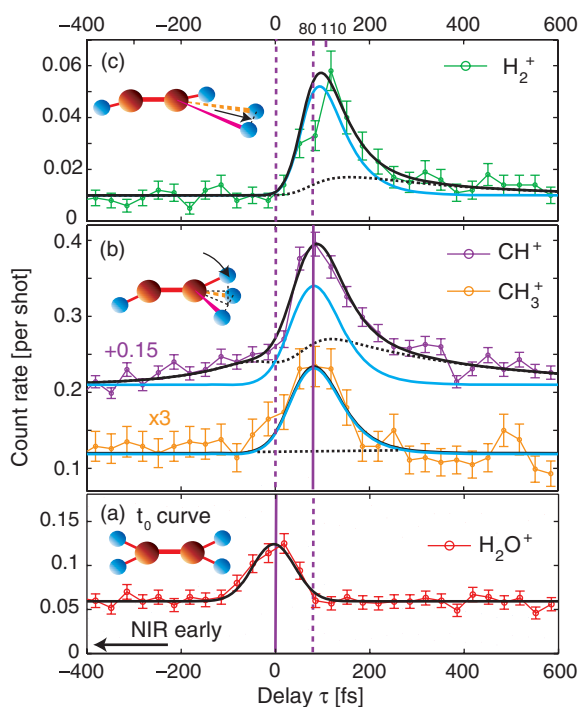


Figure 3. (a) Ion yield for H_2O^+ . This transient signal was confirmed to define time zero t_0 . (b) Ion yields for the ethylidene fragments CH_3^+ (multiplied by 3) and CH^+ (shifted up by 0.15). Optimum yield occurs at $\tau = 80$ fs. (c) Ion yield for the fragment H_2^+ (optimum at $\tau = 110$ fs), believed to represent fragmentation from a transient configuration succeeding ethylidene. The solid black curves in (b) and (c) represent modelled 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 ± 25 fs, and the data are found consistent with a $(50 \text{ fs})^{-1}$ ethylidene decay rate into the transient configuration yielding H_2^+ .

in figure 3(c) reflects this match, with model parameters of $t_{\text{isom}} = 50$ fs and $\tau_1 = 50$ fs for ethylidene, and a transient lifetime ($\tau_2 < \sigma$) for the H_2^+ -yielding configuration. Note that for the H_2^+ fit we had to use a shorter instrument response function (70 fs FWHM), which could be due to a higher degree of nonlinearity for the probe beam.

It is important to note that most pump-probe models are fully based on decay rates [15, 17], and do not include a delay term such as t_{isom} . However, application of such a simple model to our data (having strong transient features for CH_3^+ and CH^+ around $\tau = 80$ fs and for H_2^+ around $\tau = 110$ fs) failed to yield agreement. It is not our goal to provide a detailed and comprehensive pump-probe model for molecules undergoing isomerization, but we do want to point out that the simplest modification of the decay model (inclusion of the constant t_{isom}) already provides a robust match to the data. Note that our method is a direct measurement of the isomerization time scale, in contrast to more indirect methods such as photoelectron analysis performed on hydrogen migration in C_2H_2 (acetylene) [21, 22].

In summary, we have studied the dynamics in the EUV-pumped excited ethylene cation (C_2H_4^+), leading to formation of the transient ethylidene configuration ($\text{HC}-\text{CH}_3^+$). Application of an NIR probe resulted in ethylidene

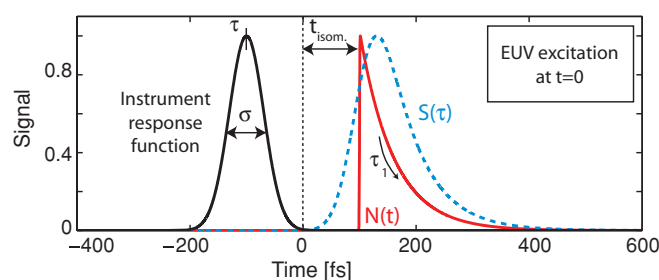


Figure 4. Model used to provide a fit to the data in figures 3(b) and (c). The population probability of the nuclear wave packet in a specific region L on the potential energy surface is labelled as $N(t)$. In this simple model, the isomerization time for the wave packet to reach this region is t_{isom} . The population of the region has a decay rate $1/\tau_1$. By convolving the instrument response function (black curve, width σ) with $N(t)$, a modelled signal S versus probe delay τ is retrieved (blue dashed curve).

fragmentation to CH_3^+ and CH^+ , which occurred favourably at a 80 fs probe delay. A model was proposed to match the data, and within the framework of this model we found an isomerization time of 50 ± 25 fs. The fragment H_2^+ was measured predominantly at a 110 fs probe delay, consistent with the concept of the ethylidene population decaying into the H_2^+ -yielding configuration. A simple rate-based model had to be expanded through inclusion of an isomerization time in order to match the data, mainly due to the measured presence of strong transient signals at positive probe delays.

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