Ultrafast Dynamics and Coherent Oscillations in Ethylene and Ethylene-\textit{d} Excited at 162 nm


Downloaded from http://pubs.acs.org on February 27, 2009
Ultrafast Dynamics and Coherent Oscillations in Ethylene and Ethylene-$d_4$ Excited at 162 nm

K. Kosma, S. A. Trushin, W. Fuss,* and W. E. Schmid
Max-Planck-Institut für Quantenoptik, D-85741 Garching, Germany
Received: April 23, 2008; Revised Manuscript Received: June 9, 2008

The fifth harmonic (162 nm, 11 fs), generated in a short argon cell from 12 fs Ti–sapphire laser pulses, was used to excite C$_2$H$_4$ and C$_2$D$_4$ in the maximum of the first $\pi\pi^*$ transition. Around 10% of the molecules were excited to the $\pi 3s$ Rydberg state instead. The subsequent motion of the wave packet, moving over the potentials from the Franck-Condon region down to the ground state, was monitored by nonresonant ionization at 810 nm with mass-selective detection of the ion yield. Five time constants (from $\approx 20$ fs in excited states to 0.6–11 ps in the hot ground state) and four coherent oscillations (CC stretch and torsion vibrations or hindered free rotation) were determined for each isotopomer. The initial relaxation follows a superposition of CC twist and stretch coordinates; this explains a surprisingly small deuterium isotope effect of the initial time constant (21 versus 24 fs). Also the vibrations in the Franck-Condon region have such a mixed character and a correspondingly small isotope shift. From the perpendicular minimum the wave packet reaches (within 17 or 21 fs for the two isotopomers) a conical intersection via a direction that also involves partial hydrogen migration. This is concluded from the detection of ethylidene (CH$_3$CH), formed simultaneously with ground-state ethylene. This carbene isomerizes in the ground state within 0.6 ps (1.6 ps for CD$_3$CD) to ethylene. Two time constants for dissociation (4.5 and 11 ps) in the hot ground state were also identified. The small yields of bimolecular reactions (photodimerization, addition reactions involving a “suddenly polarized” excited state, carbene reactions) are interpreted in terms of the short lifetimes. It is pointed out that the relaxation path starting from the Rydberg state merges into that from the $\pi\pi^*$ state; nevertheless, there is a wavelength dependence in the photochemistry of olefins, because due to a momentum effect the wave packet remembers from which state it came.

1. Introduction

To a large part, $\pi \rightarrow \pi^*$ excitation is involved in the spectroscopy and photochemistry of organic molecules. The simplest such systems are monoolefins. Ethylene is a prototype of them. Its $\pi \rightarrow \pi^*$ absorption begins very weakly around 200–210 nm, reaching a maximum near 162 nm (7.65 eV), where it is, however, superimposed by a Rydberg transition$^1$–$^4$ (Figure 1). There is now agreement that the weak and diffuse structure at long wavelengths must be assigned to a CC twist vibration and that the excited state has a minimum at 90° twist.$^2$–$^6$ Experimentally this was established by the deuterium effect on this structure at long wavelengths$^7$–$^8$ and by the resonance Raman spectrum.$^9$–$^{10}$ A CC stretch vibration is also expected to be Franck-Condon active$^9$–$^{12}$ and was tentatively assigned to some features in the spectrum of C$_2$D$_4$;$^8$ the composed nature of the vibrational structure and the different D effect on these two vibrations is considered to be the reason the C$_2$D$_4$ spectrum looks so different (Figure 1).$^8$–$^{13}$ (See, however, ref 14 where the vibrational structure was simulated without CC stretch activity. For previous controversies of assignment of the vibrational structure, see refs 3, 4, and 15.) The extrapolated 0–0 transition (hence, the minimum of the torsional potential) would be around 5.6 eV,$^5$–$^8$ 2.0 eV below the Franck-Condon region (maximum of the torsional potential). In the nomen-

* Corresponding author. E-mail: w.fuss@mpq.mpg.de. Fax: +49-89-32905-200.
geometry.) This state is easily polarized in polar media ("sudden polarization" for more recent work, see refs 24 and 25 and literature quoted), leading to a structure with a planar partially positive CH₂ group and a pyramidalized partially negative CH₂ group; the latter group also reduces its HCH angle.

Photochemical reactions with polar reagents were therefore expected. Taking also other coordinates into account, the "perpendicular minimum" of the lower state turns out to be a saddle point: the energy is further lowered on pyramidalizing one of the CH₂ groups (already in the absence of polar media) and/or allowing one of the H atoms to partially migrate to the other carbon atom.

Along one or both of these coordinates, the molecule can eventually reach a conical intersection (CI) with the ground state. If this path is barrierless (the calculations are not yet reliable enough to decide), it may explain the ultrashort lifetime of the excited state of ethylene. Compared with the measurements (see below), the calculated lifetimes are generally too long, however.

The CI provides not only an ultrafast path for internal conversion but also the branching region between reactant and product formation. Because its geometrical structure involves a 90 °CC twist, one can expect a high quantum yield of cis-trans isomerization of substituted ethylenes. If it also involves partial H migration (as predicted in refs 12, 19, 20, 26, and 29-32 but questioned in refs 27, 28, 38, and 39), completion of the migration on passing through the CI will give rise to a carbene (in this case ethylidene, CH₂CH). The photochemistry of ethylene and monoolefins has been reviewed.

Besides cis-trans isomerization, carbene products are observed as a rule. In the case of ethylene itself, an evidence is the formation of methyl-cyclopropane and 1-butene in solid or liquid ethylene, probably formed from a bimolecular insertion of ethylene into the C=C and C–H bonds of ethylene. It has been suggested, and we provide experimental evidence that ethylene is formed from the same conical intersection as that for cis-trans isomerization and internal conversion. The short-lived ethylidene is detected in this work for the first time.

Other reactions observed after UV excitation of ethylene are the eliminations of atomic and molecular hydrogen (see the reviews on olefin photochemistry). The dynamics of these dissociation reactions has been much investigated by photofragment spectroscopy in molecular beams by the group of Y. T. Lee and others. There is now agreement that they occur in the hot ground state of ethylene (after internal conversion) or ethylidene. In fact, we also observe two ground-state reactions, for the first time in time-resolved work on ethylene and ethylene-\textit{d}_4.

The dynamics of ethylene was investigated by pump-probe experiments before, but with much less time resolution. Probing was done by transient ionization, similarly as in our work. Whereas in the first work the pump wavelength was 155 nm and the time resolution was ≈350 fs, in the other three, ethylene was excited in its long-wavelength wing near 200 nm with pulses of 125–180 fs duration. Probing was done by photoionization mostly at short wavelength (±267 nm); it allowed determination of only one time constant, the lifetime of population in the Franck-Condon region. Only in the last investigation was a long wavelength (800 nm) also used for ionization (as in most of our work), so that also a second time could be determined. (At longer wavelengths and the required higher intensities, also states of lower electronic energy can be detected, in particular if also ionic fragments are measured.)

In this work we use 11–12 fs pulses at 162 nm to pump ethylene in the maximum of its ππ* band (exciting some molecules also to the π3s Rydberg state, Figure 1) and 12 fs pulses at 810 nm to probe them by (multiphoton) ionization and mass-selective detection of the ion yields; the resulting time resolution is <13 fs. We can resolve five time constants (including two after return to the electronic ground state) and four coherent oscillations (vibrations in the Franck-Condon region and in the perpendicular minimum) for each, C₂H₄ and C₂D₄. These data allow conclusions on the photochemical pathway and provide spectroscopic data not available before.

For the pump pulses we use the fifth harmonic of 12 fs pulses at 810 nm, which themselves are made by self-phase modulation in argon and chirped-mirror compression. The fifth harmonic is produced in an argon cell that is short enough to avoid pulse lengthening; this is an extension of the work, in which 10 fs third-harmonic and supercontinuum pulses were demonstrated.

2. Experimental Section

The generation of short (11 fs) pulses at the fifth harmonic from 12 fs pulses of Ti:sapphire radiation is described in ref 65 and the shortening of the fundamental in ref 67. Briefly, we focused (f = 2 m) 1 mJ pulses (810 nm, 45 fs, 1 kHz) of a commercial Ti:sapphire laser system into a cell (length 1.5 m, equipped with quartz-glass windows of 0.2 mm thickness) filled with 500 mbar Ar (instead of atmospheric-pressure of Ar as in ref 64). Under these conditions the pulses are self-phase modulated and acquire a chirp, which can be used to compress the pulses to 12 fs (determined by a commercial autocorrelator) by reflection from chirped mirrors. Part (3–10 μJ) of this radiation was used for probing. The larger part (0.7 mJ) was focused into a short (18 mm) steel cell with two pinholes (0.7 mm), which contained Ar (∼50 mbar) and was immersed in a vacuum setup (Figure 2), where the beam path was differentially pumped. In chamber B the 162 nm radiation was selected by dielectric mirrors and merged with the probe beam, using a mirror with a hole (diameter 4 mm). The two beams were focused (f = 0.7 and 1 m) into the ionization region of a time-of-flight mass spectrometer. With the estimated UV pulse energy of 4 nJ, one calculates an energy density of 0.13 mJ cm⁻² (intensity 1.3×10¹⁰ W cm⁻²) in the focus; the intensity of the probe was ≈(3–10)×10¹³ W cm⁻². The pressures of the gases (Xe for determination of the UV pulse duration and the time zero, and ethylene) were between 10⁻⁷ and 10⁻⁴ mbar, the latter for the weakest signals.

The signals are the yields of the parent and fragment ions (C₂H₄⁺, C₂H₃⁺, C₂H₂⁺, and the corresponding deuterated species) as functions of the probe delay, which was varied in steps of 3.3 fs. The time zero was taken from the maximum of the Xe⁺ signal (from added Xe) recorded in parallel with the other signals, using boxcar integrators. Details on this technique

Figure 2. Set-up for the fifth-harmonic generation. The entrance window (CaF₂) is 0.5 mm thick. The probe pulses used for the time-resolved measurements in the time-of-flight mass spectrometer (MS) merge with the UV beam at a mirror with a hole. CMC: chirped-mirror compressor. A is the first of four apertures for differential pumping. B is an evacuated box with mirrors for collimation, focusing and merging the beams.
(time-resolved intense field dissociative ionization) including evaluation can be found in refs 63 and 68 for example.

3. Results

The time-resolved data reflect the population flowing via the different locations \( L_i \) on the potential surfaces and the mass spectra \( \sigma_i \) associated with each \( L_i \). In addition, vibrations in \( L_i \) can periodically modulate the \( \sigma_i \) (probability to produce an ion of mass \( m \) from location \( i \)). The populations are modeled by rate equations, whose solutions are sums of exponentials (no matter whether the processes are consecutive or parallel) with time constants \( \tau_i \) as parameters and coefficients that result from solution of the rate equations. These sums (\( L_i \) populations) must still be multiplied by the \( m_i \sigma_i \) (which are another set of fit parameters) to get the signals. To simulate the signal also during the pump–probe overlapping time, these sums of exponentials must be convoluted with the (Gaussian) pump and probe pulses. These procedures are described in detail in refs 63 and 68 If there is in addition a periodic modulation, these functions are multiplied by (one or more) functions of the kind

\[
 f_{\text{osc}} = 1 + A \cos(2\pi \nu t - \varphi) \tag{1}
\]

where the amplitude \( A \), frequency \( \nu \) and phase \( \varphi \) are again fit parameters. In practice, one first fits a sum of exponentials (with convolution, if necessary) to the measured signals, then divides the latter by the former and takes the Fourier transform of the result (diminished by 1) to get the frequencies. These are entered into functions of type (1), which are then multiplied by the (convoluted) sum of exponentials; this complete function is then fitted to the measured data to get also the parameters \( A \) and \( \varphi \) and a final correction of the time constants \( \tau_i \) and cross sections \( m_i \sigma_i \). Evaluation in the presence of oscillations is described in more detail in ref 69 Each \( i \) and oscillation frequency \( \nu_i \) in general appear in more than one signal.

It should be noted that, in contrast to previous cases, \( \sigma_i \) eq 1 does not contain a dephasing term (exponential decay) before the cosine, because it turned out that all detected oscillations decay with the lifetime of the population at the corresponding location. It seems that there is no opportunity for a dephasing of the oscillations within the short lifetimes.

The evaluation model deserves some further explanation: We assume that on the potential surfaces one can define several contiguous regions (i.e., without gaps, locations \( L_i \)). The borders between them result from properties of the probe process, the change of ionization probability and fragmentation pattern. (The fact that this change is continuous might be a reason why the \( L_i \) populations obey rate equations, which are normally used for incoherent processes.) The locations have a certain extension, indicated by arrows in the figures. We write the “lifetimes” (of the populations within these extended regions) besides the arrows, if the traveling times of the wave packet through these windows is expected in the same range. Vibrations in these (extended) regions can modulate the ionization and/or fragmentation probability and thus modulate the signal. Hence in this model, it is not the population that oscillates (it is described by a sum of exponentials) but only the signal generation probability.

Figure 3a,b shows the parent ion signals \( \text{C}_2\text{H}_4^+ \) and \( \text{C}_2\text{D}_2^+ \). Obviously, each exhibits a doubly exponential decay. Because the pump pulse gives rise to two different kinds of excited molecules, some in the \( \pi\pi^* \) state and about 10% in the Rydberg state (Figure 1), it seems obvious that the weaker signal (which in fact has an amplitude of \( \approx10\% \) of the other) with the longer time constant \( \tau_R = 80 \) and 115 fs, respectively) belongs to the Rydberg molecules. If the Rydberg state were depleted into a nondetected state, then, to isolate the signal of the \( \pi\pi^* \) molecules, one had simply to subtract this monoexponential function (which does not contain any periodic modulation), extrapolated back to time 0 and convoluted with the laser pulses. However, in the Discussion we will show that the Rydberg population flows to the \( \pi\pi^* \) state. The signal from this indirect \( \pi\pi^* \) population is doubly exponential (time constants \( \tau_R \) and the lifetime of the \( \pi\pi^* \) state, \( \tau_i \)), with coefficients resulting from the rate equations and the assumption that the ionization probabilities from the two states are equal. This signal part is also subtracted from the measured data (Figure 3a,b); the difference (Figure 3c,d) represents the signal from the directly populated \( \pi\pi^* \) state. The result is a singly exponential decay (fit curves in Figure 3c,d, with \( \tau_1 = 21 \) and 24 fs, respectively) with some modulation. Dividing the data by the (convoluted) exponential fit curve results in the periodic functions at the bottom of Figure 3c,d, whose Fourier transforms are shown separately (Figure 3e,f). The extracted frequencies, time constants and other fit parameters (also for the fragment signals) are compiled in Table 1.

It is easy to show the two variants of evaluation (subtraction of the, back-extrapolated, slow decay versus subtraction of the full Rydberg path: the Rydberg component decaying with \( \tau_R \) and the indirect \( \pi\pi^* \) population containing \( \tau_R \) and \( \tau_i \)) result in the same time constants. (Hence the data do not tell the destination, to where the Rydberg population is depleted.) Only the interpretation of the coefficients is different. However, if there were a highly damped oscillation in the directly populated \( \pi\pi^* \) state, it would only be revealed by subtracting the full Rydberg path. Therefore we preferred this method in Figure 3. (An overdamped oscillation was not detected, however.) For the later locations, this method seemed not necessary, so that we simply subtracted the back-extrapolated slow decay in Figure 4.

Figure 4 shows early time data for the fragments \( \text{C}_2\text{H}_3^+ \) and \( \text{C}_2\text{D}_2^+ \). This stronger earlier part also contains the time constants \( \tau_R \) and modulation found already from the parent signal. Obviously the mass spectra of \( L_1 \) and \( L_2 \) also contain these fragment ions. To reveal additional information, we first subtract the slower \( \tau_R \) decay, with the results shown in Figure 4c,d (solid circles). Then we subtract the \( L_1 \) contributions, i.e., an exponential with time constant \( \tau_1 \) modulated with frequencies \( \nu_1 \), \( \nu_2 \) and \( \nu_3 \) (curve with early maximum and without data points in Figure 4e,d). The residue is a doubly exponential function (time constants \( \tau_1 \) and \( \tau_2 \) with a simple modulation \( \nu_2 \) (crosses and the unmodulated curves with late maxima in Figure 4c,d; shown also in a linear scale in Figure 4e,f), which describes filling up a location \( L_2 \) from \( L_1 \) (with time constant \( \tau_1 \)), an oscillation in this region and the depletion of \( L_2 \) (lifetime \( \tau_2 \)). Figure 4c,d shows how these two contributions (from \( L_1 \) and \( L_2 \)) add up to the total signal (from which the Rydberg contribution has been subtracted). Figure 4e,f displays the \( L_2 \) contribution once more (crosses), the result of dividing it by the doubly exponential fit and, in the inset, the Fourier transform of this oscillatory part. Obviously, there is only a single oscillation frequency. As before, it was used in the time-dependent fit functions to simulate the periodic parts and the partial and total signals, as shown in Figure 4.

The \( \text{C}_2\text{H}_3^+ (\text{C}_2\text{D}_3^+) \) fragment signal looks similar in this time range as the \( \text{C}_2\text{H}_2^+ (\text{C}_2\text{D}_2^+) \) signal (which has a better signal-to-noise ratio) and does not contain additional information. This short-time part is therefore not shown.

At longer times, in the picosecond range, the two fragments reveal very weak tails, nonmodulated exponential decays with
time constants $\tau_3$ and $\tau_4$. To detect them, we raised the probe intensity by a factor of 3 (to $\approx 10^{14}$ W cm$^{-2}$) and the pressure up to $\approx 10^{-4}$ mbar (from the normally used $10^{-7}$ to $10^{-6}$ mbar) and did more averaging. They are shown in Figure 5. Whereas the C$_2$H$_3^+$ signal shows both $\tau_3$ and $\tau_4$ (the latter more clearly, Figure 5a,b), the fragment C$_2$H$_2^+$ only contains $\tau_3$ (Figure 5c,d).

The effect of the probe intensity is demonstrated with C$_2$D$_3^+$ as an example in Figure 5b, where the small symbols show data recorded with standard probe intensity ($\approx 3 \times 10^{13}$ W cm$^{-2}$). Evidently, reducing the intensity by a factor of 3 lowers the ion yields to levels, where $\tau_3$ can barely be recognized and the $\tau_4$ window (L$_4$) is below the detection limit.

The parent-ion signal decays to 0. That is, the ion yields at negative and long positive delay times coincide. The former is
obviously due to multiphoton ionization by the probe; it was subtracted from the measured data. For the fragment ions the long-time signals are slightly higher (about $10^{-4}$ of the maximum) than those at negative time. Because this “pedestal” depended nonlinearly on the UV intensity (varied by a factor of 2, by changing the pressure in the Ar cell), it cannot be due to one-photon excited molecules; therefore we subtracted the pedestal from the fragment signals. All the rest, i.e., the signals from all $L_i$ are linear in the pump intensity and the ratios of signals stay perfectly constant. The absence of a long-time signal means that no end product was detected.

The probe energy was also varied (by a factor of 3, Table 1). An example is also shown in Figure 5b. The corresponding variation of the signal intensity (more precisely: the ionization probability) could inform on the order of ionization of the different $L_i$ and hence on their relative energies. For this purpose, one should add up the parent and fragment signals; unfortunately, each signal was separately measured and normalized. We instead compare the dominant signals: the parent from $L_1$ and $L_R$, and $C_2H_4^+$ from $L_2$ and $L_3$. The former pair was found to have the same order of ionization (the signal ratios do not change with the probe energy, Table 1), so that the two locations have roughly the same energy. As to $L_3$ and $L_4$, the probe-intensity dependence is less conclusive, probably because the fragmentation pattern also changes with the intensity. Nevertheless it can be recognized from Table 1 that $L_3$ and $L_4$ are below $L_2$, because the signals from the former are by more than 2 orders of magnitude weaker than those from $L_2$. Also the fragment intensity from $L_1$ relative to that from $L_2$ should not be used for conclusions, because fragmentation in the former is very minor and certainly intensity dependent, whereas from $L_2$ the fragments dominate. In section 4.2 we conclude from the drastic increase of fragmentation that $L_2$ is much below $L_1$.

One could expect that the $\sigma_i$ from corresponding locations $L_i$ coinide for the two isotomers. This is the case within a factor of 2 for the higher probe intensity (Table 1). For the fragments at lower intensity there are more deviations, perhaps due to their strong sensitivity to the intensity. (The intensity might have been slightly different from day to day.)

In the context of the isotope shifts, the error limits of the time constants and frequencies would be interesting. In previous experiments we used for this purpose the standard deviation found, when each of $\pm 10$ scans was evaluated and the results averaged. In the present case this is difficult, however, due to the multipstep evaluation procedure (subtraction of the $L_0$ contribution, for $L_2$ also subtraction of the $L_1$ contribution, division by the exponential parts, etc.); as a consequence not only is the analysis of each scan tedious, but the errors of the different quantities will also be interdependent. Nevertheless, to get an estimate at least for the more important numbers ($\tau_i$ and the vibrational wavenumbers), we instead averaged the measured data of 8 scans each and then evaluated them. Then the same was done with another such set (for $C_2H_4$ it was measured at the higher probe intensity, for $C_2D_4$ on another day) and the results compared. The ($\pm$) deviation from the average was

- for $C_2H_4$: 3% for $\tau_1$ and $\tau_2$; 5%, 0.5%, 1% and 3% for $\nu_2$, $\nu_3$, $\nu_4$, $\nu_5$,
- for $C_2D_4$: 4% for $\tau_1$; 0.6% and 3% for $\nu_4$ and $\nu_5$.

In view of the small deviations it is probably safe to estimate an error limit of $\pm 5\%$, also for the time constants and wavenumbers, for which the fluctuation was not investigated.

### 4. Discussion

#### 4.1. Generation of the Short 162 nm Pulses

It was previously considered difficult to produce short pulses in the deep UV or even vacuum UV. In this region the refractive-index dispersion of windows, nonlinear crystals and even gases is larger than at longer wavelengths; it gives rise to chirping and pulse lengthening. Compression methods for chirped pulses in the UV are not yet satisfactory (see, e.g., the limited success with a prism compressor in ref 66) and would first require some development (such as that using flexible mirrors65). Our method generating the third66 or fifth harmonic65 in a short gas cell, which introduces only little dispersion, leaves the duration of the pulses unaffected, or even shortens them a little due to the nonlinearity of the process. (It was shown in ref 66 that even tunable radiation can be generated in a variant of such a setup.) Starting with pulses of 700 $\mu$J and 12 fs at 810 nm, we obtained 11–12 fs pulses at 162 nm with an estimated energy of 4 nJ, with still some room for optimization.65

It was enough to pump ethylene. Its absorption cross-section in this region ($\sigma \approx 3 \times 10^{-17}$ cm$^2$, Figure 1) implies a saturation energy density of $h\nu/\sigma = 40$ mJ cm$^{-2}$; 0.3% of it (section 2) will excite 0.3% of the molecules. This requires only mild focusing (to 3 $\times$ $10^{-3}$ mm$^2$, which is the focus cross section estimated in section 2). This energy and the percentage of excited molecules was even sufficient to detect very weak signals such as those originating from molecules after their return to the ground state (section 4.2.3); for ionization from there, five more probe photons are required than from the Franck-Condon region. Previous experiments59–62 did not detect such signals.

Short time constants can in principle also be extracted by deconvolution from measurements with longer pulses, and this has been done in the previous experiments on the dynamics of ethylene,59–62 if several linearly independent (ion) signals are available, more than one such constant can be deduced.63,69 The potential and limitations of this method are discussed in ref 69. But high-frequency periodic oscillations cannot be extracted by

| TABLE 1: Lifetimes $\tau_i$ of Population in the Locations $L_i$, Ionization Cross-Sections $\sigma_i$ To Produce an Ion of Mass $m$ (in Parentheses in Column 1) from $L_i$ and the Oscillation Frequencies from $L_i^*$ |

<table>
<thead>
<tr>
<th>$L_i$ (C$_2$H$_4$):</th>
<th>$L_R$</th>
<th>L$_i$</th>
<th>L$_i$</th>
<th>L$_i$</th>
<th>L$_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_i$</td>
<td>80 fs</td>
<td>214.1 fs</td>
<td>16.5 fs</td>
<td>0.60 ps</td>
<td>5.0 ps</td>
</tr>
<tr>
<td>C$_2$H$_4^+$ (28 u)</td>
<td>0.1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.07</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4^+$ (27 u)</td>
<td>0.08</td>
<td>1</td>
<td>0.3</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>0.2</td>
<td>1</td>
<td>2.3</td>
<td>0.018</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4^+$ (26 u)</td>
<td>0.07</td>
<td>1</td>
<td>0.7</td>
<td>0.001</td>
<td>0</td>
</tr>
<tr>
<td>0.08</td>
<td>1</td>
<td>1.6</td>
<td>0.002</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$\nu$/cm$^{-1}$</td>
<td>631, 1113, 1572</td>
<td>1263</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C$_2$D$_4^+$):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$, $\nu_2$, $\nu_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_4$, $\nu_5$, $\nu_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$/cm$^{-1}$</td>
<td>512, 891, 1263</td>
<td>1190</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C$_2$D$_4$):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$, $\nu_2$, $\nu_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_4$, $\nu_5$, $\nu_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$/cm$^{-1}$</td>
<td>512, 891, 1263</td>
<td>1190</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Estimated error limits for the time constants and frequencies are $\pm 5\%$. The $\sigma_i$ values printed in italic are for a probe intensity of $10^{13}$ W cm$^{-2}$, the others for $\approx 3 \times 10^{11}$ W cm$^{-2}$. The picosecond time constants $\tau_i$ and $\tau_4$ were determined with the higher intensity, which raises the corresponding signals (Figure 5b).
deconvolution. To detect them, short pulses are needed. It is shown also in this work how much information is obtained from such oscillations.

4.2. Assignment of Time Constants and Oscillation Frequencies. The observation windows $L_i$ are locations (regions) on the potential surfaces, which are to be identified by the assignment. The evaluation in section 3 has delivered population lifetimes $\tau_i$ for them and for some $L_i$ also oscillation frequencies. The $L_i$ are also associated with different mass spectra (fragmentation patterns), ionization probabilities and orders of ionization, and these properties help to assign the $L_i$ to different locations or regions on the potential surfaces: Electronic relaxation lowers the electronic energy and therefore reduces the ionization probability (signal intensity) and raises the order of ionization; the latter is determined from observing the signal on variation of the probe intensity. Because the total energy is conserved during relaxation, vibrational excess energy is released, and ionization of such a hot molecule gives rise to a

Figure 4. Fragment ion signals. (a, c, e) $C_2H_2^+$; (b, d, f) $C_2D_2^+$. (a, b) full signals and a fit curve to the slower decay (time constant $\tau_B$, with convolution). (c, d) Signal (full circles) after subtraction of the slower decay, simulated by the full-fit curve; subtraction of the $L_1$ contribution (curve with early maximum) yields the $L_2$ contribution (crosses), which is fitted by exponentials (time constants $\tau_1, \tau_2$, with convolution). (e, f) The data after subtraction of the Rydberg contribution (full circles) and after subtraction of the $L_1$ contribution (crosses) and their exponential simulation are again shown; dividing the $L_2$ data by the fit curve (minus 1) results in the oscillatory part (open circles), whose Fourier transform is plotted in the inset; their simulation by a function of type (1) is also shown.
hot ion that fragments before detection; the degree of fragmentation is thus also a measure of the electronic (or vibrational excess) energy of an individual $L_i$. The fit parameters $m$ and $\sigma_i$ reflect both the ionization probability and the fragmentation pattern (for details see ref 63).

Coherent oscillations can also help to identify the $L_i$, if independent spectroscopic information is available. They result from superposition of stationary vibrational states of the molecule in the location $L_i$. However, there is a chance to observe an oscillation only, if the vibration modulates the ionization or fragmentation probability. This is not expected, for example, if in the probe transition the lower and upper potentials are parallel, as is the case on ionization from a Rydberg state. There are also a number of other reasons why some oscillations may remain unobservable.  

For the assignment we start with knowledge of the potentials from spectroscopy and quantum chemistry (Figure 6). Initial excitation at 162 nm mainly populates the one-electron excited $\pi\pi^*$ (V) state (symmetry $B_{3u}$ in $D_2h$ if the $z$ axis is chosen to coincide with the CC bond and the $x$ axis perpendicular to the molecular plane). According to Figure 1, the lowest Rydberg state ($\pi3s$ or $R3s$, $B_{1u}$) state is excited in parallel with about 5–10 times less probability. The $\pi3s$ state is slightly lowered on CC twisting, reaching a minimum near $25–30^\circ$ and rising again beyond. On the other hand, the $\pi\pi^*$ potential is lowered by about 2 eV by twisting by 90°. The two potentials intersect each other at a torsional angle of $\approx35^\circ$. Therefore population can flow easily (i.e., with very little activation energy) from the Rydberg $\pi3s$ state to the $\pi\pi^*$ surface and from there further down (Figure 6).

According to the present understanding, the way down from the Franck–Condon region of the $\pi\pi^*$ state involves not only CC torsion $q$ (which gives rise to a horizontal tangent at $q = 0$ and hence to only slow initial acceleration) but also CC stretching. The latter is not indicated in Figure 6. Near $q = 90^\circ$, the V and Z states become nearly degenerate and easily
exchange population. After reaching \( q = 90^\circ \), the molecule takes a new relaxation direction to reach a conical intersection (CI) with the ground-state (S\(_0\)) surface. The new direction involves pyramidalization of one CH\(_2\) group and/or partial migration of an H atom from one C to the other (see Introduction). After passing through the CI, the molecule can either directly reach the \( S_0 \) minimum of C\(_2\)H\(_4\) or, if H migration is involved, temporarily arrive at a structure corresponding to the carbene CH\(_3\)CH (ethyldene, not indicated in Figure 6). Ethyldene very rapidly rearranges on a barrierless path in the ground state back to ethylene (section 4.2.3). In the hot \( S_0 \), H and H\(_2\) eliminations can take place (section 4.2.3).

### 4.2.1. Franck–Condon Region

The parent-ion signal contains strong contributions from observation windows (L\(_2\) and L\(_1\)) with time constants \( \tau_{L2} \) and \( \tau_1 \), whereas it does not show the time constants \( \tau_2 - \tau_4 \). That is, from these locations L\(_4\) and L\(_1\) the ionization probability is highest, and fragmentation probability is lowest. Obviously they represent the Franck–Condon region. The signal contribution from L\(_4\) is about 10 times smaller than that from L\(_1\). This is practically the same as the estimated ratio (5–10) of excitation probabilities of the \( \pi\pi^* \) and \( \pi 3s \) states (see above and Figure 1). Therefore we assign L\(_4\) to the Rydberg \( \pi 3s \) state (lifetimes \( \tau_{L4} = 80 \) and 115 fs for C\(_2\)H\(_4\) and C\(_2\)D\(_4\), respectively) and L\(_1\) to the \( \pi\pi^* \) state (lifetimes \( \tau_1 = 21 \) and 24 fs, respectively) (Figure 6). This assignment is supported by the oscillations, which are observed in the \( \tau_1 \) window but not in L\(_4\): Although vibrational coherence is certainly also generated on exciting the Rydberg state, it should not be observed on probing by ionization, because of the parallel potentials, as explained above.

On excitation of the \( \pi\pi^* \) state, a coherent superposition can be expected for Franck–Condon active vibrations. This will be mainly the torsion (twist, \( \nu_4 \)) and probably also the CC stretch (\( \nu_2 \)); the resonance–Raman spectrum also suggests some activity of the symmetric scissors vibration (\( \nu_3 \)) and its antisymmetric counterpart (\( \nu_{12} \)) and out-of-plane wagging (\( \nu_9 \)).\(^{5,10}\) In \( S_0 \), full deuterium substitution reduces all these frequencies by a factor of \( 1.41 - 1.33 \) except the CC stretch vibration (\( \nu_2 \)), which is reduced by a factor of \( 1.07\)\(^{72}\) as the inverse ratio of the square root of the moving masses. For the coherent oscillations \( \nu_{\alpha}, \nu_{\beta} \) and \( \nu_c \) observed in the \( \pi\pi^* \) state (L\(_1\)) the corresponding factors are 1.23, 1.25 and 1.24, respectively (Table 1, Figure 7a). Hence not one of them involves a pure hydrogen vibration; all must be mixed and contain some CC stretch. From the wavenumbers one may suppose that the CC stretch dominates in \( \nu_{\beta} \) (1110 cm\(^{-1}\) in C\(_2\)H\(_4\)); then the torsion will dominate in \( \nu_{\alpha} \) (630 cm\(^{-1}\) in C\(_2\)H\(_4\)), and \( \nu_c \) (1570 cm\(^{-1}\) in C\(_2\)H\(_4\)) will be the combination vibration of the two. The latter wavenumber would be too high to assign it to a CC stretch (ground-state value 1623 cm\(^{-1}\);\(^{72}\) which should be drastically reduced in a \( \pi\)-antibonding state).

The wavenumber of \( \nu_4 \) is by 9% smaller than the sum \( \nu_\alpha + \nu_\beta \), which is in the range of common anharmonic shifts.

This assignment is also supported by the recurrence times of the wave packets calculated after excitation to this energy region by Viel et al. and Brill et al.\(^{12,34}\) The CC distance oscillates with a period of \( 25 - 30 \) fs, corresponding to a wavenumber of \( 1330 - 1110 \) cm\(^{-1}\); the torsion has a recurrence time near \( 45 \) fs (740 cm\(^{-1}\)). The calculation also predicts a small amplitude for the scissors vibrations (similar frequency as CC stretch; but note that we need a strong participation of the CC stretch vibration to explain the small isotope shift that we observed) and a practically negligible amplitude for wagging. The calculation further points out that the CC distance shortens on twisting (after lengthening at the initial zero twist), so that the two motions are not separable. This can explain the mixed character of the vibrations, concluded above from the small isotope shift, and also the observation of a combination vibration. Interestingly, Barbatti et al. find in their surface-hopping study a periodicity of \( \approx 20 \) fs (1660 cm\(^{-1}\)), well consistent with our combination vibration of 1570 cm\(^{-1}\) in the \( S_1 \) population, if excited at 160 nm (Figure 4 in ref 35); because \( V \leftrightarrow Z \) relaxation only takes place at a certain geometry (near \( q = 90^\circ \)), this periodicity must reflect a vibration, which contains the torsion. Our findings thus also confirm the quantum chemical calculations of\(^{12,34,35}\)

In the spectra (Fourier transforms, Figure 3e,f) of the oscillations in the Franck–Condon regions the relative intensity of the combination frequency over that of the fundamentals is not the same for C\(_2\)D\(_4\) and C\(_2\)H\(_4\). This is not unexpected, if the anharmonic interaction between CC stretch and torsion differs for the two isotopomers. Such interactions usually depend on frequency differences and hence on isotopic substitution. Probably one can interpret in the same way the different intensity ratios of CC stretch (which is weak in C\(_2\)D\(_4\)) over that of CC torsion (which is weak in C\(_2\)H\(_4\)). The narrow width of the CC stretch of C\(_2\)D\(_4\) (Figure 3f) is probably an artifact of the Fourier transform, because it is not reflected in the dephasing time in the simulation of the time-dependent data. Also the peak near 2100 cm\(^{-1}\) for C\(_2\)H\(_4\) may be spurious, although it would fit to the next member (\( \nu_4 = 2 \)) in the sequence \( \nu_2 + \nu_4 \).

The isotope effect on the time constants (Figure 7b) will be discussed in section 4.2.5.

### 4.2.2. Departure from \( S_0 \)

The time constant \( \tau_2 \) is not contained in the parent-ion signal but only in the two fragments. This means that from L\(_2\) ionic fragmentation is complete (in contrast to L\(_3\) and L\(_4\), from which the parent ion dominates, Table 1), indicating that L\(_2\) is much lower in energy than the Franck–Condon region. Because the next two windows (L\(_3\) and L\(_4\)) are already on the \( S_0 \) surface (section 4.2.3), \( \tau_2 \) must be the
time for leaving $S_1$. The oscillation observed in $L_2 (\nu_d = 1260$ and 1190 cm$^{-1}$ for C$_2$H$_4$ and C$_2$D$_4$, respectively) must then be a vibration in the lower part of the $S_1$ surface. The isotope shift (6%) indicates that it is a pure CC stretch vibration. Interestingly, Foo and Innes found in the long-wavelength part of the UV spectrum of C$_2$D$_4$ a progression displaced by 1250 cm$^{-1}$ from the main (\nu_2) progression.\(^8\) They assign this shift to a \nu_2 quantum, i.e., to a CC stretch vibration in the lower part of $S_1$. The agreement with our 1190 cm$^{-1}$ seems to us good enough (see end of section 3 for the estimated accuracy) to support our identification of \nu_d and location L$_2$ (see next paragraph, however). Furthermore the increase of the CC stretch wave-number from L$_1$ to L$_2$ (\nu_h compared to \nu_2) by 15–30% is fully consistent with the theoretical prediction\(^12,19–21\) that the CC bond is shorter at $\varphi = 90^\circ$ than at 0°, implying a stronger bond in the twisted structure. It is even more strengthened and shortened, when an H bridge forms on the way to H migration.\(^20\)

The agreement of our CC stretch frequency with the spectroscopic value for the region near the perpendicular $S_1$ “minimum” (C$_2$H$_4$ with D$_{2d}$ symmetry) does not necessarily mean that our L$_2$ is exactly there. If \tau_2 is the time for leaving $S_1$, L$_2$ should extend to the S$_1$/S$_0$ CI; a change of ionization probability (hence a termination of the observation window L$_2$) will take place especially there, where the electronic energy quickly drops and the electronic state is changed. Hence in L$_2$ there will also be some pyramidization and/or H migration in addition to the 90° torsion. In fact, quantum chemistry predicts that the D$_{2d}$ structure is not a minimum (which would imply some residence time) but a saddle point.\(^19,21,26,27\)

During a drastic geometrical change such as pyramidization and/or H migration any initial twist vibration will strongly change its character and wavenumber (from an initial value near 800 cm$^{-1}$ in the D$_{2d}$ geometry\(^7\)). Furthermore, near this structure the zwitterionic state begins to be populated, in which the twist vibration has a much higher frequency (note the strong curvature of the Z potential in Figure 6). Any initial coherence would be rapidly lost by such frequency variations. It is therefore not surprising that a coherent twist oscillation (\nu_4) and its combination with CC stretching (\nu_2) is not observed from L$_2$. (In fact, a \nu_4 oscillation has been observed in $S_1$ of C$_2$F$_4$, where the zwitterionic state seems to be higher in energy and not involved in the relaxation process.\(^7\)) It is also not surprising that any \nu_3/\nu_4 mixing is completely different between the two windows L$_1$ and L$_2$, as indicated by the different isotope effect. In L$_1$ the twist is a hindered free rotation; along the large angular excursion the CC distance changes (see above) so that the two motions couple. In L$_2$ the twist amplitude is much smaller (Figures 6 and 7a), so that the CC distance remains constant and the two motions are decoupled.

In a previous investigation of the ultrafast dynamics of ethylene (pumping by 130 fs pulses at 198 nm), Stett et al.\(^62\) also found a second time constant with values (\tau_2 \approx 15 and 25 fs for C$_2$H$_4$ and C$_2$D$_4$, respectively) very similar to ours. The cutoff in the photoelectron spectrum, measured by a coincidence technique from this window, indicates that the probe laser (792 nm, 1.56 eV) does not reach the energy minimum of the parent ion but a higher state. Indeed, the electronic ground state of the ion is raised by geometric distortion. In Figure 8a, we adopt the calculated ion energies of 1.3 eV (above the ion ground state) for D$_{2d}$ (perpendicularly twisted) geometry\(^74\) and the value 1.2–1.4 eV calculated for CH$_3$CH$^+$ or a bridged variant of it;\(^75\) these energies are 11.8 eV above neutral C$_2$H$_4$. Using the 0.85 eV cutoff energy of the photoelectrons in five-photon ionization,\(^62\) we obtain an electronic energy of L$_2$ of 4.8 eV (Figure 8b). (We tacitly assume ionization with $\Delta \nu = 0$, i.e., parallel potentials for the neutral molecule and ion in this region. This assumption seems necessary to explain the sharp cutoff observed.) This value is entirely conceivable for the region between the perpendicular D$_{2d}$ minimum (5.5 eV\(^8\)) and the S$_1$/S$_0$ CI: Furthermore, it is fully consistent with the twisted-pyramidalized CI of 4.5 eV of the recent high-level calculations\(^5\) (see also Figures 5 and 6 there\(^\text{20}\)). This experimental evidence hence also supports the assignment of L$_2$ to a region extending to the last CI from around the D$_{2d}$ minimum. Furthermore, we can conclude on the molecular structure in L$_2$ before reaching the CI: Because the photoelectrons were measured in coincidence with the C$_2$H$_2^+$ signal and because H$_2$ elimination from the C$_2$H$_4^+$ ion takes place only after partial or complete H migration,\(^74,76\) such a rearrangement must have happened in the neutral molecule, too, before vertical ionization. A similar conclusion on the structure after passing the CI is drawn in the next section.

### 4.2.3. Ground-State Processes

The signal parts with long time constants \tau_3 and \tau_4 (reflected in the tails of the two fragment ion signals, Figure 5) are already very weak, for both fragments by 2–3 orders of magnitude weaker than from L$_2$ (Table 1, Figure 5). This indicates that ionization from L$_3$ and L$_4$ requires 1–2 more photons for ionization than from L$_2$. (This conclusion is supported by the probe-intensity dependence of the C$_2$D$_2^+$ and C$_2$D$_4^+$ signals; the latter is illustrated in Figure 5b. The evidence from the nondeuterated signals is not so clear-cut however.) So, \tau_3 and \tau_4 are most probably time constants of reactions in the hot ground state. (See the end of this section for an interpretation, why both signals decay to 0.) Several reactions are known from hot C$_2$H$_4$ resulting after internal conversion.\(^40,41\)

The branched first step in this scheme can give rise only to one observable time constant (inverse of the sum of the three rate constants), which would be the lifetime of the hot ethylene. The subsequent (exothermic) step in (2a) would be too fast to be observed after the slow (strongly endothermic) first step. Although the second step in (2b) (less endothermic than the first) is energetically not accessible at 193 nm, RRKM calculations predict that it is 8–12 times faster than the first with the excess energy available with 157 nm (7.9 eV) excitation.\(^52\)}
is probably similar to our 162 nm (7.65 eV), so that also this step will not be observed. Similar considerations apply to the third line, because CH3CH decays primarily back to ethylene (see below), faster than it is formed. So only one of the two time constants \( \tau_3 \) and \( \tau_4 \) can be explained by Scheme 1.

Here one should recall the possibility that CH3CH forms not only from ethylene (reaction 2c) but also directly from the S1/S0 CI. If this is the case, this path is much faster (17 fs) and kinetically independent from reaction 2c. Ethylidene rearranges rapidly to ethylene\(^{77}\) in a nearly barrierless\(^{78,79}\) process; but H2 and probably H elimination from it is also observed (Scheme 2).\(^{78}\) This means that dissociation is competitive with rearrangement.

The three reactions will again give rise to only one observable time constant. It is independent of that characterizing reactions 2. We conclude that already the fact that two ground-state time constants (\( \tau_3 \) and \( \tau_4 \)) are observed points to formation of ethylidene directly from the CI, independently of the path (2c).

Reaction 3a is strongly exothermic (by \( \approx 3 \) eV\(^{80}\)) and barrierless or nearly so.\(^{78}\) We can expect that it is faster than the endothermic reactions (2). This is confirmed by RRKM calculations, which predict rates of \((6-8.5) \times 10^{12} \) s\(^{-1}\) for it.\(^{52}\) Therefore we assign our \( \tau_3 \) to the lifetime of hot CH2CH (caused by the set of reactions (3)) and our \( \tau_4 \) to the lifetime of hot C2H4 (set of reactions (2)).

This assignment is also supported by the fact that the longer time constant (\( \tau_4 \)) is only contained in the C2H4\(^+\) signal but not in the C2H3\(^+\) signal (Figure 5). This point shall be explained by Figure 9: It is generally accepted that H2 elimination from the C2H4\(^+\) ion takes place only after hydrogen migration, i.e., from the ethylidene ion (left-hand side in Figure 9).\(^{74,76}\) Hence vertical ionization of hot CH2CH will reveal its short lifetime (\( \tau_3 \)) in the C2H2\(^+\) ion (also in the C2H2\(^+\) ion, see Figure 9), whereas from ethylene in its hot ground-state (lifetime \( \tau_4 \)) vertical ionization and subsequent fragmentation will primarily lead to C2H3\(^+\), so that \( \tau_4 \) will be detected only in this signal, as is indeed the case (Figure 5). (Such a preferential elimination of H over that of H2 was also found, when C2H4 was generated as H2CCCH2\(^+\) with D\(_2\) signal by multiphoton ionization that was two-photon resonant with Rydberg states.\(^{81}\)) This also means that the ionic dissociation is kinetically controlled; if it were thermodynamically controlled—i.e., only by the excess energy, independent from which location on the potential it starts—both channels would be equally probable, because the appearance potentials of the ions C2H3\(^+\) (13.22 eV) and C2H2\(^+\) (13.14 eV) are practically identical.\(^{82}\) Also our observation of different kinetics of the C2H3\(^+\) and C2H4\(^+\) signals points to kinetic control of C2H4\(^+\) dissociation.

The D isotope effect on \( \tau_4 \) is larger (2.2, Figure 7b) than for a barrierless hydrogen motion (1.41) but probably consistent with the assignment to the endothermic H elimination. Also the D effect on \( \tau_3 \) (2.67) indicates an activated process. Perhaps this is because the (endothermic) H2 elimination contributes to \( \tau_3 \). It indicates that also the ethylidene \( \rightarrow \) ethylene rearrangement by H migration is not completely barrierless, although some calculations predict that.\(^{78}\) A minor barrier seems to us consistent with some photochemical observations (see below). It is also suggested by a similar deuterium effect (3.2) for H migration in the homologue dimethylcarbene at room temperature in pentane.\(^{77}\) In the same work\(^{77}\) a lifetime of CD3CD of 500 ps was deduced, on the basis of the assumption of a rate for the scavenging reaction; because this lifetime is by 3 orders of magnitude longer than ours, we suppose that the scavenging process in ref 77 probably took a different path.

With the given interpretation, all the hot ground-state products (ethylene and ethylidene) will eventually end in acetylene (reactions 2 and 3). It will certainly still have some excess energy. It is well conceivable that this end product was not detectable, because (1) it has an even higher ionization energy (11.4 eV) than ethylene (10.5 eV),\(^{83}\) so that one more photon (altogether 8) would be needed for ionization, and (2) with the available excess energy it would fragment after ionization, so that its signature would only appear in lower-mass fragment ions that were not investigated. It is therefore not surprising why the C2H3\(^+\) and C2H4\(^+\) signals both decay to 0.

We can now summarize the main basis of the assignment of the L\(_0\): L\(_1\) and L\(_R\) are the two states (\( \pi\pi^* \) and Rydberg \( \pi\delta^* \)) directly populated by the primary excitation, as known from spectroscopy. L\(_2\) is a state much lower in energy, as indicated by the drastic change of the fragmentation pattern (no parent ion from L\(_2\)); this location probably extends from the V\(_1\)-Z\(_0\) intersection to the last CI. Vibrational frequencies (from coherent oscillations), the time-resolved photoelectron spectra from literature and the quantum-chemical calculations are consistent with this assignment. L\(_3\) and L\(_4\) are located on the S0 surface (with CH3CH and H2CCCH2 structure, respectively); the main evidence is the ionization probability, which is by 2–3 orders of magnitude smaller than from L\(_2\). The lifetimes are also in the predicted range for isomerization (CH3CH) and dissociation.

---

**SCHEME 1: Ground-State Reactions of Hot Ethylene**

\[
\begin{align*}
\text{H}_2\text{CC} + \text{H}_2 & \rightarrow \text{HCC} + \text{H}_2 \quad (2a) \\
\text{H}_2\text{CCH}_2 & \rightarrow \text{HCC} + \text{H}_2 \quad (2b) \\
\text{H}_2\text{CCH} & \rightarrow \ldots \quad (2c)
\end{align*}
\]

**SCHEME 2: Ground-State Reactions of Hot Ethylidene**

\[
\begin{align*}
\text{H}_2\text{CCH}_2 & \rightarrow \ldots \quad (3a) \\
\text{H}_3\text{CCH} & \rightarrow \ldots \quad (3b) \\
\text{H}_2\text{CCH} + \text{H}_2 & \rightarrow \ldots \quad (3c)
\end{align*}
\]
(CH$_3$CH, H$_2$CCH$_2$). The expected end product (HCCH) was not detected.

In Figure 10, we summarize the complete path of the molecule from the Franck-Condon region down to the ground state. The Rydberg part (see Figure 6) is omitted from this figure. As already said, the L$_1$ window (departure from the Franck-Condon region) reaches down to perhaps not far from the V-Z intersection. In this region the L$_2$ window begins, reaching as far as to the S$_1$/S$_0$ CI. From the observation of reactions of ethylidene, we conclude that this CI is displaced from the perpendicular (D$_{2b}$) minimum in a direction involving H migration (outside the drawing plane of Figure 10). From the CI the path branches (1) to completion of this migration (perpendicular to the drawing plane) and the displacement of the CI into this direction. The path starting in the Rydberg state (Figure 6) is omitted. The two ground-state reactions, which were not yet assigned in Figure 7b, are now also identified. The pyramidalization of one CH$_2$ group, predicted theoretically, is not indicated. As argued in section 4.2.5, the turn to a new direction (to H migration and pyramidalization) does not occur so sharply (as indicated) in the perpendicular minimum but begins earlier and more smoothly.

4.2.4. Results of Spectroscopic Relevance. As explained in the Introduction, the UV spectrum of ethylene keeps being investigated. A difficulty is the diffuseness of the vibrational structure, in particular in the nondeuterated isotopomer. The broadening caused by the short lifetime (21 and 24 fs) is 230 cm$^{-1}$ for C$_2$H$_4$ and 200 cm$^{-1}$ for C$_2$D$_4$, which can be compared with the observed width of 400 cm$^{-1}$ of vibrational peaks (near 180 nm, Figure 1; for the width at low temperature, see below) for the nondeuterated isotopomer. A certain spectral congestion seems to contribute to the widths. This is certainly also why the spectra of the two isotopomers only bear little similarity (Figure 1). Furthermore, the maximum of the $\pi\pi^*$ absorption is covered by the Rydberg $\pi 3s$ band with its pronounced structure, and the assumption is widespread that the $\pi\pi^*$ band below it is a continuum (Figure 1). This is not justified, however, as demonstrated by the spectra in condensed phase (Figure 11), in which Rydberg transitions are broadened and displaced to higher energies: Also around the $\pi\pi^*$ maximum near 162 nm, these spectra show a clear vibrational progression (680 cm$^{-1}$). Unfortunately the corresponding spectra of C$_2$D$_4$ are structureless or nearly so. In contrast, in our method we probe by ionization from the excited state, where the Franck-Condon factors are different from those of the S$_0 \rightarrow$ S$_1$ transition. Therefore we can find some vibrations not detected in normal UV spectra, in particular also for the deuterated isotopomer.

At the long-wavelength end of the spectrum, there should be no congestion that could contribute to the broadening. In fact, the width found for a peak near 190 nm in C$_2$H$_4$ at $-78^\circ$ is $\approx 280$ cm$^{-1}$, this implies a lifetime $\approx 18$ fs of population near the perpendicular minimum. This is well consistent with our $\tau_2$ and the $\tau_3$ of Stett et al. (which we attribute to departure from S$_1$), but less well consistent with the $\tau_1 \approx 10$ fs measured in ref$^{21}$ with excitation at 198 nm (to an energy of $\approx 0.7$ eV above the perpendicular minimum).

There is agreement that the prominent progression is formed by CC twisting in a potential with minimum (in a cut in this direction) at 90$^\circ$ and maximum at 0$^\circ$. In the long-wavelength wing the spacing ($\approx 800$ cm$^{-1}$) corresponds to one vibrational quantum near the minimum.2,4,7 Actually, each vibrational level there is double, with wave functions with and without node below the barrier.$^{80}$ Near and beyond the spectral maximum, the structure corresponds to hindered free rotation, and for symmetry reasons in a cryogenic matrix or liquid, Figure 11) must correspond to two quanta. We find for the latter region (our observation window L$_1$) 630 and 510 cm$^{-1}$ for the two isotopomers, the former perhaps slightly less than in the matrix. Probably the matrix contributes to the hindering potential and thus raises the frequency. Recent calculations of the spectrum via the wave packet recurrence time found 680 cm$^{-1}$ or 650 cm$^{-1}$ for C$_2$H$_4$, very well consistent with our results. From the small deuterium effect (which was not possible to identify in the UV spectra and which was not yet investigated theoretically), we conclude that the twist in this region is actually mixed with the CC stretch (section 4.2.1). This is in agreement with the calculations, which predict that the CC bond is longer at 0$^\circ$ than at 90$^\circ$. The amplitude of the twist “vibration” in the Franck-Condon region comprises both angles and more. This is illustrated in Figure 7a.

The mixing of CC twist and stretch vibrations implies that in the latter the isotope effect should be larger than expected for a pure CC stretch. This is in fact observed in L$_1$ (Figure 7a), which is near the Franck-Condon region for 162 nm excitation. But in L$_2$ (the region from the perpendicular minimum to the CI) the observed vibration is a pure CC stretch, according to the small isotope effect (Figure 7a). In the long-wavelength part of the UV spectrum, this vibration was only observed with C$_2$D$_4$. Near $\varphi = 90^\circ$ the torsional amplitude is in fact much smaller than above the barrier (Figure 7a); on small
torsional excursion, the CC distance is not expected to vary much, so that the two vibrations will not couple.

Resonance Raman spectra suggest activity of more vibrations, including wagging (pyramidalization) and rocking (planar bend).\(^9,10\) In fact, such activity is expected, if the perpendicular minimum is actually a saddle point (see Introduction) toward pyramidalization and H migration. Simulations of the UV spectrum can perhaps reveal them, if they use experimental numbers for the more evident vibrations. Our data might help in this respect. So far, the published simulations used widely different numbers for excited-state vibrations.\(^{14,15,87–94}\)

### 4.2.5. Ultrafast Dynamics and Implications for the Potentials

The lifetime \(\tau_k\) (80 and 115 fs for the two isotopomers) found for the Rydberg \(\pi\pi^*\) state, excited at 162 nm (excursion energy 4400 cm\(^{-1}\) over the origin), is consistent with \(\tau_k \approx 100\) fs for \(C_2D_4\) deduced from a line width near the origin\(^8\) and a similar estimate in ref 71. A slight shortening at higher energy is expected, if there is a minor activation energy. In fact, the Rydberg potential has a minimum at a twist angle of \(\varphi = 25–30^\circ\) \(^71\) and rises by about 1.3 eV at \(\varphi = 90^\circ\) (Figure 6). (This value is taken over from the potential of the ion.\(^72\)\) At \(\varphi \approx 35^\circ\) it intersects with the \(\pi\pi^*\) \((B_{1u})\) state slightly above the \(\pi\pi^*\) state \((B_{3u})\) minimum, which can explain a minor barrier (Figure 6). Obviously the population can easily flow around the lower cone of the interaction (with a temporary distortion of \(\delta = b_{1g}\) symmetry, i.e., a CH\(_2\) pyramidalization) to the \(\pi\pi^*\) state and merge there with the population that has been excited directly to this state. This path seems to us evident, although in the spectroscopic literature (e.g., in refs 8 and 92) the leakage out from the Rydberg state was called predissociation. This view of merging populations has important implications for the photochemistry of olefins, where the \(\pi\pi^*\) band often precedes the \(\pi\pi^*\) band (section 4.2.6).

The previous experimental studies of the ethylene dynamics had less time resolution and extracted the time constants by deconvolution. With excitation at 155 nm\(^59\) or near 200 nm\(^60\), they found \(\tau_1 \approx 40\) fs, \(30\) fs, \(20\) fs\(^61\) and 10 fs\(^62\). Our \(\tau_1\) (21 fs) is within the error limit of the first three experiments and slightly out of this limit for the last one.\(^62\) According to refs 35 and 36, not much difference of lifetimes for different excitation wavelengths is expected. According to ref 69 there are \(\approx 100\) to \(>250\) fs (summarized in ref 36), whereas a method using semiempirical surfaces suggests 50 fs.\(^33\) Only the latter value would be consistent with our \(\tau_1 + \tau_2\). In the case of the ab initio surfaces, \(^{12,34–38}\) it seems to us that the initial geometrical (from \(\varphi = 0^\circ\) to \(90^\circ\) and CC stretch) relaxation is fast enough and that the actual bottleneck in the calculations concerns the departure from \(S_1\). If the latter step is too slow, it also influences the population in the Franck–Condon region due to the reversibility of the \(V\rightarrow Z\) relaxation. Perhaps in many calculations some minor barrier before the \(S_1/S_0\) CI causes the bottleneck (see later in this section). Also the following feature of the potentials may play a role:

The 17 fs for \(\tau_2\) seems to us so fast (the shortest time ever found for \(S_1\rightarrow S_0\) relaxation) that the absence of a barrier alone is not sufficient for explanation: If the wave packet arrived at the perpendicular minimum and then had to search around to find the new direction toward the CI, this would probably take some time, perhaps connected with some oscillations in the preceding directions. (Trajectory calculations might show that.) If, however, there were already an early (although minor) acceleration into the new direction, this time would be saved. In fact, the electronic \(V\rightarrow Z\) relaxation around the CI between the two surfaces involves an acceleration toward an asymmetric \((b_{1u})\) scissors coordinate,\(^25,35\) which can be interpreted as an incipient H migration, i.e., a component of the direction toward the last CI. Such minor features may still be difficult to find out by high-level calculations. For clarity, this early and smooth turn to a new direction in the \(\tau_2\) (17 fs) window is not indicated in Figure 10. An early acceleration toward the last CI has already been previously suggested to explain short lifetimes.\(^83,95,96\) At the end of this section, we argue that in \(L_2\) slopes in additional directions are also needed to explain other features of the relaxation process.

The small isotope effect (Table 1 and Figure 7b) observed (and already found in ref 62) in both \(\tau_1\) and \(\tau_2\) is remarkable. It means that during both phases not only hydrogen moves (e.g., along a twist coordinate) but also CC stretching or contraction is strongly involved. Hence the small isotope effects in the lifetimes and in the vibrations are likely to have the same origin: As already explained in the context of the vibrations (sections 4.2.1 and 4.2.4), according to the calculations\(^{12,19–21}\) in the Franck–Condon region \((L_1)\) the CC bond length initially expands and then toward \(\varphi = 90^\circ\) contracts again and does so further on the way to a H-migration CI. It would be desirable to check by calculating the dynamics also of \(C_2D_4\) whether this feature is responsible for the small deuteronium effect for lifetimes and vibrational frequencies. In the previous experiment of Stert et al. (which had less time resolution), the deuteronium effect on \(\tau_1\) and \(\tau_2\) was also found to be small, namely within their error limit.\(^62\) For the Rydberg lifetime \(\tau_R\) the D effect is normal, as expected for a motion along a pure twist via a nearly negligible barrier (see above). The D effect for the ground-state reactions was already discussed in section 4.2.3.
The ground-state processes, which we found, indicate that one of the time constants ($\tau_1$) represents the lifetime of the carbene CH$_2$CH and the other ($\tau_4$) that of hot ethylene, implying that both species are formed from the same S$_1$/S$_0$ CI (section 4.2.3). This means that the CI involves a partial H migration. More strictly speaking, the intersection-space region involving such a migration seems easily accessible for the wave packet (probably supported by an early acceleration into this direction near the V/Z CI, see above), although perhaps a region without it (but with twist and pyramidalization, for instance) might be competitive. An H-migration CI was already suggested by Evleth and Sevin and by Ohmine$^{29,30}$ and its importance pointed out once more by Freund and Kissinger,$^{26}$ although they predicted a less symmetric structure. Later calculations preferred the one-sided pyramidalization (after a 90° twist).$^{21,27,37−39}$ Recent high-level calculations point out the importance of H-migration for understanding hydrogen scrambling before dissociation.$^{30,35}$ However, they suggest that this CI (with imposed Cs symmetry) is not the minimum of the intersection space but a saddle point within it$^{20,35}$ (see also refs 27 and 31), whereas at a less high level and without symmetry constraint, the twisted-pyramidalized CI is at higher energy than the H-migration CI.$^{32}$ The result that releasing the Cs symmetry constraint lowers the H-migration CI was already obtained earlier.$^{26}$ The strong ethylidene signal in our experiment indicates that the H migration channel is at least competitive, perhaps even dominant. (It is remarkable in this context that the semiempirical dynamics calculation of Granucci et al.$^{33}$ used a low-energy H-migration CI and obtained a realistic S$_1$ lifetime, whereas the higher-level dynamics calculations, which did not have this CI or placed it at higher energy, obtained much longer lifetimes.$^{12,34−38}$) But we suppose that the landscape of the S$_1$ potential in the region between the perpendicular minimum and the last CI is rather flat in several directions; this would explain why a momentum acquired in the Franck–Condon region can influence the photochemical outcome in olefins (section 4.2.6).

The general picture of a wave packet relaxing down along potential surfaces (Figures 6, 7, and 10) deserves additional comments. The wave packet is accelerated by the slopes, so that electronic energy is converted in this way to nuclear motion in this direction. Figures 7 and 10 suggest that on the way from the FC region (L$_1$) all excess energy is deposited in the twist coordinate and (as concluded above from the small deuteron effect) in part also to CC stretching. If no new coordinates were activated in L$_2$ to accept kinetic energy, the molecule would, also in L$_2$, keep performing hindered free rotation (with amplitudes $\varphi > 180^\circ$) just as in the FC region. But the different isotope effect in L$_2$ indicates that the twist energy has dropped to some extent (amplitude $\varphi < 180^\circ$; see sections 4.2.2 and 4.2.4). Obviously the cut in twist direction (Figures 6, 7, and 10) only provides an incomplete picture, even with taking CC stretching into account; there must be additional downslopes. Candidates may be the pyramidalization and CH bending (or beginning H migration), which we suggested to be initiated on entering L$_2$.

It should be noted that with the involvement of more coordinates, the wave packet does not become diffuse (which would prevent observation of coherent oscillations), and thus the process does not involve intramolecular vibrational energy redistribution (IVR) in the statistical sense; statistical IVR is only expected later, when the wave packet is reflected from slopes in other regions of the potential. The conversion of electronic to nuclear kinetic energy may be facilitated before and after the last CI, where there are slopes in a number of coordinate directions. But the energy distribution resulting immediately after passing the CI is still not necessarily statistical.

A final question is whether the measured times are not too short for the applicability of the Born–Oppenheimer approximation of separate time scales for electronic and nuclear motion, and thus for the possibility to draw potentials. Indeed, our times are shorter than the periods of some vibrations. (E.g., for a CC stretch around 1200 cm$^{-1}$ or 0.15 eV the period would be 28 fs.) Nevertheless the electronic time scale is still much shorter, as to conclude from the energy difference between electronic states, which is several electronvolts, unless one is near a CI. In the latter region, electronic motion is slow, and this is just why the Born–Oppenheimer approximation breaks down and the wave packet can jump there to the lower surface.

4.2.6. Implications for Photochemistry. The fact that we observed a signal not only from hot ethylene (L$_4$) but also from ethylidene (L$_3$) after passing through L$_2$ implies that both species are formed from the same funnel, i.e., from the same region of the S$_1$/S$_0$ intersection space. Certainly also more generally the typical olefin reactions (cis→trans isomerization and carbene formation, besides internal conversion back to the reactant) originate and branch from the same CI or from a region nearby. Hence in the CI, H migration or an analogous alkyl-group migration has partially taken place (i.e., an H or alkyl bridge has formed), as pointed out above. This idea is also supported by the fact that it can explain several photochemical observations:

(1) In the condensed phase, reactions from the hot ground state are normally partially or completely suppressed, if the collisional cooling rate (typical time constant $\approx$10 ps, see, e.g., refs 97–99) is comparable to, or faster than, the reaction. H and H$_2$ elimination from ethylene have very similar activation energies (endothermicities) (see the energy diagrams in refs 52, 80, and 100) and should have similar rates. Nevertheless, the H channel is much more suppressed than H$_2$ elimination in condensed phase and even already in the gas by buffer gas.$^{41,101}$ This would not be understandable, if H$_2$ were formed from hot ethylene alone, even if this path can lead via ethylidene. However, if ethylidene is directly formed from the CI (i.e., not via ground-state ethylene), H$_2$ can form with very little activation energy (Figure 9), which implies much less temperature (and hence cooling-rate) sensitivity than via ethylene. The observation that H elimination is largely suppressed in the condensed phase also supports our assignment of a lifetime ($\tau_3$) of several picoseconds to this dissociation; an assignment to a subpicosecond time ($\tau_3$) would not be consistent with a suppression of this channel. Conversely, the survival of H$_2$ elimination in the condensed phase supports the assignment of the subpicosecond time ($\tau_3$) to this process.

(2) Photolysis of liquid or solid ethylene also gives rise to methycyclopropane, a typical product of a bimolecular reaction of a ground-state carbene (ethylidene) with the double bond of the olefin.$^{41,45}$ Already previously this product was taken as evidence for ethylidene formation from the CI.$^{45,47}$ Also the formation of butene-1 has been interpreted as a carbene insertion into the CH bond of ethylene.$^{45}$

(3) On the one hand, cis→trans isomerization and carbene formation in the photolysis of ethylene and other olefins was already repeatedly suggested to take place from the same CI$^{17,20,26,30,31,46,47,61,102,103}$ On the other hand, the yield ratio of carbene products to other reactions is larger, if alkylated olefins are irradiated at longer wavelengths, in the $\pi \rightarrow \sigma^*$ (or $\pi \rightarrow 3s$ Rydberg; the transition has a mixed character$^2$) band preceding the $\pi \rightarrow \pi^*$ band in these compounds (reviews: refs 43 and 44 see also refs 40–42); branching in the Franck–Condon region...
has been suggested in these cases. However, we argue (section 4.2.5 and refs 102 and 103) that the Rydberg/σ∗ and πτ∗ states exchange population via a low-lying intersection of the potentials, and the wavelength dependence is to be interpreted by the wave packet momentum, which depends on the initial state.102,103 Such a dynamical mechanism assumes that the momentum is conserved over a certain time and that the region of the CI is flat enough to permit an influence of the momentum on the branching. In ethylene itself, there is direct spectroscopic evidence that the π3s and πτ∗ potentials cross at low energy, so that population can easily flow (within τp = 80 fs) from the former to the latter state, as discussed above (section 4.2.5).

We can also draw some conclusions from the short lifetimes that we measured:

The quantum yield of photodimerization of ethylene to cyclobutane is not measurable in the gas phase, and in liquid ethylene it is slightly below 10−3 (calculated from the relative yield of cyclobutane101 and the quantum yield of H2). This seems natural in view of the small τ1 compared to a collision frequency. The latter is not well-defined in a condensed phase. But as a measure we can invoke one of the fastest collisional processes, cooling of the vibrational temperature, which has typical time constants around 10 ps (see, e.g., refs 97–99). Taking the ratio of our τ1 and the 10 ps estimate of the collision time, one can expect just the quantum yield that has been found, if the reaction is very efficient in a close encounter. (In fact, if the two double bonds are fixed in one molecule in a short distance, such as in norbornadiene, the photochemical [2 + 2]-addition is ultrafast.109) Photodimerization is more efficient with other olefins110,111 (see in particular the reviews in refs 105 and 106). In fact, they are likely to have longer excited-state lifetimes; some examples of longer lifetimes were found by Mestdagh et al. and by Hirayama and Lipsky.101,102,104 Substitution by alkyl groups lowers the π3s Rydberg state (which also has πσ∗ character) to slightly below the ππ∗ state, and population flows from the former to the latter (which is lowered along the twist coordinate) only via a small barrier (which is increased by lowering the Rydberg state)102,103 and some olefins even fluoresce from the π3s/πσ∗ state, if the excess energy is not too high (e.g., tetramethylethylene107–109), a measurable fluorescence yield (∼10−6) was even found from propylene,110 whereas from ethylene it could never be detected. One can also expect that the excited-state lifetime is prolonged by delocalization, extending the π system by attaching a phenyl or a carboxyl group, for instance. In fact, good dimerization yields are obtained from such compounds.105,106 Another effect that may enhance the dimerization yield is the direct excitation of van-der-Waals dimers (or molecule pairs fixed in another way, e.g., in a crystal106) to delocalized (“excimer”) states, typically in the long-wavelength wing of the spectrum. In this case the molecule does not have to wait for a collision. An example is the photodimerization of cyclohexene;102,104 the same mechanism was suggested for the dimerization of 7-dehydrocholesterol.111

Other bimolecular reactions are the expected addition reactions of polar reagents (e.g., methanol) to ethylene or other olefins in their zwitterionic excited state, which at 90° twist is nearly degenerate with the ππ∗ state and can undergo sudden polarization.17,22,23 The search for such reactions has not been very successful, and often it turned out that the addition products sometimes found were formed in the ground-state of a strained photoproduct such as the trans isomer of a cyclic olefin.105,106 The reason is now clear: The perpendicular excited state is too short-lived (τ2) to allow substantial yields of bimolecular reactions. To conclude from cyclohexene and norbornene, also in other simple olefins, the departure from S1 through the last CI is barrierless and the time constant is also not substantially longer than in ethylene. With certain substituents (e.g., with several phenyl groups), however, the perpendicularly twisted form is stabilized and its lifetime can be much longer; in such cases, evidence for sudden polarization effects have indeed been found (see ref 24 and literature quoted therein).

Another bimolecular reaction is the addition of ethylidene (formed in its S0 state from the CI) to ethylene. Its lifetime (τ1) is also short. (To our knowledge it is the first time it has been measured directly and a spectroscopic signature of ethylidene was detected.) But it is ≈ 30 times longer than τ1 or τ2. In fact, in solid ethylene, methycyclopropane and 1-butene (if this is also considered a carbene reaction product) are formed in substantially higher yields than cyclobutane.101 It was demonstrated that ethylidene (generated from another source) is long-lived enough to be trapped, for instance by reaction with CO in a cryogenic matrix, although its direct detection by time-resolved spectroscopy failed due the (supposed and now determined) short lifetime.113

5. Conclusion

This work demonstrates that shortening the pulses (in particularly the UV pump pulses) can reveal important new details in photochemical dynamics. Whereas previously, short time constants have been extracted from measurements with longer pulses by the help of deconvolution, it has only now been possible to nail down the small isotope effect on the lifetimes (an upper bound for it was found in ref 62), which in turn provides valuable information on the relaxation path and the potential. For resolving the coherent oscillations, short pulses are even indispensable; they cannot be extracted by deconvolution. For example, the 1570 cm−1 vibration with its 20 fs period requires a resolution around 10 fs. In the Franck–Condon region, the isotope effect on the torsion vibration (hindered free rotation) was found to be small; the vibration must therefore be strongly mixed with the CC stretch, similarly as the relaxation coordinate. In contrast, the vibration during departure from the S1 state is a pure CC stretch, which can be rationalized by the fact that the amplitudes of hydrogen vibrations are much more limited than in the Franck–Condon region.

The vibrational structure in electronic transitions of ethylene has been studied for decades, with the aim to find out the excited-state potentials. Such data are also used to test ab initio calculations, which are being pushed to higher and higher levels and which in turn provide a better understanding of the potentials and dynamics. We provide for the first time a set of vibrational data for both, C2H4 and C2D4, in the Franck–Condon region and in the region before departure to the ground state. They may also serve to calibrate simulations of UV and other spectra, to find out more vibrations.

Our results suggest that the initial relaxation on the ππ∗ (V) surface involves CC torsion as far as to 90° (within slightly more time than τ1), but from the beginning intimately coupled with stretching of the CC bond, which initially expands and then contracts again. (At large torsion the V state probably equilibrates with the zwitterionic (Z) state. However, our probing method cannot distinguish the V and Z states.) During τ2 already before a twist of φ = 90° is reached, the wave packet is gradually accelerated toward a new direction, which eventually (still within τ2) leads to a conical intersection (CI) with the ground-state surface. This additional distortion (besides a twist of 90° and some CC stretching) involves not only pyramidal-
ization of a CH₂ group (according to theory) but also partial hydrogen migration. This conclusion was deduced from the observation of CH₂CH (ethylidene) as a primary product besides hot ethylene. (The assignment was inferred from the detection of two ground-state reactions (time constants τ₁ and τ₂), indicating that there are two primary products.) It is well-known that the slope directions near the last CI decide on the fate of the reaction path and the type and yield of products. We use the observation of products to conclude on the slope directions.

In quantum chemistry the H-migration CI is still under debate.

Our data also support a scenario where the region extending from the perpendicular (D₃h) minimum to the last CI is energetically flat along the coordinates for H migration, pyramidalization and twist. This is how we explain that the initially excited state (Rydberg or ππ*). Previously, the wavelength dependence (i.e., the violation of the Kasha rule) was interpreted by assuming a branching in the Franck–Condon region. In contrast, we point out that the Rydberg state delivers its population (within τ₀) via a CI, which at least in ethylene is spectroscopically well-known and easily accessible.

We also discuss bimolecular reactions in view of the excited-state lifetimes that we found. The departure from the S₁ state (within τ₂ = 17 fs in ethylene) seems to be generally very short (<100 fs) in simple olefins (section 4.2.6), so that bimolecular reactions have little chance. This explains why the search for chemical consequences of sudden polarization (in the S₁ minimum) was not overly successful. The same interpretation might be valid for dienes. For longer-chain polyenes, however, a different explanation must be invoked: Although their 2A minimum) was not overly successful. The same interpretation (11) Ben-Nun, M.; Martinez, T. J. Chem. Phys. 2003, 119, 1397.


Dynamics and Oscillations in Ethylene and Ethylene-\textsubscript{d}\textsubscript{4}

JP803548C