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### ADVERTISEMENT



## Time-resolved dissociative intense-laser field ionization for probing dynamics: Femtosecond photochemical ring opening of 1,3-cyclohexadiene

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The concerted photochemical ring opening of 1,3-cyclohexadiene was investigated in the gas phase by low-intensity pumping at 267 nm and subsequent probing by high-intensity photoionization at 800 nm and mass-selective detection of the ion yields. We found five different time constants which can be assigned to traveling times along consecutive parts of the potential energy surfaces. The molecule is first accelerated in the spectroscopic state 1B along Franck-Condon active coordinates, then alters direction before changing over to the dark state 2A. All constants including that for leaving the 2A surface are below 100 fs. These times are shorter than appropriate vibrational periods. Such a maximum speed is evidence that the pathway is continuous leading from surface to surface via real crossings (conical intersections) and that the molecule is accelerated right into the outlet of the 2A/1A funnel. On the ground state it arrives as a compact wave packet, indicating a certain degree of coherence. The experimental method promises a high potential for investigating dynamics, since many consecutive phases of the process can be detected. This is because the fragmentation pattern depends on the location on the potential energy surface, so that monitoring several different ions permits to conclude on the population flow through these locations. Ionization at the intensities used is normally considered to be an effect of the electric field of the radiation. But in our case it is enhanced by resonances in the neutral molecule and in particular in the singly positive ion, and it is not sensitive for the length of the molecule (different conformers of the product hexatriene). The ionic resonances explain why hexatriene has a much richer fragmentation pattern than cyclohexadiene. Coulomb explosion is observed from an excited state of a doubly positive ion. Its mechanism is discussed. © 2000 American Institute of Physics. [S0021-9606(00)00819-9]

#### I. INTRODUCTION

Pericyclic reactions are not only important for organic chemistry, but they can also serve as model systems in reaction dynamics since it is easy to figure out qualitative potential energy surfaces for them on the basis of the Woodward-Hoffmann rules. An example is the photochemical electrocyclic ring opening of 1,3-cyclohexadiene. It has recently been investigated quantum chemically,<sup>1–4</sup> by resonance-Raman spectroscopy<sup>5–9</sup> and by ultrafast spectroscopy (transient absorption in solution<sup>10–13</sup> and transient ionization in the gas phase<sup>14,15</sup>). The molecule is excited in the UV spectral range (267 nm in this work) in a  $\pi\pi^*$  transition to the ("bright") 1B<sub>2</sub> state, which very rapidly decays to the ("dark")  $\pi\pi^*$  state 2A<sub>1</sub> (see also Sec. III and Fig. 2). The 2A<sub>1</sub> surface is higher than 1B<sub>2</sub> in the Franck–Condon region, but after a crossing with 1B<sub>2</sub> reaches a minimum or stationary point along the reaction coordinate. This so-called pericyclic minimum as well as a maximum of the ground-state surface at a similar geometry are characteristic of photochemically allowed, ground-state forbidden pericyclic reactions.<sup>16,17</sup> Both result from an avoided crossing of two



The energetic distance  $\Delta E$  of the 2A minimum (far from the Franck–Condon region we drop the subscripts 1 and 2, because of the reduced symmetry) from the 1A maximum is more than 1 eV.<sup>1</sup> According to the Landau–Zener formula (see, e.g., Ref. 16),

$$P = \exp\left(-\frac{\pi^2 \,\Delta E^2}{hv \,\Delta s}\right),\tag{1}$$

a molecule passing this geometry with a velocity v will cross over to the lower surface with a probability P;  $\Delta s$  is the magnitude of the difference of the asymptotic slopes. The larger  $v \Delta s$ , the larger is P. Using the fairly high values  $\Delta s = 5 \text{ eV}/\text{\AA}$  and  $v = 2 \times 10^{13} \text{\AA/s}$ , one obtains with the above  $\Delta E$  the very small  $P = 4 \times 10^{-11}$ . That is, the molecules will oscillate more than  $10^{10}$  times in the upper well before reaching the lower surface. This is unrealistically long. Times in the lower picosecond range for ring opening

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and internal conversion have been measured for the cyclohexadiene derivative 7-dehydrocholesterol,18 for cyclohexadiene itself and a dialkyl derivative.<sup>8,9,19</sup> More recently evidence has been presented for even shorter reaction times in the gas phase<sup>14,15</sup> and in solution.<sup>10-13,20</sup> (The discrepancy to the previous work is resolved in Refs. 13 and 20.) Here, as already in the brief account of this work,<sup>15</sup> we report a 2A lifetime  $t_{2A} = 77$  fs for cyclohexadiene in the gas phase. This is shorter than an appropriate vibrational period. This means that already the first attempt to cross is successful. Thus, according to (1)  $\Delta E \approx 0$ ; that is, there must be a real crossing between the surfaces and there is a continuous pathway from the upper to the lower surface. In fact, such a pathway passing through a conical intersection between the 2A and 1A surfaces is just what quantum chemical calculations have predicted.<sup>1</sup> From the short  $t_{2A}$ , it was further inferred in Ref. 15 that the conical intersection is easily accessible, in particular without any barrier, and surmised that it is situated near the line of steepest descent of the 2A surface. Here we discuss this suggestion (Sec. VIC) in the light of recent MCSCF calculations.<sup>3</sup>

The data were measured by transient ionization in the gas phase with mass-selective detection, pumping by weak frequency-tripled Ti-sapphire laser radiation (267 nm) and probing by the fundamental (800 nm) at high intensity. The nonresonant ionization has the advantage that there are no dark states. The various ion signals showed time behavior different from each other, thus providing more information than with a single signal alone. In fact, we obtained time constants for several consecutive "phases" of the ring opening. This is an advantage over transient absorption which normally only probes a single electronic transition.

The probe intensity used was in a range (2  $\times 10^{13} \,\mathrm{W \, cm^{-2}}$ ) where multiple ionization is observed and where the ionization is considered to be caused by the electric field of the laser light. This intense-laser field ionization (IFI) depends on the length of a bond (which can expand during the ionization process) $^{21-23}$  or (comparing different chemical species) on the length of the molecule.<sup>24</sup> Therefore we expected to detect in this way also the length changes of the product Z-hexatriene resulting from a thermal singlebond isomerization, following the photochemical step (Scheme 1). But although this process was detectable by resonance-enhanced photoionization<sup>14</sup> (see also Sec. V D and Ref. 15), the IFI signal turned out to be insensitive for it. Another surprise was that the intense-laser field ionization seems to be enhanced by intermediate resonances (Sec. VIB).

After presenting the experimental method, in Sec. III we will briefly introduce the potential energy surfaces and in Sec. IV intense-laser field ionization and its potential for probing dynamics. In Sec. V we present the results with some conclusions being drawn in each subsection separately.

#### **II. EXPERIMENTAL METHODS**

All the experiments were conducted in a gas-phase reaction chamber at room temperature, employing the widely used<sup>25,26</sup> femtosecond pump-probe setup with transient photoionization combined with mass-selective detection of ion yields.

The radiation source is based on a Ti-sapphire laser oscillator (Spectra-Physics, Tsunami) followed by a one stage Nd-YLF pumped (527 nm) Ti-sapphire stretcher–amplifier– compressor device (Quantronics, Series 100 and 4800), which supplies ultrashort pulses at 800 nm with energy up to 700  $\mu$ J at a repetition rate of 1 kHz. This beam is split by means of a dichroic mirror into two. One part is used as input for frequency doubling and tripling in a commercial frequency converter (CSK Optronics) with 0.5 mm thick LBO and 0.3 mm thick BBO crystals. The third harmonic (267 nm) serves for pumping and the remaining part of the fundamental radiation for probing.

The duration of the probe pulse, measured with an autocorrelator by frequency doubling (APE, Pulsecheck), was 110 fs (full width at half maximum). The pump pulse had a Gaussian shape with a length of 130 fs as determined by difference frequency mixing with the 800 nm pulse in a 0.1 mm BBO crystal. The unfocused pump beam (diameter 1 mm) and the probe beam focused to a spot size of 100  $\mu$ m (by a lens with a focal length of 50 cm) were colinearly combined and guided into the photoionization chamber using a dichroic mirror. The probe had a peak intensity in the focal plane of about  $2 \times 10^{13} \,\mathrm{W \, cm^{-2}}$  and the pump about  $10^9 \text{ W cm}^{-2}$ . The latter corresponds to 0.13 mJ cm<sup>-2</sup>; this is 0.1% of the saturation energy  $(h\nu/\sigma)$  of cyclohexadiene, so that 0.1% of the molecules will be excited. In all the experiments, the polarization of the probe laser was parallel to the mass spectrometer axis. The polarization of the pump laser could be rotated by a half-wave plate, selected for a small wedge angle. In most of the experiments the polarization was set to the magic angle of 54.7° relative to that of the probe laser. The half-wave plate, however, lengthens the pump pulse to 145 fs; therefore in some experiments (to be indicated) this plate was not used.

The delay between pump and probe pulses was varied with a resolution of 6.7 fs by a motorized translation stage under computer control. The time-zero was determined as the maximum of the transient ion signal for Xe which is due to pure nonresonant (2+2) multiphoton ionization under the given conditions. Two ion signals (normally a Xe peak and one of the cyclohexadiene-related signals) were simultaneously recorded in each pulse using two boxcar integrators. This method provided synchronization of different scans with an accuracy of  $\pm 2$  fs. The pump and probe beams were alternately blocked by two synchronized choppers. Ion signals were periodically measured with pump only  $(I_{pu})$ , probe only  $(I_{pr})$  and with both lasers together  $(I_2)$  to determine the transient ion signal S at a given delay time t,  $S(t) = I_2(t)$  $-I_{pu}-I_{pr}$ . Each signal is averaged over 1000 pulses. The resulting signal-to-noise ratio was better than 300. For a given mass the background  $(I_{pu}+I_{pr})$  was typically kept less than 30% of the maximum of the signal by limiting pump and probe intensities. The ion signals and the pump and probe energies (measured by photodiodes), recorded by gated integrators, were stored in a computer for further analysis.



FIG. 1. Setup for photoionization and mass-selective detection. The upper part is equipped with  $CaF_2$  windows (W) for the laser beam (LB), two grid electrodes (GR1, GR2) to accelerate the ions generated in the focal region and a gas feed (GF) through precision needle valves. A wall (SW) separates the gas cell (upper part) from the high vacuum chamber (lower part) with the microchannel plate (MCP). The slit helps to maintain the pressure difference. DT is the field-free drift tube and MS a magnetic shielding (mu metal).

The ionization chamber combined with a linear time-offlight mass spectrometer is sketched in Fig. 1. In its upper part the ions generated in the focal region of the laser beam are accelerated in two steps by the fields between the two grid electrodes (GR1, GR2) and the separation wall (SW). Then, in the lower part, the ions travel through a drift tube (DT), which has a slit at its upper end and is closed by a grid at the lower end, and are detected by a two-stage microchannel-plate (MCP, Galileo). The gases were independently fed through precision leak valves into the upper part of the chamber. The gas flow is set to provide a pressure in the range  $3 \times 10^{-5} - 3 \times 10^{-7}$  mbar in the upper part and  $10^{-7}-10^{-9}$  mbar near the MCP. The pressure ratio is roughly given by the ratio of cross sections of the slit and of the pump. The background pressure is  $<10^{-9}$  mbar. The spacing between the grids is 10 mm, the field strength 600 V/cm. The focus is centered between the grids. The spacing of SW and GR2 is 5 mm and the field strength between them 4800 V/cm. The ratio of the electric fields is 1:8, which is optimum for spatial focusing. The field-free drift tube is 250 mm long. The ion of mass 80 has a signal peaked at 3.6  $\mu$ s time of flight with a pulse width of 8 ns. To pass the acceleration region between the focal zone and slit, such ions require about 450 ns (extraction time). Ions produced by thermal dissociation of some ionic precursor in less than about 1% of the extraction time cannot be distinguished from prompt ions produced immediately by the probe pulse.

If the ions generated in the focal zone have an initial kinetic energy with a horizontal component, they will be forced on parabolic trajectories which may end at the separating wall outside the slit area and therefore are lost. This favors ions with vertical initial speed and favors the detection of double peaks from Coulomb explosions.

All the experiment was performed at a gas temperature of 293 K. Diffusion (molecular velocity $\geq 100 \text{ m/s}$ ) and gas flow were sufficient to replenish the irradiated volume in the millisecond between the pulses and avoid any accumulation of products.

Cyclohexadiene (Fluka) was used after degassing without further purification. According to gas-chromatography mass-spectrometry it contained about 1% of impurities, which did not disturb the measurements, however, since they either absorb at shorter wavelengths than the pump radiation (1,4-cyclohexadiene) or only contribute a time independent signal (benzene, i.e., the dehydrogenation product). Hexatriene (product of ring opening) was present in concentrations of less than 0.3%. Z-Hexatriene used for some comparison experiments was recovered from the commercial (Fluka) mixture of Z- and E-isomers by scavenging E-hexatriene with maleic anhydride.<sup>27</sup>

#### **III. QUALITATIVE POTENTIAL ENERGY SURFACES**

The electrocyclic ring opening of cyclohexadiene is a prototype of the more general class of photochemical pericyclic reactions. It is easy to construct general, though qualitative, potential energy surfaces for them (Fig. 2): According to the Woodward–Hoffmann rules in the interpretation of van der Lugt and Oosterhoff (see, e.g., Ref. 16), we have the following.

- (1) The first excited state (1B) of the educt correlates with the first excited state of the product.
- (2) The ground state (1A) of the educt correlates with a twoelectron excited state (2A in the figure) of the product, and vice versa.
- (3) An avoided crossing of the correlation lines between 1A and 2A creates a high barrier in the ground state (which justifies the denotation "ground-state forbidden" for the reaction) and a collection well for the excited states. The latter is called pericyclic minimum. It is biradicaloid in character and has the same nature for all photochemical pericyclic reactions, no matter which was the primary excited state.

Figure 2 represents this general scheme. But the crossing is not avoided everywhere. In a suitable section (different from the drawing plane) of the potential surfaces there will be a real crossing with the shape of a double cone (broken lines in Fig. 2), and for the cyclohexadiene/hexatriene case<sup>1</sup> and several other pericyclic reactions<sup>28</sup> it has been localized by *ab initio* calculations. In contrast to the biradicaloid structure at the pericyclic minimum with its two decoupled electrons, at the subsequent conical intersection (CI) four elec-



FIG. 2. Schematic potential energy surfaces of cyclohexadiene/hexatriene  $C_6H_8$  and of the parent ion  $C_6H_8^+$ . The arrows indicate pumping with one 267 nm photon and nonresonant 800 nm probing. The asterisk (\*) indicates the position of the conical intersection (outside the drawing plane). Ionization of the molecule from the 2A state results in the formation of a ground-state ion but with an excess vibrational energy of about 2.5 eV, which is partly due to the difference in the energies of the 1B and 2A states of the neutral and partly due to the release of energy when the ion runs downhill from the crossing region. This excess energy is enough to overcome the 2 eV barrier for dissociation of the parent ion  $C_6H_8^+$  into  $C_6H_7^+$ +H.<sup>31</sup> The horizontal broken line with arrows indicates the threshold for this fragmentation.

trons are decoupled, and the manner of recoupling decides between formation of different products and the educt.<sup>28</sup> So the CI not only provides a fast outlet of the funnel to the ground state, but is also a branching point determining quantum yields (product formation versus internal conversion) and the probability of the different photoproducts.

The upper part of Fig. 2 also shows potential energy curves for the ions. The ground states of the two ions belong to different symmetry species (just as the highest occupied orbitals of the neutral molecules) and therefore do not correlate with each other. The two states are above the neutral ground state by about 8.3 eV (ionization energy 8.25 eV for cyclohexadiene<sup>29</sup> and 8.32 eV for hexatriene<sup>30</sup>). According to the photoelectron spectra, the first excited state is higher by 2.5 eV<sup>29</sup> or 1.7 eV<sup>30</sup> in the case of cyclohexadiene and hexatriene, respectively. The next higher state can also be inferred from the absorption spectra of the ions.<sup>31</sup> As in Ref. 31 they are correlated in Fig. 2 with the ground states of the complementary ion.

The fragmentation energy of the ions is also expected to depend on coordinates, so that it could be represented by kind of potential energy surfaces. Such surfaces are, however, not known. The horizontal broken line only indicates the minimum energy (2 eV<sup>31</sup>) for fragmentation to  $C_6H_7^+$ .

#### IV. DISSOCIATIVE INTENSE-LASER FIELD IONIZATION FOR PROBING MOLECULAR DYNAMICS

Femtosecond time-resolved multiphoton ionization combined with mass selective detection has proved to be a powerful tool in time-resolved studies of chemical reaction dynamics.<sup>25,26,32,33</sup> But it was not recognized before<sup>33</sup> that, as we show here, the different ions can represent different locations on the potential energy surface; instead, it was often supposed that the different ionic fragments reflect a dissociation of the neutral molecule. Originally we chose nonresonant ionization at long wavelength (800 nm) expecting that there will thus be no dark states since the process will not depend on resonances. Indeed we detect signals from all states theoretically expected to be populated. On the other hand, ions sometimes have absorptions at very long wavelengths. By such a resonant ionic excitation with photodecomposition we interpret (Sec. VIB) why hexatriene has a fragmentation pattern which is drastically different from that of the reactant cyclohexadiene. This is another great advantage over UV photoionization where the two isomers show mass spectra which are practically indistinguishable.<sup>34</sup>

A third advantage turned out in the course of this work: Most of the many ions differ in their time behavior. Hence there must be a number of different neutral precursors of the ions. (All signals generated from a single precursor must be proportional to each other, since one entity can only have one time behavior, even if it contains several time constants.) These precursors cannot be chemical species since only two (reactant and product) are present. Hence they must be locations on the potential energy surface. The many signals thus permit us to deduce the population flow through a number of such locations. Note that this conclusion does not depend on the interpretation of the ionization mechanism presented below. It is also worth mentioning that the many time constants are not extracted from a single signal (multiexponential decay); but most signals contain only one or two time constants; each time constant is contained in several signals, so that there is redundant information.

Nonresonant ionization requires high intensity. We used about  $2 \times 10^{13}$  W cm<sup>-2</sup>. Under such conditions ionization is usually assumed to be caused by the electric field of the laser radiation (amplitude about 1.3 V Å<sup>-1</sup>).<sup>35,36</sup> It is often accompanied by extensive fragmentation. It can be called dissociative intense-laser field ionization (DIFI). In a classical model<sup>35,36</sup> the Coulomb potential for the electron and the field of an intense laser superimpose to create an ionization barrier which for strong fields is low enough to cause efficient ionization of an atom or molecule. This model predicts the threshold intensity  $I_{BSI}$  for ionization of atoms by barrier suppression:<sup>35</sup>

$$I_{\rm BSI} = A({\rm IE})^4 Z^{-2}, \tag{2}$$

where  $A = 4 \times 10^9 \text{ W cm}^{-2} \text{ eV}^{-4}$  is a numerical constant, IE the ionization energy, and Z the charge of the resulting ion. Following DeWitt and Levis,<sup>36</sup> we also use it for molecules.

(According to Schröder *et al.*,  $A = 2.3 \times 10^9 \text{ W cm}^{-2} \text{ eV}^{-4}$  for diatomic molecules.<sup>37</sup>) For cyclohexadiene with IE = 8.25 eV for the ground state, the threshold intensity calculated from (2) is  $I_{BSI} = 1.8 \times 10^{13} \text{ W cm}^{-2}$ .

If the ionization efficiency mainly depends on the ionization energy, we can expect an enhanced ion signal from every electronically excited state independent of its electronic and vibrational nature (no dark excited state, as mentioned above). Since IE changes along the reaction path (because the ionic and neutral surfaces are not parallel), the ionization probability will depend on the location on a potential surface. This interpretation-as also the model on which Eq. (2) is based—tacitly assumes that the ionization process is vertical. A position dependence is even expected if the process is only vertical in a first step (as often in multiphoton processes), and such a dependence is sufficient to allow measuring time constants. In the following four paragraphs we consider three reasons (excess vibrational and electronic energy, photochemistry of the ion) why also the fragmentation pattern depends on the location on the PES.

The Franck-Condon principle which is valid for vertical transitions implies that most of the vibrational energy of the neutral precursor is transferred to the ion. This is immediately obvious for the fraction of the energy contained in the many Franck–Condon inactive modes (selection rule  $\Delta v$ =0). In case of a compact wave packet running down along the potential energy surface, the kinetic energy is even completely conserved during ionization; this is a consequence of the original Franck principle<sup>38</sup> which postulates conservation of nuclear position and momentum in a vertical electronic transition. The case of the wave packet is probably appropriate for the ultrashort processes described here. One source of the excess energy is transformation of electronic to vibrational energy when a molecule runs down a potential energy surface or when during internal conversion or chemical reaction it crosses from an initially excited state to a lower state. (Note that the total energy is conserved since collisions are negligible in the gas phase in the fs time scale.) A similar situation has already been found in alkylbenzenes, where ionization from the vibrationally hot triplet state primarily produced fragments, but not the parent ions.<sup>39</sup> This picture is also supported by the recent femtosecond photoelectron/ photoion coincidence studies of benzene, where after the  $S_2 \rightarrow S_1$  internal conversion the photoelectron spectrum only indicated high-energy ions,<sup>40</sup> just as expected if the excess vibrational energy of the neutral molecule is transferred to the ion. Similarly, the photoelectron spectrum of hexatriene only indicates ions with excess energy, if it is measured at a delay (after UV excitation) after which some of the initial electronic energy has already been converted to vibration.<sup>41,42</sup> If the vibrational energy thus transferred to the ion exceeds the threshold for fragmentation, the parent ion will not be observed anymore, but a fragment instead. Thus when the neutral molecule runs down the potential energy surfaces, more and more electronic energy is converted to vibration, and the ions observed will be lighter and lighter. In fact, we observed the lightest fragments at the latest times, i.e., after recovery of the ground state (Sec. VD). Hence, if the fragmentation thresholds are suitable, ionic fragmentation can serve to roughly determine the vibrational energy and thereby help to distinguish different electronic states.

It may be asked why the excess vibrational energy does not cause dissociation of the neutral molecules before it is transferred to the ion. In fact hot-ground-state reactions have often been observed, in the case of cyclohexadiene, for instance, a H migration and H<sub>2</sub> elimination.<sup>43</sup> But they take a time of the order of nanoseconds,<sup>14,43,44</sup> much beyond the time scale of the pump-probe delay. In other words, singlephoton excitation at 267 nm does not cause prompt dissociation of cyclohexadiene (two-photon excitation ionizes it), so that *all fragmentation observed* must have *occurred in the ion*. Although in the ion it may also be slow, only its result will be monitored by the probe, since all processes taking place after ionization, but within a time much shorter than (e.g.,  $\leq 1\%$  of) the time needed for extraction (about 450 ns for mass 80, 280 ns for mass 30), will not be time-resolved.

Another consequence of the Franck-Condon principle is that at some locations of the potential energy surface the ion is generated with excess electronic energy. (The minimum number of probe photons required is then, of course, larger.) This situation is typical of a photochemical reaction where the molecule runs down a descending excited-state surface (its slope drives the reaction!), whereas the ionic groundstate surface rises, being usually more similar to the groundstate surface of the neutral. For example, ionization from the pericyclic minimum of cyclohexadiene/hexatriene leads to the top of a barrier ( $\leq 1.5 \text{ eV}^{31}$ ) in the ion (Fig. 2). (It may be worth noting that, despite the increased distance of ionic and neutral surfaces, the ionization energy from the pericyclic minimum is still smaller and the ionization probability larger than in the ground state.<sup>14</sup>) The excess electronic energy plus the vibrational energy transferred from the neutral (about 1 eV, the calculated energy difference between the Franck-Condon region and the 2A minimum) exceed the first fragmentation threshold  $(2 \text{ eV}^{31})$  of the ion. Hence the parent ion will not be generated from the 2A minimum.

Besides the excess electronic and vibrational energy, another source of fragmentation is *photodissociation of the ion*. Resonances in the ion will, of course, depend on its geometry (see also Sec. VIB) and hence—to the degree to which ionization is vertical—also on the position on the surface of the neutral. Usually the absorption of long-wavelength photons is more probable in ions than in neutrals due to the higher density of electronic states in the ions. Ionic photofragmentation is operative in experiments with both nanosecond and femtosecond pulses (see the review of Weinkauf *et al.*<sup>45</sup> and the discussion in Ref. 46).

To summarize this interpretation, the ionization probability depends on the location on the potential surface, because the ionization energy depends on it (due to the nonparallel surface of neutral and ion), and the fragmentation pattern changes with geometry for three reasons.

- (1) Due to the excess vibrational energy released on the way down the potential energy surfaces. This energy is transferred in a vertical ionization to the ion and there causes fragmentation.
- (2) Due to excess electronic energy in the ion, since typi-

cally a higher part of the ionic surface is reached in a vertical transition from a reactive surface of the neutral.

(3) Due to photochemistry of the ion. Its resonances (which can be at long wavelengths) depend on its geometry, and its ground-state surface is reached without geometry change from the neutral by vertical ionization.

Whereas a dependence on the location on the potential can also occur at lower intensities, a special feature of field ionization at laser intensities comparable or higher than  $I_{BSI}$ is multielectron dissociative ionization, i.e., multiple ionization followed by dissociation through Coulomb explosion of the charged fragments.<sup>47</sup> Organic molecules under these conditions usually produce all possible fragment ions,  $CH^+, CH_2^+, CH_3^+, C_2H^+, C_2H_2^+$ , etc., including atomic carbon and hydrogen ions.<sup>47–50</sup> With appropriate resolution some fragment ions show a doublet splitting corresponding to the recoil energy acquired in the Coulomb explosion, and such a splitting proves the formation by this process. Such a structure is easily observed with the light atomic ion  $H^+$ . The splitting arises, because in any Coulomb explosion which takes place in the ionization zone between the acceleration grids, some charged fragments are ejected toward and some away from the detector. The two groups of ions will differ in their arrival time, and from this difference the kinetic energy of the ions can be calculated.

Recently it has been found that DIFI is dramatically enhanced in various molecular and cluster systems at some critical internuclear distances, larger than equilibrium ones.<sup>21,23,50–52</sup> Corkum and co-workers proposed to use the DIFI sensitivity to atomic distances as a probe in time-resolved studies of a dissociative system.<sup>22</sup> However, as explained above (see also Secs. V A and VI B) the DIFI fragmentation pattern not only changes along a dissociation coordinate, but more generally depends on the position on the potential energy surface and on structural changes which the molecules experience during photoisomerization.

#### **V. RESULTS**

In this section we also present, besides results, some immediate conclusions at the end of each subsection and a model for evaluation in Sec. V D.

#### A. Mass spectra

Whereas with low-intensity photoionization (e.g., at 267 nm) the mass spectra of cyclohexadiene (CHD) and Z-hexatriene (HT) are almost indistinguishable (also with REMPI<sup>48</sup>), they show a rather different fragmentation pattern when the molecules are ionized by an intense-laser field (Fig. 3): The yield of the parent ion is practically the same for both isomers if ionized at 800 nm with an intensity around  $2 \times 10^{13}$  W cm<sup>-2</sup>, but in HT the light fragments with masses around 51, 39, and 27 are more abundant by about a factor of 10, and the atomic ions C<sup>+</sup> and H<sup>+</sup> by two orders of magnitude, than in CHD.

Formation of the atomic ions  $C^+$  and  $H^+$  is typical of intense-laser field ionization of organic compounds. It is usually attributed to dissociative multielectron ionization.<sup>21,51</sup> In fact, the  $H^+$  signal in the time-of-flight spectrum (Fig. 4) has



FIG. 3. Photoionization mass spectra of 1,3-cyclohexadiene (CHD, solid lines) and *tZt*-hexatriene (*tZt*-HT, dashed lines) obtained by irradiation of a gas sample with 110 fs laser pulses at 800 nm and intensity of about 2  $\times 10^{13}$  W cm<sup>-2</sup>. The spectra are normalized to the intensity of the parent ion. They were recorded under identical conditions (sample pressure and laser intensity) giving a similar parent ion yield in both cases. The arrow marks a peak at M/Z=40.5 amu which is most likely due to the doubly ionized isotopic species  ${}^{13}CC_{5}H_{8}^{++}$ .

a characteristic doublet shape; the splitting is due to recoil energy originating from the Coulomb explosion of a doubly charged precursor ion.<sup>21,51</sup> Using the peak-splitting time  $\Delta t$ , the kinetic energy  $E_{kin}$  of the ions can be calculated by the following equation (see, e.g., Refs. 21 and 54):

$$E_{\rm kin} = C(\Delta t^2/m)(\Delta U/d)^2 q^2, \qquad (3)$$



FIG. 4. Time-of-flight spectra ( $H^+$  signal) of CHD (solid line) and *tZt*-HT (dashed line) obtained under the conditions of Fig. 3. The intensities are normalized. The actual  $H^+$  intensity in CHD is about 100 times smaller than in HT. The asymmetry between the components of high and low kinetic energy is just the other way around than in previous observations. This difference can be attributed to the discriminating properties of the slit used by us at the entrance of the mass-spectrometer flight tube (Ref. 53).

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where  $C = 0.120 \text{ eV} \,\mu\text{s}^{-2} \text{ amu cm}^2 \text{V}^{-2}$ , *m* is the molecular mass,  $\Delta U/d$  the electric field across the first pair of acceleration grids and q the charge in units of the elementary charge. The splittings in Fig. 4 are  $\Delta t_{CHD} = 11.3 \pm 0.3$  ns and  $\Delta t_{\rm HT} = 15.0 \pm 0.3$  ns. For the  $\Delta U/d = 422$  V cm<sup>-1</sup> employed, this corresponds to a kinetic energy of the H<sup>+</sup> ion of 2.74  $\pm\,0.15$  and  $4.82\pm\,0.20\,\text{eV}$  in case of CHD and HT, respectively. Double ionization is confirmed by the peak at mass 40 with its satellite at M/Z = 40.5; the latter is due to HT<sup>++</sup> with a single <sup>13</sup>C and shows the correct abundance. This signal is obviously due to a stable state of this ion, whereas the H<sup>+</sup> is launched from a dissociative electronic state. The H<sup>+</sup> peak was also noticed in a recent work;<sup>24,55</sup> but its origin from a Coulomb explosion was not recognized and a different interpretation was presented. Double ionization was also observed in aniline, pyridine and furan.<sup>56</sup>

We cannot exclude that some other light fragments such as those with the masses 51, 39 and 27 are also due to double ionization and subsequent Coulomb explosion. If so, their recoil-energy splitting seems not to be resolved by our instrument. However, we assume that they are actually photochemical products of the singly positive ion. Some of the ions thus produced may have vibrational excess energy and may be metastable; i.e., they decompose during the extraction time (100–500 ns), thus giving rise to broad peaks. The broad group of peaks around mass 12 may be such a case, too, although other workers<sup>21,51</sup> prefer to assign it to Coulomb explosion. Levis *et al.* ascribe the broadening to recoil in some impulsive dissociation of the neutral;<sup>55</sup> but such a process seems to us less probable when many bonds have to be broken, such as in this case.

We will discuss in Sec. VIB why HT is more liable to ionic photodissociation and multielectron ionization and thus shows more light fragments than its isomer CHD. The observed drastic difference between the DIFI mass spectra of the two molecules (Fig. 3) has a practical consequence: It allows us to monitor the appearance of the photoproduct and its identification. This expectation is confirmed by Fig. 5 where the transient IFI mass spectrum, recorded at 400 fs delay after one-photon excitation of CHD at 267 nm, is presented together with the DIFI spectrum of not pre-excited HT. The two spectra are obviously very similar not only in the presence of the light fragments and their pattern, but also in their recoil structure (the lower part of Fig. 5). The only difference is that the 400 fs spectrum also shows a strong depletion (i.e., a decrease compared with negative delays) of  $HT^{++}$ . This is not unexpected, since it will be hot when produced from hot neutral HT, so that the corresponding ions will decompose. The similarity of the spectra clearly shows the presence of some form of hexatriene at 400 fs. It can be concluded that the ring opening is already complete at this time.

#### B. Time dependence

To monitor the dynamics of the photochemical ring opening of CHD, we recorded the delay-time dependence of various ion yields. All the transient ion signals were found to be proportional to the pump energy, which confirms that they are produced by absorption of a single UV photon. The time



FIG. 5. Transient time-of-flight spectrum of CHD (dashed line) recorded at 400 fs delay after single-photon pumping at 267 nm with 145 fs laser pulses. The spectrum is obtained with photoionization by delayed pulses at 800 nm and intensity of about  $2 \times 10^{13}$  W cm<sup>-2</sup>. The solid curve shows a spectrum of static *tZt*-HT recorded under identical conditions but with 800 nm only (see Fig. 3). The spectra are normalized to the intensity of the H<sup>+</sup> ion in each case. The numbers near the peaks indicate the mass values.

constants do not depend on the ionizing probe energy, although the relative height of the H<sup>+</sup> pedestal decreases with lowering of the probe energy. According to Sec. IV and Fig. 3, we can expect that the parent ion  $C_6H_8^+$  (mass 80) and the fragment  $C_6H_7^+$  (mass 79), which is also the strongest one in electron-impact<sup>57</sup> and low-intensity photoionization<sup>34</sup> mass spectra, will contain information about the temporal history of electronically excited states, whereas the light fragments including atomic ions will reflect the product appearance and processes in the ground state.

Typical transient signals for the former two ions are presented in Fig. 6 in a singly logarithmic scale. The broken curve shows the response function calculated for (1+3)-multiphoton ionization (3 is the minimum number of probe photons required to ionize the 1B state) on the basis of the measured pulse shapes and time zero. The signals of the masses 80 and 79 instantaneously grow with the pump pulse, reach their maxima at 26 and 60 fs and then decay to values near zero. After the pump-probe overlapping region both ions show exponential decay over more than two orders of magnitude with decay time constants of  $43\pm3$  fs for the parent and  $77\pm7$  fs for the fragment ions. These values are averaged over at least 10 independent scans. They do not depend on the intensities and relative polarizations of the pump and probe beams. Only at higher pump energies a small negative pedestal at long delay can be seen for both masses owing to a partial depletion of the educt. In order not



FIG. 6. Relative ion yield in CHD for the parent  $C_6H_8^+$  and fragment  $C_6H_7^+$  ions versus the time delay between the 130 fs pump at 267 nm and the 110 fs probe at 800 nm. The symbols show the experimental data and the lines represent singly exponential fits to them. The broken curve is the response function calculated for a pump pulse of 130 fs FWHM and a probe pulse of 110 fs FWHM assuming that three probe photons are used for ionization. The shape of the transient signals for the parent and fragment ion at mass 79 does not depend on the relative polarizations of the laser beams. Note: The data are slightly offset in such a way as to have a zero pedestal at long delay.

to distort the singly exponential decay in the logarithmic scale in such cases, the data presented in Fig. 6 have been offset to have a zero pedestal at long delay.

In contrast to the masses 80 and 79, the signals at lighter masses depend on the relative polarization of pump and probe. Therefore their kinetics was studied with magic angle  $(54.7^{\circ})$  between pump and probe polarizations. Figure 7 shows the transient signals for the parent ion and the ionic



FIG. 7. Relative ion yield in CHD for the parent  $C_6H_8^+$  (dashed curve) and fragments  $C_3H_3^+$  (squares),  $C_2H_3^+$  (triangles) and  $H^+$  (circles) ions versus the time delay between the 145 fs pump at 267 nm and the 110 fs probe at 800 nm. The solid lines show one-parameter single-exponential fits to the tail of fragment ions using a fixed time constant of 77 fs. In this fitting only the pedestal values were varied; two-parameter fitting gives for  $H^+75\pm7$  fs and for the 27-amu and 39-amu fragments the little bit longer decay of 90  $\pm 10$  fs. The data were recorded with a relative angle of 54.7° between pump and probe polarization.



FIG. 8. Anisotropy *r* of the H<sup>+</sup> signal in CHD versus delay time *t* between the 267 pump and the 800 nm probe. *r* has been calculated from the transient H<sup>+</sup> signals recorded for parallel  $(S_{\parallel})$  and orthogonal  $(S_{\perp})$  polarization by using Eq. (3). For normalization, r=0  $(S_{\parallel}/S_{\perp}=1)$  has been assumed for the region of the minimum around 1700 fs. The solid curve shows a single-exponential fit to the data in the region 500–1300 fs, giving an anisotropy decay rate of  $1.72\pm0.22$  ps<sup>-1</sup>.

fragments with the masses 39, 27 and 1 measured under these conditions. These fragment ions  $C_3H_3^+$ ,  $C_2H_3^+$  and  $H^+$ show practically the same steep growth as the parent ion, but delayed relatively to it. The delay is most pronounced for H<sup>+</sup> where it is as large as 170 fs.  $H^+$  reaches a maximum at 200 fs and then drops to a positive pedestal value. The fragment ions  $C_3H_3^+$ ,  $C_2H_3^+$  behave similarly, but are less delayed and more broadened as compared with H<sup>+</sup>. They reach their maxima at 110 and 140 fs, respectively, and then decay to a positive pedestal. A pedestal indicates that the end product contributes to the signal. As shown in Fig. 7, the decaying part of all three signals can well be approximated by a single exponential with time constant of 77 fs, the same as for the decay of the fragment ion  $C_6H_7^+$ . After 400 fs none of the monitored signals shows any change over at least 60 ps (with probing under the magic angle).

The *polarization dependence* was studied in detail for the H<sup>+</sup> signal. It is typical of orientational relaxation of freely rotating anisotropic molecules.<sup>58,59</sup> Its kinetics is most easily seen in a plot of the rotational anisotropy r,

$$r = (S_{\parallel} - S_{\perp})/(S_{\parallel} + 2S_{\perp}), \tag{4}$$

where  $S_{\parallel}$  and  $S_{\perp}$  are the transient ion signals with the polarizations of the pump and probe parallel and perpendicular, respectively. Figure 8 shows for H<sup>+</sup> the decay of *r* versus the delay time *t*. Although the experimental conditions for one given polarization were very stable, there is some uncertainty of the absolute signal values in different runs, due to a variation of the spatial overlap for pump and probe beams after realignment to change the polarization. Therefore in evaluating the anisotropy we set for simplicity  $r=0(S_{\parallel}/S_{\perp}=1)$  for the region t=1.7 ps where *r* has a minimum, and normalized the experimental data accordingly. This assumption can influence only the absolute values of the anisotropy, but does not change the rate constants. In the region 0 < t < 0.3 ps, the

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anisotropy has a constant value of 0.33, then it drops to the minimum around t = 1.7 ps and thereafter recovers to about 0.02. Such oscillatory behavior is typical of orientational relaxation of freely rotating anisotropic molecules.<sup>59</sup> A signal beginning at a positive r (near 0.4) and then decaying means that the dipole moments for the pump and probe transitions (the latter will be identified in Sec. VIB) are (nearly) parallel, whereas with perpendicular transition moments r starts from a negative initial value. The minor initial rise and slightly delayed decay which were observed probably mean that the two dipole moments form a small nonzero angle with each other. In the decaying part (0.5-1.2 ps) the data can be fitted by a singly exponential decay with a rate of  $k_r = 1.72 \pm 0.22 \text{ ps}^{-1}$ . Using the equation given in Ref. 59, such a decay rate would be expected from a molecule of moment of inertia  $\theta = 171$  amu Å<sup>2</sup> rotating at room temperature. This  $\theta$  is very near the values calculated for cyclohexadiene (184 amu  $Å^2$  for an axis perpendicular to the ring; the other two  $\theta$  are half as large) and the *cZc* conformer of hexatriene whose moments of inertia are certainly very similar. The *tZt* conformer would have  $\theta = 35$ , 321 and 356 amu  $Å^2$  along its three axes. Hence we can conclude that at least a large fraction of the product identified in Sec. VB as hexatriene (at 400 fs) is the cZc conformer. So at this time this (expected) primary product has not yet undergone single-bond isomerization to other conformers. From the observation of the *cZc* moment of inertia we can also infer that the strong field of the probe laser does not automatically stretch the molecule during multiple ionization to its longest (tZt) conformer.

Evidence has been presented that in solution the conformer isomerization begins in the subpicosecond range; but a time constant  $\tau_{\rm conf}$  could not be given since this process competes with vibrational cooling.<sup>11,13,60</sup> So we expect  $\tau_{\rm conf}$ between 1 ps and 400 fs in the gas phase. Therefore we re-assign the time constant of  $580\pm60$  fs found in the gas phase<sup>14</sup> by transient resonance-enhanced multiphoton ionization (REMPI) to the single-bond isomerization. It is probably the shifting of the UV spectra and increase of absorption during this process<sup>11–13</sup> which sensitizes REMPI for this isomerization.

In the temporal region  $\geq 600$  fs, the DIFI signals (Fig. 7) do not change. This is surprising, since the length of hexatriene increases from its *cZc* to its *tZt* conformer by nearly a factor of 2, and a length dependence was expected for field ionization. Obviously, with our intensities *there is no strong dependence of the DIFI signals on the length of hexatriene*. In Sec. VI B we point to the dominating influence of resonances in the hexatriene ions.

#### C. Simulation by a rate-equation model

It was explained in Sec. IV that different locations on the potential energy surfaces have different ionization probabilities and fragmentation patterns. In an ideal situation, each region would give rise to just one ion. Then a decay of one signal would be connected with the rise of another one with the same time constant. Actually each fragment ion contains contributions from different precursor states. These contributions can be extracted by kinetic modeling, as done in the following.

To derive information about the dynamics of cyclohexadiene ring opening from the kinetics of various ion signals, we assume that the pathway is not branched and describe the population at each location (level, observation window) by rate equations. It is common to model the dynamics in femtosecond transition-state spectroscopy by rate equations (see Ref. 61 and references therein, and Ref. 62). Although such a model ignores coherences,<sup>63</sup> it is powerful in providing the nature of population flow. A justification is that we observed exponential decays (which are solutions of rate equations) in some examples (Fig. 6) over 2.5 orders of magnitude. On the other hand, signs of a coherent effect were observed, too (compactness of the H<sup>+</sup> signal; see the end of this section).

The ion signals are then calculated from these timedependent populations (resulting from the rate equations) by convolution with the measured pump and probe pulse shapes.<sup>61,64</sup> According to Sec. II, the pump pulse is well described by a Gaussian (full width  $\tau_{pu}$  at half maximum). The time-dependent population of the *i*th level  $N_i(t)$  produced by this finite-length pump pulse is then given by

$$N_{i}(t) = \int_{-\infty}^{t} n_{i}(t-t') I_{\rm pu}(t') dt', \qquad (5a)$$

where  $I_{pu}(t) = I_{pu}^0 \exp(-\alpha_{pu}t^2)$  is the normalized intensity of the pump pulse,  $\alpha_{pu} = 4 \ln 2/\tau_{pu}^2$ ;  $n_i$  represents the population resulting from the rate-equation calculations with an infinitesimally short pump pulse,  $n_i(t)$  being a sum of exponentials. Then convolution with a probe pulse of length  $\tau_{pr}$  gives the contribution of the *i*th level to the intensity of the ion signal at mass *M* at a pump–probe delay time *t*:

$${}^{M}S_{i}(t) = {}^{M}\sigma_{i} \int_{-\infty}^{\infty} N_{i}(t') I_{\mathrm{pr}}^{m}(t'-t) dt', \qquad (5b)$$

where  $I_{\rm pr}(t) = I_{\rm pr}^0 \exp(-\alpha_{\rm pr}t^2)$  is the normalized intensity of the probe pulse,  $\alpha_{\rm pr} = 4 \ln 2/\tau_{\rm pr}^2$ ,  ${}^M \sigma_i$  is the effective cross section to produce the ion of mass *M* from the *i*-th level and *m* the effective order of the ionizing process. (Also in DIFI, one finds that the ion yields are proportional to a power of  $I.^{24}$ ) It can be shown (using Heaviside's step function to match the integration limits, then invoking that convolution is commutative and associative) that Eqs. (5a) and (5b) can be contracted to

$${}^{M}S_{i}(t) = {}^{M}\sigma_{i} \int_{-\infty}^{t} n_{i}(t-t') I_{\text{instr}}(t') dt', \qquad (5c)$$

where the instrumental function  $I_{instr} = I_{instr}^0 \exp(-\alpha_{instr}t^2)$  is the correlation of the pump with a suitable power (*m*) of the probe pulse,  $\alpha_{instr} = 4 \ln 2/\tau_{instr}^2$ ,  $\tau_{instr}^2 = \tau_{pu}^2 + m^{-1}\tau_{pr}^2$ . The latter relation shows that the exact value of *m* practically does not matter, as long as  $m \ge 3$ : Inserting m = 4 instead of 3 and the pulse lengths of Sec. II,  $\tau_{instr}$  just decreases by 2%. Therefore we did not determine this parameter, but chose it (see Scheme 2) according to energy considerations. Since the solutions of the rate equations are a sum of exponentials, Eq. (5c) results in an analytical expression (containing the error



FIG. 9. Time constants (in fs) resulting from the kinetic simulation of the experimental data (see Figs. 10 and 11) of the cyclohexadiene ring opening with assignments to regions or levels (their numbering is encircled) of the potential energy surfaces. Note also the interpretation of these times as traveling times in Sec. VI.

function) which can be directly used in fitting to the measured data using commercial evaluation software. Parameters resulting from the fit are the time constants  $\tau_i$  and the ionization probabilities  ${}^{M}\sigma_i$ .

It was found that the main features of the early kinetics for all ions can be reproduced by the rate equations using six levels connected by five time constants (Scheme 2; see also Fig. 9). These five constants are a minimum set to achieve a good fit. Only two (43 and 77 fs) of them can be directly read from the exponential tails of suitable signals (Figs. 6, 7 and Sec. V B). The smaller one is from the tail of the parent ion. However, a simple convolution of an exponential function with a time constant of 43 fs with the instrumental function noticeably deviates from the experimental parent-ion



FIG. 10. A comparison of experimental data (from Fig. 6) for the parent (squares) and fragment  $C_6H_7^+$  (circles) ions with the results of the simulation. The dashed curve shows a single exponential decay (time constant 43 fs) convoluted with a one-photon pump pulse (130 fs FWHM) and a three-photon probe pulse (110 fs FWHM). The solid curves result from simulation using the first three levels of Fig. 9 and the ionization cross-sections  $^{80}\sigma_i$  and  $^{79}\sigma_i$  of Table I. The order *m* of the ionization process is assumed to be 3 for forming mass 80 and 5 for forming mass 79.

signal, giving a longer delay (a broken line in Fig. 10). The assumption of a preceding short-lived ( $\tau_1 = 10$  fs) level with higher ionization probability ( ${}^{80}\sigma_1 > {}^{80}\sigma_2$ , Table I) than in the following 43 fs removes the deviation and perfectly reproduces the parent ion signal. Only the levels 1 and 2 give rise to the parent ion. The third time constant  $\tau_3 = 77$  fs is mainly from the tail of the fragment ion C<sub>6</sub>H<sub>7</sub><sup>+</sup>. The simulation also reproduces the full temporal behavior of this signal, in particular also its early appearance, if we assume a rather high contribution from locations 1 and 2 (expressed by the quantities  ${}^{79}\sigma_1$  and  ${}^{79}\sigma_2$ ). As mentioned, this is probably due to photodissociation of the parent ion produced from these early levels.

To describe the time behavior of H<sup>+</sup> (Fig. 11), we must introduce into the rate-equation model at least *three more levels*. The first of them, level 4 with lifetime  $\tau_4$ , does not contribute intensity to the H<sup>+</sup> signal ( ${}^{1}\sigma_{4}=0$ ), but gives rise to a shift without broadening. The fifth level with lifetime  $\tau_5$ is responsible for the H<sup>+</sup> spike and the sixth one with an "infinite" (>50 ps) lifetime accounts for the H<sup>+</sup> pedestal. The steepness of the leading front of the H<sup>+</sup> signal is close to the experimental response limit and the decay of the trailing edge coincides with the lifetime ( $\tau_3$ ) of the third level. This is expected if  $\tau_4, \tau_5 \ll \tau_3$ . To reproduce the shift of the H<sup>+</sup> signal, the model requires  $\tau_4 + \tau_5 = 55$  fs. With  $\tau_4 \ge 35$  fs and  $\tau_5 \le 20$  fs the model reasonably well reproduces both the steep leading front and the decay of the H<sup>+</sup> signal (the solid line in Fig. 11). However, the calculated signal is still

	CHD (1A <sub>1</sub> )		
	$\downarrow h v_{pu}$		
(L1)	CHD (1B <sub>2</sub> , FC)	$\underline{m_1hv_{pr}}$	parent and fragment ions
	$\downarrow \tau_1$		
(L2)	CHD (1B)	$m_2h v_{pr}$	parent and fragment ions
. ,	$\downarrow \tau_2$		
(L3)	CHD (2A)	$\xrightarrow{m_3h v_{pr}}$	fragment ions
. ,	$\downarrow \tau_3$		-
(L4)	(1A, near CI)	$\xrightarrow{m_4h v_{pr}}$	fragment ions
	$\downarrow  au_4$		-
(L5)	HT (1A, resonance)	$\xrightarrow{m_{5}h_{V_{pr}}}$	fragment ions
	$\downarrow \tau_5$		-
(L6)	cZc-HT (1A <sub>1</sub> )	$m_6h v_{pr}$	fragment ions
× · /	× 1/		<b>U</b>

SCHEME 2. Levels (observation windows) used in the kinetic simulation. The first level (L1) is the initially excited state  $1B_2$  of cyclohexadiene in the Franck–Condon (FC) region, and the sixth level (L6) is the primary photoproduct of the ring opening: the ground state  $1A_1$  of *cZc*-hexatriene. To account for the main features of the kinetics of all the fragments, we must introduce at least four intermediate levels, L2–L5. L4 and L5 are two intermediate regions on the ground-state surface; the former is near the conical intersection (CI) and the latter location shows some resonance with the probe laser. The parameter  $m_i$ , entering in Eq. (5b), indicates the order of the ionization process. The simulation is not very sensitive for the value of  $m_i$  [ $\geq$ 3, see near Eq. (5c)]. The  $m_i$  values used are indicated in the captions of Figs. 10 and 11 which compare the experimental data with the simulation. A set of parameters, for which the kinetics of all the ions within the 6-level rate-equation model can be well simulated, is presented in Table I.

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TABLE I. Experimental results and simulation parameters for the six-level rate-equation model.  $\tau_i$  is the lifetime of level *i* (traveling time through observation window *i*) and  $M_{\sigma_i}$  the relative ionization cross-section to produce an ion of mass *M* from this level.  $\tau_{\text{prod}}$  is the time (calculated from  $\tau_1$  and  $\tau_5$ ) needed to form 63% of the product in its ground state (ring-opening time),  $\tau_{\text{rot}}$  the time constant for rotational anisotropy decay of the H<sup>+</sup> signal. The infinity sign stands for lifetimes >50 ps.  $\tau_{\text{prod}}$  and the level lifetimes  $\tau_1$  to  $\tau_5$  are also given in Fig. 9.

level (i)	1	2	3	4	5	6
$\tau_i/\mathrm{fs}$	10±5	43±3	77±7	≧35 <sup>a</sup>	$\leq 20^{a}$	$\infty_{\rm p}$
$^{80}\sigma_i$	1.0	0.23	0	0	0	0
$^{79}\sigma_i$	1.0	0.87	0.53	0	0	0
$^{39}\sigma_i$	1.0	0	0	0.7	0.7	0.05
$^{27}\sigma_i$	1.0	0	0	0.9	0.9	0.096
$^{1}\sigma_{i}$	0	0	0	0	1.0	0.068
$ au_{ m prod}/ m fs$		205				
$ au_{ m rot}/ m fs$		580±75				

 $^{a}\tau_{4} + \tau_{5} \approx 55$  fs.

<sup>b</sup>This level comprises the conformers of Z-hexatriene, not distinguished by probing at 800 nm. Relaxation from cZc hexatriene to a high-temperature equilibrium of conformers proceeds with a time constant of  $\tau_{conf}$ =580 ±60 fs, as is detectable by REMPI at 280–300 nm (see Sec. V D).

broader than the experimental one. This inconsistency can be removed by simulating the H<sup>+</sup> signal with a modified sixlevel kinetic model with a single bottleneck for the third level ( $\tau_3$ =77 fs, lifetimes of all preceding levels assumed <4 fs; note that the preceding levels do not contribute to the H<sup>+</sup> signal) and with an artificial time offset of +103 fs. The results of the calculation for  ${}^1\sigma_5:{}^1\sigma_6=1:0.016$  are shown by the dotted line in Fig. 11. This description approximates a "coherent" motion of a nonbroadening wave packet on the potential surfaces with only one bottleneck: the departure from level 3. In photodissociation of iodobenzene Zewail and coworkers observed a similar delay and ascribed it to a coherent motion of the wave packet.<sup>65</sup>

Fitting to the experimental data not only yields the time constants for the various steps, but also their sequence. Special considerations are then required to assign each level to a definite location on the potential energy surfaces.

#### VI. DISCUSSION

Some conclusions and interpretations were already given at the end of the foregoing subsections and in Fig. 9.

# A. Assignment of the time constants to the different observation windows

The lifetimes resulting from the rate equations should not be understood as times for passing a bottleneck (if there is any) or for leaving a discrete level, since traveling times are of the same order of magnitude. Therefore we wrote them in Fig. 9 near some arrows meant to represent observation windows of nonvanishing extension and without sharp limits.

As explained in Sec. IV, an ion generated from the region of the 2A minimum will have sufficient excess energy ( $\geq 2 \text{ eV}$ ) that it will dissociate and will *only* be detected as the *fragment* C<sub>6</sub>H<sub>7</sub><sup>+</sup>. Therefore the rate (43 fs)<sup>-1</sup> deduced from the exponential decay of the *parent* ion can be assigned to the departure from the region before (or from a region



FIG. 11. A comparison of experimental data (from Fig. 7) for the fragments  $C_3H_3^+$  (squares),  $C_2H_3^+$  (triangles) and  $H^+$  (circles) with the results of the simulation. The dashed curve shows the experimental signal for the parent ion  $C_6H_8^+$  (curve 1 of Fig. 10). The solid curves result from the simulation using all six levels of Fig. 9 and the ionization cross-sections  ${}^M\sigma_i$  of Table I. The order *m* of the ionization process is assumed to be 5 for ion formation from the first level and 6 from the others. The dotted curve shows the  $H^+$  signal simulated by the six-level rate-equation model with one single bottleneck of 77 fs for leaving the third level (lifetimes of all other levels are shorter than 4 fs) and +103 fs temporal offset, assuming  ${}^1\sigma_5$ :  ${}^1\sigma_6$  = 1:0.016. This model approximates a nonbroadening "coherent" motion of a wave packet on the potential energy surfaces with the departure from the 2A surface as the only bottleneck.

after which the conversion of electronic energy of the 1B state to vibration is becoming substantial). Most likely this region terminates near the crossing point between the 1B and 2A surface, where there is a sharp change in the slopes of potential curves. So we assign this *time of* 43 fs *to the departure from the 1B state*.

The first level with its lifetime of  $\tau_1 = 10$  fs must correspond to departure from the *Franck–Condon region*, because the same lifetime was deduced from the fluorescence quantum yield,<sup>5</sup> and according to the spectrum the fluorescence in fact came from the Franck–Condon region. The second level (lifetime of  $\tau_2 = 43$  fs) then must be related with the later parts of the 1B surface probably until the crossing between 1B and 2A.

The third time constant ( $\tau_3 = 77$  fs) was determined from the decay of the fragment ion C<sub>6</sub>H<sub>7</sub><sup>+</sup>. As mentioned, a strong contribution to this signal is expected from the 2A state, in addition also from the shorter-lived 1B region. The slow decay can therefore be attributed to departure from the 2A state (or more generally: a region following the 1B state). Quantum chemistry supports this assignment since it predicts that the 2A state has the longest lifetime;<sup>1</sup>  $\tau_3$  is in fact the longest time in the sequence found (Fig. 9).

Much stronger fragmentation is already observed from level 4 ( $\tau_4 \ge 35$  fs). (A column of the table roughly indicates

the fragmentation pattern of the level concerned.) This is plausible if some electronic energy was again converted to excess vibrational energy, as expected if the molecule has already reached the ground-state surface. A similar statement can be made about level 5 ( $\tau_5 \leq 20$  fs). The maximum of the H<sup>+</sup> signal during this time will be attributed in Sec. VI B to a resonance, which helps to localize this level more accurately. We also recall that the mass spectrum measured during this time requires that this level lies on the product side (end of Sec. V A), i.e., on the right-hand side (Fig. 9) of the 2A minimum and on the ground-state surface.

Level 6, comprising the different conformers of Z-hexatriene, shows no time dependence detectable by the method of this work ( $\tau_6 > 50 \text{ ps}$ ), because the conformers seem to give the same signals. According to the end of Sec. V B, isomerization from the *cZc* hexatriene to a high-temperature equilibrium of conformers takes place within 580 fs (measured previously<sup>14</sup>). The population of level 6 *calculated from*  $\tau_1$  to  $\tau_5$  reaches 63% ( $=1-e^{-1}$ ) of its maximum after 200 fs. This time can be denoted the time of photochemical ring opening of cyclohexadiene.

The H<sup>+</sup> signal, mostly generated from level 5, deserves a special comment: Its delay and compactness was not possible to model well enough by rate equations; instead we introduced an artificial delay which is probably a manifestation of the coherent motion of a wave packet after leaving the 2A state down through the conical-intersection region and further on the ground-state surface to a region (level 5) where multiple ionization is maximal. The existence of a compact wave packet around 200 fs implies that equipartition of internal energy cannot yet be complete at this time. On the other hand, around 600 fs is the molecule already isomerized to the other conformers with a rate as statistically expected with equipartition.<sup>13</sup> So intramolecular vibrational redistribution seems to proceed in this interval.

The ion signals in Figs. 10 and 11 are complementary to each other and together result in a complete picture of the reaction: Whereas mass 80 (parent ion) monitors the 1B state alone and mass 79 reflects the populations of 2A and 1B with no contribution from the ground state,  $H^+$  appears only when the ground state of the product is reached. The other fragments  $C_2H_3^+$  and  $C_3H_3^+$  are produced from both the Franck–Condon region of the 1B state and the ground state of the product. It is noteworthy that the 2A state contributes to only one ion,  $C_6H_7^+$ .

The possibility of determining a time constant as short as  $\tau_1 = 10$  fs requires a special justification: It was the only time constant deduced from data during the overlap of the pump with the strong probe radiation, and the latter could in principle modify the potential energy surfaces via intensity-induced level shifts. But as already mentioned in Sec. V B, the time constants do not depend on varying the probe intensity. Furthermore  $\tau_1$  was also independently determined from the fluorescence quantum yield.<sup>5</sup> Another justification comes from measurements with Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub>, where the lifetimes of initially excited state (30 and 46 fs) could not only be extracted from within, but also from outside the pump–probe overlapping region.<sup>66</sup> Probably shifts of levels relative to each other, or changes of slopes, are

unimportant in view of the large widths and steep slopes connected with the short lifetimes.

#### B. Interpretation of the enhanced multielectron ionization in hexatriene and a comment on Coulomb explosion

In Sec. VA we reported on strongly enhanced twoelectron ionization (followed by Coulomb explosion) in hexatriene as compared with cyclohexadiene. It is responsible for the drastically different mass spectra of the two compounds (Fig. 3). The difference was unexpected, since the two molecules have the same ionization energy. Let us discuss possible mechanisms responsible for it. Recently it has been found that the rate of multielectron dissociative ionization in intense fields rapidly increases, by several orders of magnitude, as the internuclear separation is extended to a certain critical distance.<sup>21-23</sup> A different phenomenon, not involving bond stretching, is the observation that longer hydrocarbons give higher ion yields than shorter ones (see Ref. 24 and references therein). tZt-Hexatriene is nearly twice as long as its ring-closed isomer cyclohexadiene (terminal C-C distance 5.7 vs 3.1 Å). So we could expect an enhanced multiple ionization of the longer molecule. However, our experimental findings disagree with this idea. First of all, the anisotropy decay of the H<sup>+</sup> signal shows that the hexatriene product rotates at a speed which is only consistent with the moments of inertia of the cZc conformer, but not with those of the tZt conformer (Sec. V B). The subsequent  $CZc \rightarrow tZt$  isomerization with the concomitant elongation from 3.1 to 5.7 Å then proceeds with a time constant of 580 fs (Sec. V D) as determined by REMPI probing in the  $UV^{14}$ (see Sec. V B). It is most remarkable that during this time the H<sup>+</sup> and other signals do not change. This means, the *intense*laser field multielectron ionization is not sensitive for the length of the molecule in this case! (We already concluded in Sec. V B in the context of polarization dependence, that the strong field does not stretch the product hexatriene to its longest conformer tZt.)

To explain the enhanced yield for multiple ionization in hexatriene, we instead invoke an intermediate resonance in the singly charged positive ion. The first allowed transition  $({}^{2}B_{1} \rightarrow {}^{2}A_{2})$ ; see Fig. 2) in the hexatriene cation (HT<sup>+</sup>) has a cut-off at about 700 nm and probably at even longer wavelengths in the hot ion, while in the cyclohexadiene ion (CHD<sup>+</sup>) the cut-off for the corresponding band  $(^{2}A_{2})$  $\rightarrow^2 B_1$ ; Fig. 2) is at shorter wavelengths (about 530 nm).<sup>31</sup> Thus the probe wavelength of 800 nm is close to resonance with HT<sup>+</sup> which will not only enhance the ionic photofragmentation, but also seems to help reaching the second ionization limit. The corresponding resonance in CHD<sup>+</sup> is farther away. It is rather unusual to postulate an intermediate resonance for intense-laser field ionization, a process which has been believed to be a field-induced process which is insensitive for resonances. (Resonances with Rydberg states have previously been seen in DIFI of H2.67,68) Note, however, that the resonance in HT<sup>+</sup> concerns the second electron, which has already a rather high ionization energy, so that the intensity for barrier-suppression ionization [Eq. (2)] might not be reached. (Also for the first electron, our intensity is just only at the threshold, since we are now dealing with ionization from the ground state.)

Strong evidence for the suggested resonance is the rotational anisotropy (Sec. V B): Ionization without any intermediate resonance will either not depend at all on the molecular orientation or, if a length dependence is assumed, will be sensitive for anisotropy of the molecular shape. In the latter case, it is the rotation around an axis in the "ring plane" of the nearly ring-like molecule cZc-hexatriene which should show up in the signal. However, the rotation around an axis perpendicular to the ring was observed. This is just what is expected for a resonance whose transition dipole moment is in the ring plane. The suggested  ${}^{2}B_{1} \rightarrow {}^{2}A_{2}$  transition of the hexatriene ion in fact has just a polarization nearly in this plane: Its direction is near the line connecting the two terminal carbons. This is parallel to the dipole moment of the pump transition in cyclohexadiene. In Sec. V B we found in fact that pump and probe transitions are nearly parallel. A small angle between the two can be rationalized by assuming that the cZc-hexatriene is slightly distorted from  $C_2$  symmetry due to steric crowding.

In principle it would be consistent with this interpretation that the two signals  $C_6H_8^+$  and  $C_6H_7^+$  formed from the excited states do not depend on the polarization: To form these ions, no resonance is involved. But a more trivial rationalization of this insensitivity is that the rotational anisotropy does not strongly change before about 500 fs (Fig. 8), i.e., at a time when both ion signals have already decayed to near zero.

It is tempting also to interpret by a resonance why there is a location (level 5) on the potential energy surface giving rise to a transient maximum yield of doubly charged ions and the consecutive products such as H<sup>+</sup>. In this case one needs a resonance which is tuned by the ring-opening coordinate. Such a feature exists in the ion and in the neutral: The ground state of HT<sup>+</sup> correlates with the second excited state  $(2^2B_1 \text{ around } 4 \text{ eV})$  of CHD<sup>+</sup> and vice versa, and along the ring-opening coordinate there is an allowed crossing.<sup>31</sup> Hence the (strongly allowed) ionic transition  $1^2 A \rightarrow 2^2 B$  is tuned through zero and through the laser frequency during ring opening of the neutral molecule; the end is the imperfect resonance discussed above for static HT<sup>+</sup>. For the neutral, the  $1A \rightarrow 2A$  transition grows from zero energy at the conical intersection to several eV; but its oscillator strength is very small. The much stronger transition  $1A \rightarrow 1B$  begins with little above 1 eV at this point (as to conclude from the calculation<sup>2</sup>) and will pass the laser frequency (corresponding to 1.55 eV) soon after the conical intersection. We suggest that it is this resonance, further enhanced by the one in HT<sup>+</sup>, which gives rise to the transient peak of two-electron ionization probability. An enhancement by this resonance from the neutral ground state can simultaneously explain why the double ionization is much more efficient from this ground state than from the 2A level. The opposite could have been expected, since the 2A state contains a substantial percentage of a two-electron excited configuration, so that both electrons could be detached with little ionization energy. Why a resonance is more important can be understood in terms of geometries instead of energies: Because  $HT^+$  is in resonance with the probe laser and  $CHD^+$  is not and because the HT geometry is reached only after arrival of the neutral at the ground state.

Resonances in the neighborhood of a conical intersection, tuned through the 800 nm probe wavelength, were already used to explain a number of observations including coherent oscillations in metal carbonyls, for instance  $Cr(CO)_5$  produced by photodissociation of  $Cr(CO)_6$ .<sup>69</sup>

We can conclude that level 5 is not characterized by a property of the ground-state surface alone, but it corresponds to a position on it where the distance to the 1*B* surface is around 1.55 eV (probe photon) and where there is a similar resonance in  $HT^+$ . The existence of this "label" on the ground-state surface allowed us to determine the time needed after departure from the 2*A* surface through the conical intersection until this position, which itself cannot be very far from the intersection as to conclude from the small energetic distance to the 1*B* surface (Sec. V D). It also permitted us to detect the compactness of the wave packet (Sec. V D).

The resonance in HT<sup>+</sup> excites a  $\pi$  electron. This is only the very first step for reaching the ionization limit of the second electron, and many additional photons have to follow. If it is the  $\pi$  electron which continues to be excited until ionization, the product will be the ground states of HT<sup>++</sup> and CHD<sup>++</sup>. They are observed (Figs. 3 and 5) and hence are both stable enough, unless they have excess vibrational energy (Sec. V A). (The properties of HT<sup>++</sup> in its ground and some excited states have been calculated in Ref. 70.) Coulomb explosion must hence originate from an electronically excited state. We suppose it is a state (1) in which both electrons have been removed from a single CH bond, (2) which is populated by transition from a precursor state with a single hole in the CH bond and the second hole probably delocalized in the  $\pi$  system (Fig. 12); the transition can either be photon-induced (by excitation of the last CH electron into the other hole) or induced by curve crossing. This assumption can explain the following observation: The H<sup>+</sup> recoil energy (2.7 eV, Sec. VA) due to Coulomb explosion of CHD<sup>++</sup> indicates a distance between the two charges of 5.3 Å before ejection of the H<sup>+</sup> ion, whereas for HT<sup>++</sup> we calculate from 4.8 eV the smaller distance 3.0 Å using Coulomb's law. The suggested assumption predicts that this ejection distance only depends on the CH bond strength and length in the precursor state and on its energy; the Coulomb repulsion curve is always the same (Fig. 12). In fact, in  $CHD^{++}$  with a single hole in a CH bond of a  $CH_2$  group the remaining electron can delocalize in the  $\pi$  system and the CH bond will therefore be long and weak (see the flat potential curve with its minimum at a large CH distance in Fig. 12). In  $HT^{++}$  such a delocalization is not possible since the  $\sigma$  orbital of the CH bond is in the nodal plane of the  $\pi$ orbitals.

So the process begins with ionization of a first  $\pi$  electron and continues with excitation of a second such electron; but later-on it can branch: It either continues in this direction until reaching a stable doubly charged ion or it begins to involve one and eventually even two  $\sigma$  electrons to lead to Coulomb explosion.

In view of the strong difference in the fragmentation patterns of hexatriene and cyclohexadiene which we found under conditions of intense-laser field ionization it is interesting to discuss the recent results of Levis and DeWitt et al.24,71 They studied dissociative photoionization of aromatics and alkyl substituted derivatives using intense 780 nm radiation and found ionic fragmentation increasing with the number of atoms<sup>71</sup> or  $\sigma$  bonds<sup>24</sup> in the molecule. For explanation, the authors invoke superexcited states<sup>71</sup> (i.e., states of the neutral parent molecule with internal energy exceeding the ionization potential) and field-induced dissociation.<sup>24</sup> We think that these two mechanisms alone would not explain all the details reported above, such as the H<sup>+</sup> originating from a Coulomb explosion or the resonances, etc. Rather one should consider also in these cases ionic transitions enhanced by near resonance. Note that according to photoelectron spectra the lowest ionic states of higher aromatics and of alkyl substituted benzenes have a smaller distance than those of benzene, and that radical ions with a  $\sigma$  hole always have very low-lying excited states.<sup>29</sup> The same can be said about aniline, furane and pyridine studied in Ref. 56. The degree of fragmentation depends on the relative rates of further excitation versus decomposition of an excited ion.

In this work, a number of features were observed which are normally considered to be typical of multiphoton processes. Among them are several resonances and nonvertical steps such as the geometrical relaxation before Coulomb explosion (Sec. VIC). It may therefore be surprising why we keep speaking about field ionization (DIFI). The main reason is that the intensity is clearly beyond the limit of Eq. (2) (or an analog for molecules), if excited states are concerned. Nevertheless, the singly positive ion is below the limit, owing to the high energy for removing the second electron, and ionic resonances play an important role in this work. So, obviously a combination of field ionization with subsequent multiphoton processes is possible. It is also conceivable that resonances which are important at low intensities can still facilitate excitation at intensities typical of field ionization.

## C. Comparison with calculated potential energy surfaces and pathways

All the lifetimes given in Fig. 9 are so short that it must be concluded from the Landau-Zener consideration in the Introduction that the pathway is continuous all the way down the different potential energy surfaces. There can be no significant gap between the surfaces, and in particular there must also be a real crossing between the 2A and 1A surfaces. So the experiment directly supports the conical intersection predicted for this case.<sup>1</sup> Figure 9 is one of the most detailed descriptions of the dynamics of a reaction. The assignment of all these numbers would not have been possible without at least the qualitative ideas about the potential energy surfaces presented in Sec. III. Recent progress in quantum chemistry now permits to calculate more accurate potential energy surfaces and to predict details of the pathway. Examples are the work of the groups of Bernardi, Olivucci and Robb.<sup>1-3,28</sup> The results can be compared with the experiments.

The calculations of the 1B surface<sup>2</sup> showed, after a steep initial slope accelerating the molecule in the direction of



FIG. 12. Suggested potential energy curves for the Coulomb-repulsive state (repulsive curve, right-hand side) and precursor states of CHD<sup>++</sup> and HT<sup>++</sup>. Open and solid circles indicate holes and electrons, respectively. The creation of the last  $\sigma$  hole from a  $\pi$  hole probably takes place at a curve crossing at the CH distances indicated in the figure. The transition to the Coulomb-repulsive curve can either be purely diabatic (e.g., after the absorption of the last photon) or optical (by absorption from a lower state). In a dressed-states description, the latter case involves a curve crossing, too.

Franck–Condon active coordinates, a flatter region which is crossed by the 2A surface (schematically shown in Figs. 2 and 9). Only in this second region the  $\sigma$  bond (C1-C6, numbering as in hexatriene) initially not affected by the  $\pi\pi^*$  excitation begins to open. That is, the direction of the path changes. In Sec. VIA we assigned the first two time constants to these two regions on the basis of energetic and spectroscopic arguments. Recently we also found a confirmation of the direction change in the effect of substituents on  $\tau_1$  and  $\tau_2$ .<sup>72</sup>

On the 2A surface the initial calculations<sup>1</sup> showed a minimum energy path (MEP) first leading to the 2A minimum and then changing direction toward the 2A/1A conical intersection (CI). Whereas in the 2A minimum the molecule has a geometry similar to cZc-HT, with the  $C_2$  symmetry conserved, in the CI (more precisely, the energy minimum of the CI space) the symmetry is broken, one of the terminal C atoms forming a triangular structure (three-electron threecenter bond) with the other two terminal C atoms. According to the calculation, the time to find this special geometry is lengthened by a negative activation entropy ( $\Delta S^a$  $= -2.0k_B$ ). The minor activation energy found ( $\Delta E^a$ = 0.04 eV) was at the limit of accuracy and is not confirmed by recent calculations.<sup>3</sup> Its influence on the 2A lifetime could anyway be neglected in view of the large excess energy ( $\approx 1$ eV) released along the path from the Franck-Condon region down to the 2A minimum. With  $\Delta S^a$  and transition-state theory, one estimates a 2A lifetime of 1200-450 fs using in the pre-exponential factor  $(k_B T/h)$  a temperature of 300-800 K, the latter calculated from the assumption that the excess energy is equipartitioned. So the experimental rate  $(77 \text{ fs})^{-1}$  seems to be faster, though not much, than the maximum predicted by statistics. This is conceivable if the molecule is accelerated by the slope of the potential energy sur*faces directly to the funnel* and its outlet, so that statistical energy redistribution is not required to find the direction.

The same conclusion can be drawn from comparison of the 2*A* lifetime with the period of a vibration much contributing to the reaction coordinate. The MEPs before and after the 2*A* (symmetric) minimum have large components of nonplanar torsions, all of which having wavenumbers of the order of 100 cm<sup>-1</sup> (in the ground state; magnitudes of curvatures are, however, not drastically different in excited states). 77 fs correspond to only a fraction of their periods ( $100 \text{ cm}^{-1} = 333 \text{ fs}$ ). This suggests that the funnel outlet is just somewhere early along the line of such a vibration. Hence also this consideration infers that the molecule does not have to search around.

Since the direction changes along the reaction path, the idea of the steepest slope directly leading the molecule to the funnel infers a valley which guides the molecules around a smooth curve to the new direction. They would not follow a sharp curvature, due to the momentum in the direction of initial acceleration. Recent calculations<sup>3</sup> indeed confirm this idea: Already early on the path which appeared to be a MEP before<sup>1</sup> there is a large negative curvature towards the funnel. The deflection of the path even seems to begin before the first conical intersection.<sup>72</sup> This is probably characteristic for pericyclic reactions,<sup>72</sup> whereas two examples of *cis*–*trans* isomerizations showed a less smooth or even abrupt change of direction.<sup>3</sup>

A recent study investigates the quantum dynamics on the 2*A* surface of cyclohexadiene and finds broadening or contraction of the wave packet depending on the initial width near the 1B/2A intersection.<sup>73</sup> The narrow wave packet observed after passing the 2A/1A conical intersection (the end of Sec. VI A) probably also infers a small width immediately before.

#### **VII. CONCLUDING REMARKS**

Originally Corkum and coworkers suggested using dissociative intense-laser field ionization (DIFI) for ultrafast spectroscopy.<sup>22</sup> The idea was to profit from the extreme sensitivity of multiple ionization for the dissociation (Coulomb explosion) coordinate, which thus provides an observation window for motion along this direction. Recently Castleman and coworkers studied the proton transfer in the hydrogenbonded dimer of 7-azaindole by DIFI;<sup>74</sup> depending on the progress of reaction of the neutral dimer, Coulomb explosion after ionization separated the monomers either with or without a transferred hydrogen. Our work demonstrates that the potential of DIFI to study dynamics is even broader: The DIFI signals can also be sensitive for reaction coordinates (such as the ring opening of cyclohexadiene) which have nothing to do with the direction of Coulomb explosion (the ejection of H<sup>+</sup> from a doubly charged ion). This sensitivity has various origins which were discussed in the text. All of them are, however, related to the Franck-Condon principle, which rationalizes why the ionization probability and fragmentation pattern depend on the location on the potential energy surface. For this mechanism to hold, only the first step must be (more or less) vertical; it does not matter if before the last step a bond must be extended, as suggested in Sec. V B to explain the difference of Coulomb recoil energy for the two isomers.

DIFI usually gives a signal for every part of the potential energy surface being passed, and it gives rise to many different ions which often differ in temporal behavior, thus providing more information than methods based on only one transition such as transient absorption or fluorescence. This is the reason why we obtained an unprecedented number of details on the dynamics of the ring opening of cyclohexadiene. A similarly detailed picture was obtained for H migration in cycloheptatriene<sup>75</sup> and for dissociation of some transition metal carbonyls and subsequent isomerization.<sup>66,69,76</sup> With low-intensity photoionization or with REMPI, this nonselectivity and generation of many ions is not common.

Whereas photoionization with mass-selective detection is often used for time-resolved probing, it was apparently not recognized before, that different ions monitor different locations on the potential energy surface; instead, it was often attempted to correlate the ionic fragments with a supposed dissociation of the neutral, an assumption which at least for cyclohexadiene is invalid. Reference 77 shows that transient DIFI is consistent with transient absorption, although the latter would probably provide comparably rich information only if it were measured at many different wavelengths.

As already pointed out, the levels used in the kinetic equations actually represent observation windows, each characterized by a set of probabilities ( $\sigma$ ) to produce the observed ions. Traveling times required to cross each window are expected to be of the same order of magnitude as the observed times. It is even probable that all the time is used for traveling and there is no bottleneck anywhere on or between the surfaces. It seems that a new observation window can open not only when the molecule enters another electronic state, but also if it changes direction on a given surface (note the two times assigned to the 1*B* surface). This phenomenon probably occurs if the difference of slopes of ionic and neutral potentials abruptly changes.

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