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Ultrafast dynamics of the photochemical ring opening of 1,3-cyclohexadiene studied by multiphoton ionization

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Abstract

Femtosecond time-resolved studies of the ring opening of 1,3-cyclohexadiene are presented. After absorption of a single UV photon in the region 250-270 nm $(1A_1 \rightarrow 1B_2 \text{ transition})$, the reaction is investigated using time-delayed single- and multiphoton ionization with probe pulses in the region 250-415 nm. Ions are detected by a time-of-flight mass spectrometer. The parent ion is only observed during the time when the pump and probe lasers overlap. The corresponding ionizable state, which we identify as $1B_2$, has a short lifetime which we estimate to be 60 fs. The only signal detected after a delay is due to $C_6H_7^+$. It arises from dissociation of vibrationally hot parent ions which are produced by two-photon ionization of vibrationally excited products. The appearance rate constant of the product is as high as $1.7 \pm 0.2 \text{ ps}^{-1}$. It is assigned to the transition from the $2A_1$ to the $1A_1$ surface via a conical intersection, i.e. to the photochemical ring opening of 1,3-cyclohexadiene to Z-hexatriene. Measuring fragment ions generated by photoionization at suitable wavelengths may be a general method for monitoring vibrationally hot neutral molecules.

1. Introduction

The UV-induced ring opening of cyclohexadiene (CHD) to Z-hexatriene (Z-HT) is a model for a large number of photochemical electrocyclic reactions. The intense longest wavelength UV band of CHD is a $\pi - \pi^*$ transition of symmetry $1A_1 \rightarrow 1B_2$ (in $C_{2\nu}$) [1,2]. Another $\pi - \pi^*$ excitation leads to the $2A_1$ state [1], which is higher than $1B_2$ in the Franck-Condon region, but lower for a larger deformation of the molecule [3,4]. Quantum chemical calculations [4,5] have shown that after UV excitation to its $1B_2$

potential surface, cyclohexadiene is rapidly accelerated into the direction of the reaction coordinate of the ring opening; then it crosses to the 2A₁ surface, proceeding to a minimum which is common to CHD and Z-HT; from there, the reaction path requires some activation entropy to reach a conical intersection with the 1A₁ surface, where it branches to the ground state of the product or the educt. From the low fluorescence quantum yield of CHD it has been concluded that the $1B_2/2A_1$ crossing occurs within about 10 fs [6]. Time-resolved resonance Raman scattering showed that the product of the ring opening appears with a time constant of 6 ps [7-9]. By transient absorption spectroscopy, we found that the cyclohexadiene ring of dehydrocholesterol opens with a temperature-independent rate of 1/5.2 ps, from

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which we inferred an activation entropy of -3.4 kB [10]. All this is good confirmation of the quantum chemical calculations. More recent transient absorption measurements of CHD by Pullen et al. [11] and in our lab [12] indicated, however, a subpicosecond rate of product formation; the analysis is complicated in this case by superimposed thermal processes. All these measurements have been done in solution.

In this work, we measured the decay rate of excited CHD in the gas phase by using femtosecond time-resolved pump-probe two-color photoionization with mass-selective detection. At the mass of the parent ion, there was a transient signal only when the pump and probe pulses overlapped. Thus the corresponding state (certainly $1B_2$) of neutral CHD has a short lifetime. From the yield of the ions we can estimate this lifetime to be about 60 fs. Only at the mass of the fragment $C_6H_7^+$ we found a delayed signal. We assign it to the decaying $2A_1$ state and the appearance of the ground state of educt and product.

Three recent works [13-15] investigated Z- and E-HT by a related technique. In Ref. [14] the authors also mention the absence of a delayed ion signal in CHD. Although the investigated conformer of Z-HT is different from the primary photolysis product of CHD, the lifetimes of their excited states were found to be similar. In this work, we focus on the detection of highly vibrationally excited molecules. The photoionization of such molecules (cycloheptatriene/toluene [16] and azulene [17]) has already been reported previously, though without mass-selective detection and only with low time resolution.

2. Experimental

The laser system used in our experiments has been described elsewhere [10] and therefore the description here is kept brief. The primary source of radiation is a 1 kHz oscillator/amplifier Ti sapphire laser system, yielding pulse energies of 600 μ J in the range 780–840 nm, pulse width 100 fs. Its frequency ω_p is converted to tunable UV radiation by various non-linear processes:

• $\omega_s + \omega_i = \omega_p$, i.e. signal and idler in a commercial optical parametric generator (OPG, TOPAS), $(\lambda_{s,i} = 1150-2400 \text{ nm});$

• $\omega = 2(\omega_s + \omega_p)$, i.e. mixing signal + pump frequency and subsequent frequency doubling ($\lambda = 230-270$ nm);

• $\omega = 2(\omega_i + \omega_p)$, i.e. mixing idler + pump frequency and frequency doubling ($\lambda = 260-300$ nm);

• $\omega = \omega_p + (\omega_s + \omega_p)$, two-fold frequency mixing ($\lambda = 290-330$ nm);

• $\omega = \omega_p + (\omega_i + \omega_p)$, two-fold frequency mixing ($\lambda = 320-360$ nm);

• $\omega = 2 \omega_p$ ($\lambda = 390-420$ nm), frequency doubling;

• $\omega = 3\omega_p$ ($\lambda = 260-280$ nm), frequency tripling.

Pump-frequency doubling and tripling could be operated simultaneously with OPG-based frequency conversion. Crystals are optimized for efficiency. Typical UV pulse energies are up to 10 μ J, pulse duration 300 fs.

The pump and probe beams are delayed separately, combined collinearly and focused into the photoionization chamber, which was provided with accelerating grids and connected to a magnetically shielded time-of-flight tube (25 cm) and a microchannel-plate detector by a slit of $0.5 \times 30 \text{ mm}^2$. The gas pressure in the ionization chamber was about 10^{-5} mbar and sufficient gas flow was provided in the focal region to exchange the irradiated volume between subsequent laser pulses. The pumpbeam polarization could be rotated by a half-waveplate. Time-dependent signals were taken by gated integrators and processed by a PC. The mass spectrum of Fig. 1 was recorded by a fast multichannel counter. Synchronized choppers allowed us to measure ion signals periodically with pump only I_{pu} , probe only I_{pr} and with both lasers simultaneously $I_{\rm bo}$ to determine the transient ion signal S at a given delay time t, $S(t) = I_{bo}(t) - I_{pu} - I_{pr}$. Beam energies and the difference-frequency signal of the pump and probe-beams were recorded for correlation peak width measurement and normalization of the signals. The focal diameter of the laser beams was 100 μ m. Typical energy densities for the pump and probe were $\Phi_{pu} = 1 \text{ mJ/cm}^2$ and $\Phi_{pr} = 30 \text{ mJ/cm}^2$.

Commercial 1,3-cyclohexadiene (Fluka) was employed after degassing. The vapor phase contained 1-2% of each benzene and cyclohexene as impurities. They did not disturb the measurements due to the mass-selective detection.

3. Results

1.3-Cyclohexadiene (CHD) was excited in the region 250-270 nm. These wavelengths fall into the first intense band of CHD which is due to the allowed $1A_1 \rightarrow 1B_2$ transition (origin at about 267 nm) [2]. A typical time-of-flight mass spectrum of cyclohexadiene around mass 80, observed by onecolor ionization at 268 nm, is shown in Fig. 1. Three peaks are clearly seen. The strongest one corresponds to the parent ion $C_6H_8^+$ of mass 80. The peak at mass 81 with relative intensity of 6.1% is the ^{13}C isotopomer of CHD (natural abundance 6.5%), and the peak at mass 79 belongs to the fragment $C_6H_7^+$. No other signals were observed at moderate energy densities $\Phi \leq 30 \text{ mJ/cm}^2$ (intensity up to 10^{11} W/cm²). The ratio S_{80}/S_{81} of the signals at mass 80 and 81 does not depend on Φ , whereas $S_{79}/S_{80} \propto \Phi$. This fact indicates that the formation of $C_6H_7^+$ requires the absorption of one photon more than the



Fig. 1. The time-of-flight mass spectrum of cyclohexadiene around mass 80 observed with one-color ionization with 268 nm pulses of 300 fs duration. Mass 80 corresponds to the parent ion $C_6 H_8^+$, mass 81 is ${}^{12}C_5{}^{13}CH_8^+$ (natural abundance 6.5%) and mass 79 belongs to the fragment $C_6 H_7^+$. The absolute time of flight for the ion of mass 80 is 3615 ns.

generation of the parent ion. The experiment has mainly been carried out with 268 nm pump radiation. For the probing by delayed ionization, we used selected wavelengths in the region 250-415 nm. For none of the probe wavelengths was there any delayed signal at mass 80, i.e. the signal practically coincides with the cross-correlation between the pump and probe, which was separately recorded as the difference-frequency signal using a thin BBO crystal. These data indicate that the lifetime t_{CHD} . of the ionizable state of CHD is below our time resolution of about 100 fs.

Therefore, we tried to determine this lifetime t_{CHD} . by measuring the ion yield with single-wavelength ionization (260 nm). In this case, during the laser pulse there will be a competition between the ionization rate σ_{CHD} . I (intensity I in photons/cm²s) and the decay rate $1/t_{CHD}$. of the excited CHD. Their ratio is the quantum yield for ionization. Thus, by measuring the ion yield, we can deduce t_{CHD} , if the cross section σ_{CHD} . for the excited state absorption is known. For this cross section, we assume the same value $(4 \pm 2 \times 10^{-18} \text{ cm}^2)$ as for hexatriene, where it has been measured by saturating the ionization [18]. Unfortunately, this method of measurement is not feasible with CHD, since its much shorter lifetime would require much higher intensities for saturation, at which higher order non-linear processes would set in. With this assumption on σ_{CHD} . we obtain $t_{CHD} \approx 60$ fs. It is interesting that a lifetime of the 1B₂ state $t_{1B} = 10$ fs has been inferred from the small fluorescence yield [6]. We believe that the uncertainty in our t_{CHD} . (mainly due to the uncertain in σ_{CHD} .) is a factor of 2-3, but not a factor of 6. Furthermore, a previously published REMPI spectrum of CHD [19] showed linewidths corresponding to lifetimes ≥ 50 fs. Nevertheless, the two values for the lifetime can be consistent with each other. After excitation, the wavepacket is accelerated by the steep $1B_2$ potential and then crosses to $2A_1$. It may soon reach a position from where the fluorescence is too slow or at too long a wavelength, whereas ionization is still possible. Thus the temporal observation window is different for the two detection methods.

In order to avoid the fragment $C_6H_7^+$ forming by secondary absorption of the parent ion $C_6H_8^+$, we observed the signal at mass 79 under conditions



Fig. 2. Relative ion yield versus time delay between the 268 nm pump and the 294 nm probe. The dotted line with + symbols shows the parent ion $C_6H_8^+$, and the open circles are the $C_6H_7^+$. The solid curve is a single-exponential fit to the mass 79 data in the region from 0.6 to 14 ps, which gives a rise rate constant of 1.73 ± 0.17 ps⁻¹. The experimental data represent averaged values for five independent runs. The zero delay has been assigned to the maximum of the parent ion signal. The figure shows only part of the data which have been used for the fitting procedure.

where the formation of the parent ions by the pump radiation alone was negligible, i.e. at low pump energy density Φ_{pu} . The probe was stronger and could cause such secondary fragmentation of the ion. In this case, the temporal shape of S_{79} and S_{80} should coincide. In fact we confirmed this expectation, both signals having the shape of the cross-correlation function, however, only with probe wavelengths $\lambda_{pr} < 280$ nm or > 300 nm. When probed in the region 280–295 nm, the fragment $C_6H_7^+$ also shows a delayed signal.

Fig. 2 shows the transient signals for the parent $C_6H_8^+$ and the fragment $C_6H_7^+$ ions versus time delay between the pump (268 nm) and probe (294 nm). As already mentioned, S_{80} exhibits only the correlation peak, but S_{79} falls down after the initial

spike and then shows a rising feature. After about 3 ps, S_{79} does not change anymore up to about 700 ps, the largest time delay in our experiment. Note also the 50 fs delay between the correlation spikes of mass 80 and 79. A single-exponential fit to S_{79} between 0.6 and 14 ps gives a rise rate constant of 1.73 ± 0.17 ps⁻¹. Reducing the energy density (Φ_{pu}) of the pump radiation does not change the shape of the transient signals and the absolute values of the signals S_{80} and S_{79} are both $\alpha \Phi_{Du}$. This is important, as it proves that the precursors for both signals are states of the neutral species produced by absorption of only one pump photon. The shape of transient signals also does not depend on the probe energy density $\Phi_{\rm pr}$. Moreover, $S_{79} \propto \Phi_{\rm pr}^2$. This indicates the two-photon character of this probing ionization. S_{80} $\alpha \Phi_{pu}$ and $\alpha \Phi_{pr}$, and the correlation peak at mass 80 is seen even with unfocused beams. The Φ dependences can be summarized as follows: S_{80} is proportional to Φ_{pu} and Φ_{pr} , whereas S_{79} is proportional to Φ_{pu} and Φ_{pr}^2 .

The rise rate constant of 1.73 ± 0.17 ps⁻¹, within the accuracy of the fit, does not depend on the probe wavelength λ_{pr} in the region 280–294 nm when pumped at $\lambda_{pu} = 268$ nm. Essentially, the same rise rate constant has been determined for $\lambda_{pu} = 250$ nm with $\lambda_{pr} = 268$ nm.

4. Discussion

The proportionalities S_{80} and $S_{79} \propto \Phi_{pu}$ imply a single-photon pump process. This excitation initiates a sequence of events which is outlined in Scheme 1 and Fig. 3. The initial excitation populates the $1B_2$ state, which decays by internal conversion with a rate constant k_{1B} to the dark 2A₁ state. In this state, the molecule appears with an excess vibrational energy E_1 , which has been calculated to be $\approx 1 \text{ eV}[4]$. According to this ab initio calculation, the $2A_1$ surface acts as a common intermediate for CHD and cZc-1,3,5-hexatriene (cZc-HT). A conical intersection (CI) connects the 2A₁ and 1A₁ surfaces at a point between the geometry of CHD and cZc-HT. The molecule proceeds from the 2A1 minimum to the CI with a rate constant k_{2A} . It passes through the CI without delay. It is this point where the path branches to either CHD or cZc-HT. In both cases,

CHD(1A)

$$hv_{p\mu}$$

CHD(1B) $\xrightarrow{hv_{pr}} C_{6}H_{8}^{+} \xrightarrow{hv_{pr}} C_{6}H_{7}^{+}$ (1)
 k_{B}
CHD / HT(2A + E_{1}) $\xrightarrow{hv_{pr}}$ CHD / HT(S_n + E_{1})
 $\xrightarrow{hv_{pr}} C_{6}H_{8}^{+}(1A + E_{1} + E_{2}) \rightarrow C_{6}H_{7}^{+}$ (2)
 k_{2A}
 v_{1a} conical intersection
 $\xrightarrow{hv_{pr}} C_{6}H_{8}^{+}(1A + E_{3}) \rightarrow C_{6}H_{7}^{+}$ (3a)
 $\xrightarrow{hv_{pr}} C_{6}H_{8}^{+}(1A + E_{3}) \rightarrow C_{6}H_{7}^{+}$ (3a)
 $\xrightarrow{hv_{pr}} C_{6}H_{8}^{+}(1A + E_{3}) \rightarrow C_{6}H_{7}^{+}$ (3b)

Scheme 1. Photochemical and photophysical processes relevant to the formation of the ions $C_6H_8^+$ (mass 80) and $C_6H_7^+$ (mass 79). The processes (1), (2) and (3a) are illustrated in Fig. 3.

the molecules are produced in the ground state with an excess vibrational energy E_3 , which is close to the energy of the pump photons (4.5 eV).



Fig. 3. Schematic potential energy surfaces (for more detailed data see Ref. [4]) of cyclohexadiene/hexatriene relevant for the formation of the $C_6H_7^+$ fragment ion by one pump photon plus two probe photons. Asterisk (*): conical intersection. The processes (1), (2) and (3a) are those of Scheme 1. Thinner vertical arrows indicate the probe photons; where they end above the ionic ground state, the excess energy (mostly) goes into kinetic energy of the electrons. Double line arrows are the vibrational excess energies E_1 , E_2 and E_3 explained in the text.

Consider now the ionization step for probing. The ionization potential for CHD is 8.25 eV [20,21]. Therefore, the threshold wavelength for two-photon one-color ionization of the ground state of CHD is 301 nm, and the threshold wavelength required for ionization of the $1B_2$ state from its zero vibrational state at 37500 cm⁻¹ is 344 nm. Our experimental finding that $S_{80} \propto \Phi_{\rm pr}$ for wavelengths $\lambda_{\rm pr} < 340$ nm is in agreement with this spectroscopic consideration. Thus the transient signal at mass 80 is produced from the 1B₂ state as a precursor by absorption of one probe photon, as indicated in Scheme 1. From the probe radiation, the parent ion $C_6H_8^+$ can absorb one more photon, initiating the elimination of a hydrogen atom. (The cut-off wavelength for photodissociation is near 530 nm [22].) This process (1) in Scheme 1 and Fig. 3 should give a contribution to S_{79} which is proportional to the population of the 1B₂ state ($\alpha \Phi_{pu}$). Thus S₈₀ and the early part of S₇₉ reflect the population of 1B₂ and possibly of any other state which can be ionized by a single photon. The time dependence of S_{80} , in particular, shows that this state has a lifetime below our time resolution of about 100 fs. From the absolute ion yield, we estimated it to be 60 fs. Since our kinetic model (Scheme 1) contains only the two rate constants k_{1B} and k_{2A} and since the experiment shows a second rate (1.7 ps^{-1}), we associate this short lifetime with the decay of the $1B_2$ state. In this case, we should explain why the $2A_1$ state is not ionizable by a single probe photon.

We invoke two reasons for this, the potential energy hill in the ion (Fig. 3) and the Franck-Condon principle. The former is a consequence of the fact that the ring opening in the ionic ground state is forbidden by orbital symmetry, much like in the neutral molecule [22,23], although the barrier may be smaller than in the latter. As a consequence, a single probe photon may not be sufficient to ionize the molecule from the 2A₁ minimum, as indicated in Fig. 3. The Franck-Condon principle postulates a small change Δv of vibrational quantum numbers for all degrees of freedom, for which the shift of the potential surface is small. This is clearly the case for ionization of the ground states of CHD and HT, as concluded from the small Δv observed in the normal photoelectron spectrum [21]. However, we can assume this also for the $2A_1$ state, with the exception of just one degree of freedom, the reaction coordinate. A small Δv means that the vibrational excess energy of the neutral reappears in the ion, and that the photon energy required for ionization derives from the difference in electronic energies alone. Therefore, the arrows indicating the ionization in Fig. 3 start from the electronic surfaces, not from the total energies.

As mentioned, the ion signal $S_{79} \propto \Phi_{\rm pr}^2$, indicating ionization by two probe photons. Starting from the 1B₂ state, an excited dissociative state of the ion can be produced (Scheme 1 and Fig. 3). Starting from the lower states, one should realize that the excess energies E_1 and E_3 reappear in the ion; and when the $2A_1$ state is ionized, the energy E_2 released by going down the hill must be added (Fig. 3). The result is an excess energy of more than 3 eV. The dissociation of $C_6H_8^+$ into $C_6H_7^+$ + H has been reported to require only 2 eV [22]. Thus, it is obvious why the delayed ion signal shows only fragments, but no parent ion. In an alternative mechanism, the highly energized (4.6–5.0 eV) neutral molecule would first form a cyclohexadienyl radical C_6H_7 , which is then ionized by the probe. The formation of the radical is endothermic by about 3.3 eV [24]. However, the excess energy ($\leq 2 \text{ eV}$) of the energized molecule is too small to extrude the hydrogen atom within picoseconds. A rate of 0.2×10^9 s⁻¹ has been measured for H₂ elimination from 1,4cyclohexadiene after excitation with 6.4 eV photons (193 nm), and RRKM calculations gave a value of 10^9 s^{-1} for about 4 eV excess energy [25]. Moreover, no formation of cyclohexadienyl radicals has been observed in the 248 nm (KrF laser) photolysis of gas-phase 1,3-CHD [26].

Thus we can expect that the delayed part of S_{79} consists of the sum of signals from the $2A_1$ and $1A_1$ states. The populations of both states will change with the same rate, k_{2A} but $2A_1$ will contribute a decaying signal and the hot ground state (subscript hg) an increasing one:

$$S_{79} \propto \sigma_{2A} \exp(-k_{2A}t) + \sigma_{hg}(1 - \exp(-k_{2A}t)).$$
 (1)

Here, each of the two-photon ionization cross sections σ is the product of the absorption cross sections of the two consecutive steps involved. The relative size of the two terms in Eq. (1) will depend on the transition probabilities of each step. The $1A_1 \rightarrow 1B_2$ absorption of the product Z-HT is intense and is shifted to longer wavelengths, with its maximum at 280 nm [26], when the molecule contains the excess energy released by the ring opening. If we assume that the $2A_1 \rightarrow S_n$ transition (to an assumed real intermediate state S_n) has less intensity, we can understand why the (rising) signal from the population of the ground states dominates S_{79} most strongly at $\lambda_{pr} = 280-286$ nm, dropping slightly in the wings. Thus we can conclude that the observed rate constant of 1.7 ps⁻¹ must be assigned to k_{2A} .

Inspection of Fig. 2 already indicates some contribution from the $2A_1$ state: the fit curve, extrapolated to time zero, has a non-zero value in spite of the initially vanishing population of the hot ground state. In order to find this contribution more quantitatively and also to check the consistency of the model with the detailed shape of the observed signal, we calculated the populations of the $1B_2$, $2A_1$ and hot ground states by rate equations. This model included the rate constants $\sigma_{1A} I_{pu}$ for the pumping (with the known ground state absorption cross section and pump intensity), k_{1B} for the $1B_2 \rightarrow 2A_1$ decay and k_{2A} for the $2A_1 \rightarrow$ hot ground state decay. Furthermore, the ratios of ionization cross sections σ_{1B}/σ_{hg} and σ_{2A}/σ_{hg} of the intermediate states (were used. As above, each σ is the product of the absorption cross sections of the two steps involved, which yield the fragment ion. (For $1B_2$, the second step is the absorption of the ion, causing dissociation.) The resulting signals were calculated as convolutions over the pump pulse and over the probe pulse. Fig. 4 compares such a calculated curve with the measured data. k_{2A} was kept fixed at 1.7 ps⁻¹. Varying $1/k_{1B}$ between 0 and 50 fs did not change the resulting time dependence, in particular, for the small time delay between the peaks of S_{79} and S_{80} . However, note that the 50 fs delay of the leading edge is correctly reproduced. By varying σ_{1B}/σ_{hg} we can fit the ratio peak/pedestal to the experimental data. However, assuming $\sigma_{2A}/\sigma_{hg} = 0$, the calculated curve (dotted line) deviates noticeably from the experimental data in the region of the minimum around 500 fs delay. The best fit is achieved with σ_{2A}/σ_{he} = 0.13 (solid curve). Thus under these conditions,



Fig. 4. Relative ion yield versus time delay between the 268 nm pump and the 294 nm probe. The + symbols show the parent ion $C_6H_8^+$, the open circles are the fragment $C_6H_7^+$. The solid curve shows the simulation (see text) for $C_6H_7^+$ with $1/k_{1B} = 0$ ps, $1/k_{2A} = 0.58$ ps, $\tau_{pu} = 0.30$ ps, $\tau_{pr} = 0.39$ ps, $\sigma_{1B}/\sigma_{hg} = 2.15$, $\sigma_{2A}/\sigma_{hg} = 0.13$. The broken line is calculated with $\sigma_{1B}/\sigma_{hg} = 2.24$, $\sigma_{2A}/\sigma_{hg} = 0$, while all the other parameters are kept the same. The corresponding simulation curve for the parent ion practically coincides with experimental data and is not shown. The results of the calculation are not sensitive for variation of $1/k_B$ in the range 0–50 fs.

the $2A_1$ state contributes to S_{79} , although only about 13%.

The decay rate of the $2A_1$ state did not change when CHD was pumped at 250 nm (excess energy to 2500 cm⁻¹) instead of near the origin (268 nm). This indicates that there is no early barrier, just as was found for the ring opening of 7-dehydrocholesterol [10].

5. Conclusion

We found that two steps can be distinguished in the gas phase photochemical ring opening of 1,3cyclohexadiene: the radiationless transition from $1B_2$ to $2A_1$ and the decay of $2A_1$ to the ground state. The time for the first step was estimated from the ion yield to be about 60 fs. The second step takes $1/k_{2A} = 580$ fs, as measured by the transient ionization method.

For detecting this step, we selectively monitored vibrationally excited products by two-photon ionization. The selectivity was accomplished by the detection of fragment ions. The fragments are formed, because due to the Franck-Condon principle most of the excess energy of the neutral molecule is transferred to the ion. To enhance the signal, it is helpful if one of the states to be detected has a strong intermediate resonance. In our case, this is the product Z-hexatriene. This approach could generally be useful for studying ultrafast photoinduced processes in the gas phase. It is different from another twophoton ionization technique with the detection of fragments [13,14], in which the main purpose was to suppress ion signals generated by the probe alone. Whereas our approach permitted detection of the product formation, in other techniques with ion monitoring there was no delayed signal when CHD was irradiated [14].

It was surprising at first that the $2A_1$ state was difficult to detect, although a probe wavelength of 270 nm should permit single-photon ionization of states 4.6 eV below the ionization energy IE. If one assumes IE = 8.25 eV, states 1 eV below the $1B_2$ states should be detectable. However, such a calculation does not take into account that the ionic potential energy surface is geometry-dependent and has a hill just where the $2A_1$ surface of the neutral has a minimum (Fig. 3). Such a situation will be typical for the monitoring of reactions which are photochemically allowed and ground state forbidden.

Our rate constant for product formation ($k_{2A} = 1.7 \text{ ps}^{-1}$) is an order of magnitude larger than the value derived from the appearance of resonance Raman scattering from the initial photoproduct cZc-HT [7]. However, those data are possibly limited by vibrational cooling in solution rather than electronic decay to the ground state surface. Indeed, recent transient absorption measurement in CHD show multiexponential recovery of absorption with the shortest component faster than 10^{12} s^{-1} [11,12].

According to ab initio calculations [4,5], the ratedetermining step of the ring opening is the decay 682

from the $2A_1$ minimum. From there, the molecule must overcome a small barrier, associated also with a negative activation entropy ΔS_a (i.e. a statistical factor below 1), to find the region of the conical intersection, from where it reaches the ground state surface of the educt and the product. Due to the excess energy available in the gas phase, the activation energy should play no role, whereas ΔS_{a} should still be active to slow the rate down from the limit $k_{\rm B}T/h = 6 \text{ ps}^{-1}$. The measured rate of 1.7 ps⁻¹ is already near this limit. Thus, ΔS_a seems to be smaller than predicted and also smaller than found for the corresponding ring opening in 7-dehydrocholesterol. The latter difference might be attributed to steric hindrance in the steroid, since ΔS_a is associated with the intermediate formation of a bicyclic ring [5], which is the geometry of the conical intersection. It is also worth noting that such fast rates would not be conceivable without a conical intersection, since the rate of jumping between distant electronic surfaces would be clearly slower (for a general discussion see Ref. [27]).

The $2A_1$ minimum is common to CHD and the cZc conformer of Z-hexatriene. The decay rate from the $2A_1$ state with several thousand cm⁻¹ of excess energy can be compared with the corresponding process in another conformer, the tZt hexatriene, which is 1.4 ps^{-1} at high excess energy [13,15]. Thus these two values are similar for the two conformers.

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