Electronic Relaxation and Ground-State Dynamics of 1,3-Cyclohexadiene and *cis*-Hexatriene in Ethanol

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The transient absorption induced by UV excitation of 1,3-cyclohexadiene and *Z*-hexatriene dissolved in ethanol was measured in the wavelength range 255−450 nm. Repopulation of the ground state takes 470 fs in *tZt*-hexatriene. The same process in 1,3-cyclohexadiene, accompanied by ring opening to *Z*-hexatriene, occurs in less than 300 fs. The analysis of the long-wavelength wings of the ground-state spectra reveals a cooling time constant of 7 ps for the hot product *Z*-hexatriene. The transient absorption in the UV furthermore reflects the single-bond isomerizations of this product to different conformers. The evolution of their concentrations was simulated by rate equations using temperature-dependent isomerization rates calculated with the Arrhenius law. In this model, the concentrations of the conformers reach thermal equilibrium in a few picoseconds; during the first 10−20 ps, the concentrations follow the cooling of the molecule by the solvent, staying near thermal equilibrium; and a small quantity of *cZt*-hexatriene is trapped in its potential well on a time scale of 100 ps at the final temperature (300 K). At this temperature, equilibration takes longer. This model well reproduces the time dependence of the integrated spectra in solution and recent experimental results in gas phase. In addition it allows a consistent interpretation of previous, time-resolved resonance−Raman experiments. The fact that single-bond isomerization in the hot product was not suppressed by contact with the cold solvent suggests that this could also be the case for photorhodopsin, the postulated primary conformer of the photoproduct of rhodopsin which always eluded trapping even at cryogenic temperatures.

1. Introduction

Polyenes are a basic group of molecules in photochemistry.[1,2] Their photoreactions are also essential in biochemistry (e.g., in the process of vision or in the vitamin D system). Their most important photoreactions are double-bond isomerizations and pericyclic rearrangements,[1,2] and they have been a topic of research for many years.[3] Recent theoretical and experimental results show that conical intersections between the ground and lowest excited potential energy surface play a prominent role in their dynamics.[4−7] Such crossings cause the very high rates observed for some internal conversions and photoreactions.

To elucidate the dynamics of polyenes, 1,3-cyclohexadiene (CHD) and *Z*-hexatriene (*cis*-hexatriene, Z-HT) can serve as model compounds. After absorption of UV light, 1,3-cyclohexadiene undergoes with 40% quantum yield (in pentane) an electrocyclic ring opening to all-*cis*-hexatriene (cZc-HT),[8] an unstable rotamer of *Z*-hexatriene which isomerizes in the ground state around the CC single bonds first into mono-*s*-*cis*-*Z*-hexatriene (cZt-HT) and finally to the stable di-*s*-*trans*-*Z*-hexatriene (tZt-HT). The photoexcitation of *Z*-hexatriene, which is in the *tZt* conformation at room temperature, is followed mainly by internal conversion; only a very minor part (3.4% in pentane[8]) isomerizes around the central CC double bond producing all-*trans*-hexatriene (tEt-HT). The internal conversion to the hot ground state leads again to an equilibrium conformer distribution and the consecutive steps described above for the hot photoproduct of cyclohexadiene.

Several time-resolved investigations of these reactions were already carried out, but did not lead to a consistent picture since a variety of processes such as ultrafast electronic decay, subsequent ground-state isomerizations, and cooling by the solvent occur on similar time scales. For example, when exciting 1,3-cyclohexadiene, time-resolved resonance−Raman studies seemed to indicate a ring-opening time of 6 ps and a time constant of 7 ps for isomerization of one single bond,[9,10] whereas absorption measurements showed that ring opening is complete in less than 1 ps[11] or even less than 400 fs[7,12] and that the first single-bond isomerization should take less than a couple of picoseconds. This is consistent with recent ionization experiments which showed that ring opening in the gas phase takes only 200 fs and that the first C−C isomerization occurs already during the first picosecond.[13]

Recently, *Z*-hexatriene dissolved in cyclohexane was studied by transient absorption and the concentrations of the product conformers was simulated by a kinetic model[14] which is similar to the model in our work. This study has in the meantime been extended to 1,3-cyclohexadiene.[15] The excited-state absorption of *E*-hexatriene has been investigated in two different solvents,[16] and a similar study of *Z*-hexatriene has most recently been made.[17] The S_1 lifetime in the latter case is similar to the one of this and our previous[18] work. The excited-state lifetime of *Z*-hexatriene has also been studied in the gas phase.[7,19,20]

This work reports an investigation of transient absorption after excitation of 1,3-cyclohexadiene and *Z*-hexatriene dissolved in ethanol. The range of probe wavelengths (255 to 450 nm) was larger than before[14,15] which helped to evaluate concentrations of conformers from the time-dependent integrated spectra; integration eliminates the influence of the varying temperature to the spectra. The cooling by the solvent was inferred from the analysis of the long-wavelength wing of the transient UV spectra (ground-state absorption). The time-dependent temperature and integrated spectra were used in a rate-equation model

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to deduce the conformer distribution. The duration of the electronic relaxation (i.e., the ring opening and the internal conversion), is deduced from the time-dependent measurements in the blue spectral region. This evaluation is more direct and thus probably more accurate than the previous one.[14,15] The model is also simplified. We show that the long times previously attributed to electronic relaxation[9,10] are probably due to cooling and single-bond isomerization in the ground state. Comparison with the results in cyclohexane solution[14,15] and in the gas phase,[7,19,20] shows that the solvent has no strong influence to the electronic relaxation.

2. Experimental Section

The transient absorption was investigated by conventional pump−probe spectroscopy. The preparation of the samples and a description of the laser system were already reported in refs 7 and 21. Therefore, only a brief summary is given here.

Z-Hexatriene was isolated from the commercial *cis*−*trans* mixture (40%/60%) (Fluka) by adding maleic anhydride, which reacts faster with *trans*-hexatriene (10 h, room temperature).[22] Condensing the rest from the reaction vessel led to *Z*-hexatriene with a gas-chromatographic purity of better than 99%. To avoid polymers in the solutions to be investigated, the desired quantities of 1,3-cyclohexadiene (Fluka) and of *Z*-hexatriene were taken via the vapor phase out of the stock vessel, measured by the pressure in a given volume, and then condensed into a small glass vessel, to which the desired quantity of UV-grade ethanol (Merck) was added. The concentrations of 1,3-cyclohexadiene and *Z*-hexatriene were 8 and 2 mmol/L which yielded an absorption of 52 and 55%, respectively, at the pump wavelength 267 nm for a path length of 0.1 mm in our cell. During the experiment, the solution was pumped through a flow cell, which had 2 mm thick CaF_2 windows. The short optical path length was chosen in order to minimize the absorption changes due to nonresonant two-photon absorption of the solvent.[21]

A Ti:sapphire laser system consisting of an oscillator and a regenerative amplifier provides laser pulses of 110 fs duration at 800 nm and 600 μJ energy/pulse at a repetition rate of 1 kHz. To generate pump pulses at 267 nm, 25% of the beam was split off and frequency tripled. These UV pulses were focused into the flow cell by a $f = 1$ m lens to a slightly elliptical spot with an average diameter of 0.15 mm as measured by a CCD camera. Their energy was 2 μJ. Care was taken to keep the energy the same for all measurements in order to have constant excitation conditions. The residual small variations of pulse energy and spot size led to changes of the excitation energy density of less than 10% between different experimental runs. The pulse to pulse fluctuations were around 10% as well.

The main part of the Ti:sapphire radiation pumped a commercial optic parametric three-pass generator, which produced tunable pulses in the infrared. Tunable pulses were generated over the whole wavelength region between 255 and 450 nm, by sum-frequency mixing with the residual fundamental light and subsequent frequency doubling or direct (e.g., $800^{\text{nm}}_{\text{fundamental}}\ 1500_{\text{parametric}} \xrightarrow{\text{sum}} 522 \xrightarrow{\text{doubling}} 261$) doubling of the infrared radiation. To use them as probe pulses, they were strongly attenuated and focused to a spot size of about 0.05 mm in diameter in the flow cell where they crossed the pump beam at an angle of 5°. The energies of the probe pulses before and after the cell were measured by photodiodes as a function of the pump−probe delay time. The probe signal is the ratio of the outputs of the photodiodes. The pump beam is blocked for every second laser shot by a synchronized chopper. The change of absorption is deduced from the ratio of the probe signals with and without previous excitation. Every data point is an average of 2000 such ratios.

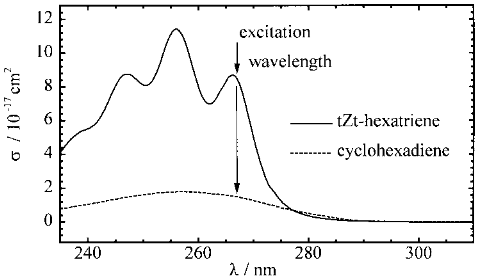

Figure 1. The absorption spectra of *tZt*-hexatriene (solid curve) and 1,3-cyclohexadiene (dashed curve) in ethanol. The arrows indicate the excitation wavelength, used for the time-resolved experiments.

Pump and probe beams were linearly polarized and the electric field vectors comprised the so-called magic angle of 55°, so that orientational relaxation did not influence the signal.[23] The cross correlation width between pump and probe pulses was 400 fs (fwhm). It was measured by nonresonant two-photon absorption in pure ethanol.[21] The flow rate of the solution was chosen so that the focal volume was replaced between two consecutive laser pulses. This was checked by slowly increasing the flow speed until the transient absorption exhibited no further change. To ensure that multiphoton effects did not affect the absorption after the cross-correlation peak, the excitation energy was varied up to 2.6 μJ, and apart from the absolute height, no variations of the time-dependent absorption curves were observed.

3. Results and Discussion

In the following, we report the transient absorption changes in the spectral region between 255 and 450 nm, which appear after exciting 1,3-cyclohexadiene and *tZt*-hexatriene dissolved in ethanol by 267 nm laser pulses. The results in the blue spectral region are assigned to electronic relaxation processes, whereas the transient absorption in the UV is dominated by the population of the ground state of product and educt, its cooling, and single-bond isomerizations.

3.1. Ultrafast Electronic Decay. *3.1.1. Transient Absorption in the Blue and Near-Ultraviolet.* Since 1,3-cyclohexadiene as well as *tZt*-hexatriene absorb at room temperature only at wavelengths shorter than 290 nm (see Figure 1), one would expect no absorption of the electronic ground state in the visible spectral region even at very high temperatures and for other hexatriene conformers. But the excitation from the S_1 to higher electronic states S_n requires less energy than the excitation from the ground state to the S_1. Therefore, excited-state absorption can also appear at longer wavelengths.

Figure 2a shows the transient absorption at 404 nm induced by exciting 1,3-cyclohexadiene (open circles). For comparison, the transient absorption of pure ethanol is depicted, too (solid circles). The differences between the two curves are in the range of the experimental uncertainties. The transient absorption of 1,3-cyclohexadiene can be well fitted by a Gaussian pulse (solid curve) with a width of 400 fs (fwhm) which coincides with the cross correlation between pump and probe pulses. The same results were obtained at the probe wavelengths 350 and 450 nm.

So 1,3-cyclohexadiene shows no delayed dynamics in this spectral region. All involved excited electronic states are depopulated on a time scale shorter than our temporal resolution. Since even a transient signal with a decay constant less than the cross-correlation width would change the Gaussian form in

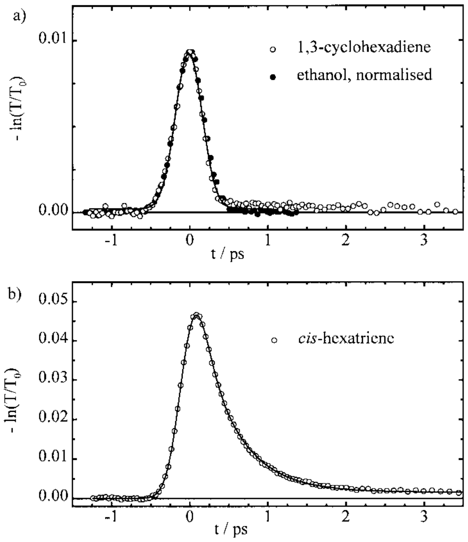

Figure 2. (a) Transient absorption ($-\ln(T/T_0)$) of 1,3-cyclohexadiene (open circles, 0.1 mm cell) dissolved in ethanol and of pure ethanol (solid circles, 1 mm cell) at 404 nm caused by excitation at 267 nm. T is the transmission of the sample at the time t after excitation and T_0 the transmission without excitation. The absorption of ethanol is normalized to the absorption maximum of the cyclohexadiene solution. The solid curve is a fitted Gaussian with a width of 400 fs (fwhm) coinciding with the cross correlation between pump and probe pulses. The absence of any delayed signal shows that the excited electronic states of 1,3-cyclohexadiene are depopulated faster than in 300 fs. (b) Transient absorption of *tZt*-hexatriene dissolved in ethanol (open circles) at a probe wavelength of 375 nm, induced by excitation at 267 nm.[18] The solid curve is a fitted function consisting of a correlation peak and an exponentially decaying component with a time constant of 470 fs convoluted with the cross correlation. The time constant reflects the lifetime of the $2A_1$ state.

a significant way as long as the signal is not too noisy, this depopulation has to be faster than 300 fs. This is in agreement with recent ionization experiments, which found a duration of 200 fs for the complete ring opening in the gas phase.[13]

The excited-state absorption of *tZt*-hexatriene has already been reported in.[18] As an example, the transient absorption at 375 nm is shown in Figure 2b (open circles). The solid curve is a fit to the experimental results. It consists of a cross-correlation peak and an exponentially decaying component convoluted with the Gaussian cross correlation. The time constant of the decay was found to be 470 ±10 fs independent of the probe wavelength between 325 and 450 nm. It has been assigned to the electronic relaxation (i.e., the internal conversion back to the electronic ground state).[18]

3.1.2. Pathway of the Electronic Relaxation. In the electronic relaxation of 1,3-cyclohexadiene, and *tZt*-hexatriene two excited states are involved: the "bright" $1B_2$ state associated with a large oscillator strength and the "dark" $2A_1$ state containing some degree of two-electron excitation.[3] The corresponding potential energy surfaces are schematically depicted in Figure 3.

The excitation wavelength employed lies in the long-wavelength wing of the absorption spectra (Figure 1), and in both cases the pump photons promote the molecules from the electronic ground state $1A_1$ to the bright state $1B_2$. According to resonance−Raman studies, the $1B_2$ state exhibits a rather steep slope along the conrotatory ring-opening coordinate in the case of 1,3-cyclohexadiene[24] and along a double-bond lengthening and single-bond shortening coordinate in the case of *tZt*-hexatriene.[25] Thereby the nuclei are strongly accelerated and the molecule quickly leaves the Franck−Condon region. The dark $2A_1$ state lies in the Franck−Condon region energetically higher than the $1B_2$ state, but it has the lowest minimum of all excited states and crosses the $1B_2$ state not far from the Franck−Condon point along the coordinates mentioned above (see Figure 3).

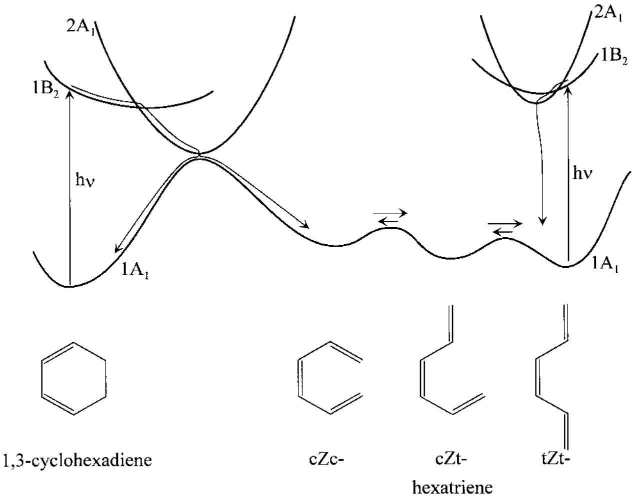

Figure 3. Schematic potential energy surfaces of the electronic ground state ($1A_1$), of the bright ($1B_2$), and of the dark ($2A_1$) states of 1,3-cyclohexadiene and *tZt*-hexatriene. For the higher energy conformers of *Z*-hexatriene, only the ground-state potential is shown. The arrows indicate the excitation, the electronic relaxation, and the isomerization possibilities. The conical intersection and the continuous pathway are indicated on the left-hand side by the close approach of the $2A_1$ and $1A_1$ surfaces, whereas on the right-hand side the corresponding features are not indicated, because in the latter case, the coordinate for the ground state (single-bond twisting) and the excited states (simultaneous twisting of a single and double bond[6]) are different.

Since their symmetry type is different, there exists a real crossing (which is conical) between them lying on the symmetry-conserving relaxation path. The resonance−Raman investigations show that the molecules leave the Franck−Condon region on a time scale of 10 and 20 fs, respectively,[24,25] and recent time-resolved ionization experiments on 1,3-cyclohexadiene found a $1B_2$ lifetime of 44 fs[13] in agreement with the low fluorescence quantum yield of 2×10^{-6}.[24] This first step of the electronic relaxation is by far too fast to produce a noticeably delayed component in the signals reported here, but the absorption from $1B_2$ to higher states contributes to the cross-correlation peak. This peak is larger in the case of excited *tZt*-hexatriene mainly due to its larger transition dipole moment, but perhaps also due to the longer $1B_2$ lifetime.

The second step of the electronic relaxation is the transition from the $2A_1$ to the ground state. The transient absorption in the blue spectral region (Figure 2) shows that this step occurs in less than 300 fs in the case of 1,3-cyclohexadiene and leads to a $2A_1$ lifetime of 470 fs in the case of *tZt*-hexatriene (previous section). The crossing of $2A_1$ with $1A_1$ is avoided along a coordinate which conserves at least the C_2 symmetry of the molecule.[2,5,26] The resulting energy gap is too large to allow such a quick jump from the upper to the lower surface. Olivucci and co-workers showed by ab initio calculations that in both cases a conical intersection should exist between the two electronic states in a nonsymmetric geometry of the molecules.[5,27] The calculated intersection is energetically easily accessible and leads to an ultrafast electronic relaxation. Concluding the other way around, the fast rates observed confirm the existence and easy accessibility of the conical intersections.

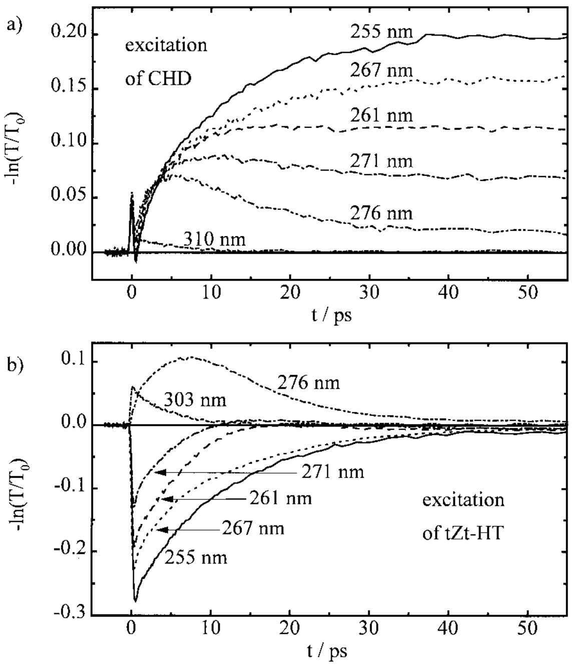

Figure 4. The transient absorption as a function of the delay time t between the probe and the pump pulse for (a) 1,3-cyclohexadiene and (b) *tZt*-hexatriene, both dissolved in ethanol, at various probe wavelengths.

In the case of 1,3-cyclohexadiene, the complete electronic relaxation happens on a time scale of one period of a low-frequency vibration. So the molecule is obviously driven by the steepest slope of the $2A_1$ surface directly to the conical intersection. Originally it was believed that the $2A_1$ minimum along the C_2 conserving coordinates, which forms the avoided crossing with the ground state, is an absolute one.[5,28] But recent calculations seem to indicate that it is rather a saddle point, and small deviations from a symmetric geometry will lead to an acceleration toward the conical intersection.[29] This is probably consistent with the maximum speed inferred from the experimental results.

In *tZt*-hexatriene, the $2A_1$ lifetime is long enough for the molecule to move a little bit around in the region of the $2A_1$ minimum before it hits the conical intersection. But also in this case there should be neither a relevant energy barrier nor an entropy bottleneck.

3.2. Ground-State Dynamics. The spectra of 1,3-cyclohexadiene as well as that of *tZt*-hexatriene extend from 290 nm to shorter wavelengths (see Figure 1). The spectra of the higher energy conformers of *Z*-hexatriene will be slightly shifted with respect to *tZt*-hexatriene, but are expected to be in the same region.

3.2.1. Transient Absorption in the Ultraviolet Region. Figure 4 shows some of the time-dependent absorption curves of photoexcited 1,3-cyclohexadiene and *tZt*-hexatriene, both dissolved in ethanol, which have been measured at a number of wavelengths between 255 and 325 nm.

In the case of 1,3-cyclohexadiene (Figure 4a), the curves show a cross-correlation peak around zero time which is caused by the nonresonant two-photon absorption of ethanol[21] and by absorption from the $1B_2$ and $2A_1$ state of cyclohexadiene to higher electronic states. According to section 3.1.1, the excited cyclohexadiene molecules arrive at the electronic ground state in less than 300 fs after excitation. In pentane, 60% of them return to 1,3-cyclohexadiene and 40% to the product *Z*-hexatriene.[8] The absorption of the former is roughly 4 times weaker than that of the latter (Figure 1) and does not change much with temperature due to its broad and unstructured shape. Therefore, the contribution of these molecules to the transient absorption after the return to the ground state is only minor. The initial product *cZc*-hexatriene isomerizes via the *cZt* to the strongly absorbing *tZt* conformer. This causes the general absorption increase observed after the cross-correlation peak (Figure 4a). Since the electronic energy has been converted to vibrational energy during the electronic relaxation, the molecules are very hot after their return to the electronic ground state. By their interaction with the solvent, the molecules cool. This causes the subsequent absorption decrease in the long-wavelength wing of the spectrum and a further increase at the maxima of the 0−0 (267 nm) and 0−1 band (255 nm) of *tZt*-hexatriene.

The transient absorption of the *tZt*-hexatriene solution (Figure 4b) is dominated by the bleaching and subsequent recovery of the cold ground-state *tZt*-hexatriene. The cross-correlation peak is here covered by the bleaching. The initially high temperature of the molecules leads to a transient increase of absorption in the long-wavelength wing (276 nm) and cooling then recovers the absorption maxima (255 and 267 nm) of *tZt*-hexatriene. The influence of the isomerizations on the signal is discussed in the next section.

All transient absorption curves in the UV after excitation of 1,3-cyclohexadiene as well as *tZt*-hexatriene can be fitted very well by double-exponential functions (cross-correlation peak excluded). This yields two time constants, one in the range between 0.6 and 3 ps and one between 4 and 12 ps, which vary strongly with probe wavelength. For both molecules there seems to exist a correlation with the spectrum of *tZt*-hexatriene, indicating that the time constants are connected to the evolution of *Z*-hexatriene after electronic relaxation. Whereas Sension et al. tried to assign them directly to particular processes,[14] we extract the information in the next sections from different features of the transient spectra.

During our investigations R. Sension and co-workers carried out similar studies on *tZt*-hexatriene and 1,3-cyclohexadiene dissolved in cyclohexane over a more restricted wavelength region between 265 and 300 nm.[14,15] Their time-dependent absorption curves are in good agreement with the results presented here.

3.2.2. Transient Spectra after Excitation of 1,3-Cyclohexadiene. To gain further insight into the evolution of the hot electronic ground-state, we derived the transient spectra at given delay times from the time-dependent absorption curves. Slight fluctuations of the excitation lead to relative uncertainties of the absorption of 5%. The probe wavelengths were determined by a spectrograph with an accuracy of 0.5 nm.

Some of the transient spectra of 1,3-cyclohexadiene are depicted in Figure 5. They clarify what could already be recognized from the time-dependent curves. The oscillator strength (or the area of the spectrum) increases mainly within the first 10 ps, whereas cooling later on results in a continuing decrease of the long-wavelength wing and the development of the spectral structure of cold *tZt*-hexatriene.

The feature of Figure 5 highlighted gray is the expected change of absorption in the limit of infinite pump−probe delay, assuming that 12% of the educt was excited and converted with 40% quantum yield to the product. It was calculated by proper scaling of the difference between the room-temperature spectra of *tZt*-hexatriene and 1,3-cyclohexadiene (both depicted in Figure 1). The excitation probability (0.12) was calculated from the parameters given in the Experimental Section, taking into

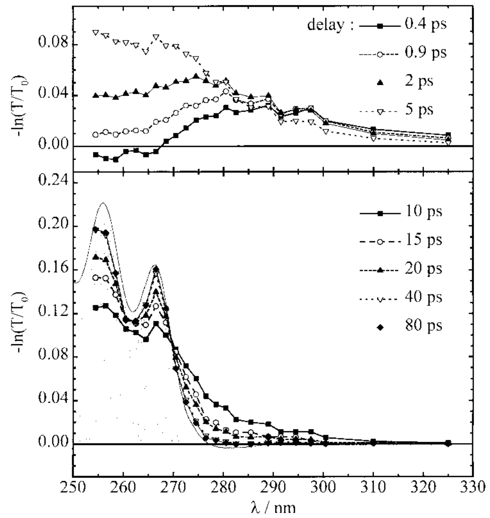

Figure 5. Transient spectra after the excitation of 1,3-cyclohexadiene. (a) Early spectra, (b) some spectra at later delay times. The gray spectrum in the background is calculated from the spectra of cold 1,3-cyclohexadiene and *tZt*-hexatriene assuming an excitation probability of 12% and a quantum yield of 40% for the ring opening.

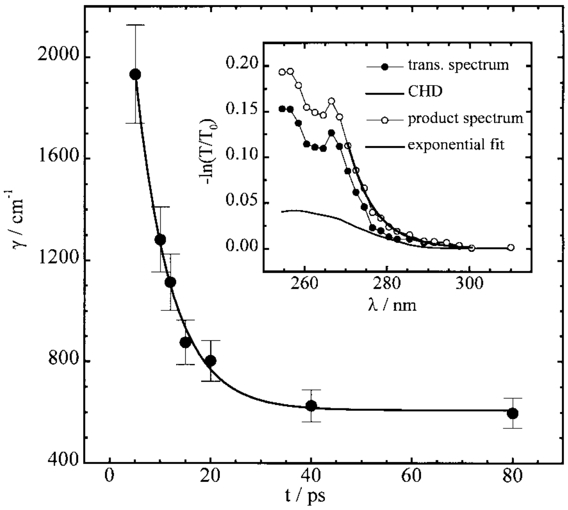

Figure 6. Inset: Transient spectrum at 15 ps delay time (solid circles), spectrum corresponding to the loss of 1,3-cyclohexadiene (thin curve), spectrum of the hot product molecules (open circles), which is the sum of both previous ones, and a fitted exponential decrease (thick curve) of the long-wavelength wing leading to the quantity γ introduced by eq 3.1. Main panel: γ for various delay times *t*. Since γ is proportional to the temperature, its time dependence reflects directly the temperature decrease of the produced *Z*-hexatriene. The time dependence can be well fitted also by an exponential drop (solid curve), resulting in a time constant of 7 ±1 ps for the cooling by the solvent.

account the orientation dependence of the transition probability[30] and the absorption of the pump pulse along its passage through the sample. The absolute error of the excitation probability is estimated to be less than 0.02.

The good agreement between the calculated spectrum and the late transient spectra shows that, after 50 ps, the molecules which performed the ring opening have almost completely isomerized to the *tZt*-conformer. In addition the excitation by short laser pulses obviously does not affect the quantum yield measured with continuous-wave light.[8]

3.2.3. Cooling by the Solvent. During the relaxation process, the electronic energy is converted to vibrational energy which is then quenched by the solvent. A convenient description employs the concept of an internal temperature.[31,32] It assumes a canonical energy distribution and a complete equilibration between all molecular vibrations, although this would only be justified after a few picoseconds. But there are only few important vibrational modes: the optically active ones and those which are connected with ground state reactions. As long as their population densities correspond roughly to a temperature, the concept is adequate. This should already be the case after some intramolecular vibrational energy redistribution has taken place. A further justification are the simulations in section 3.2.5 which only show negligible differences between microcanonical and canonical calculations.

For many molecules, the absorption cross-section far in the long-wavelength wing of their spectra exponentially decreases with wavenumber.[32,33] Neglecting the very weak $1A_1 \rightarrow 2A_1$ absorption, this is also true for *tZt*-hexatriene.[34] At high temperatures hot bands increase the absorption in the long-wavelength wing and thus decrease the logarithmic slope. Hence this slope and its change give information about the molecular temperature T and the cooling process. For evaluation, we assume that the slope is proportional to T^{-1}. This is approximately correct, if the spectral shift is dominated by a single UV-active mode (such as the symmetric C=C stretch), whereas the other modes only cause smaller shifts. The density of states (appearing in the Boltzmann factor) of overtone states of a single harmonic mode is constant. The dependence of the absorption cross-section on the wavenumber ν lower than a reference wavenumber ν_0 then reflects the thermal occupation of the corresponding vibrational levels[35,36] and can be written as

$$\sigma(\nu) = \sigma_0 \exp\left(\frac{\alpha hc(\nu - \nu_0)}{k_B T}\right) = A \exp\left(\frac{\nu}{\gamma}\right) \qquad \text{with} \qquad \gamma = \frac{k_B T}{\alpha hc}; \quad A = \sigma_0 \exp\left(\frac{-\alpha hc \nu_0}{k_B T}\right) \tag{3.1}$$

h is Planck's constant, c the speed of light, k_B the Boltzmann constant, T the temperature, and σ_0 the absorption cross-section at the wavenumber ν_0 and the temperature T. α is a proportionality factor independent of the temperature. By fitting this formula to the long wavelength wing of the spectrum, one obtains a quantity γ which is directly proportional to the molecular temperature.

To obtain the spectra of the hot product molecules, the transient spectra were corrected for the loss of cyclohexadiene, which was calculated as outlined in the previous section. The result is shown in the inset of Figure 6 for a transient spectrum at a delay time of 15 ps. The fitted exponential (eq 3.1) is depicted, too. It quite well reproduces the shape of the wing. The fit was carried out for several transient spectra with different delay times longer than 4 ps. (At earlier times the spectral wing is nonexponential due to contributions from the other conformers.) The obtained values of γ are shown in Figure 6 in dependence on the delay time *t*.

$\gamma(t)$, which reflects $T(t)$, can again be fitted by an exponential decay (solid curve in Figure 6). This indicates that the energy exchanged per time unit between the molecules and the solvent is proportional to the temperature difference. This behavior was already observed for a large number of molecules (see, for example, refs 36−38), although more accurate investigations have shown slight deviations.[39] The time constant τ_{cool}, with which the initial temperature of the arising *Z*-hexatriene drops exponentially to the ambient temperature, is determined from the fit as 7.1 ps. Extrapolating the temperature back to the time immediately after the electronic relaxation would yield 1600 K.

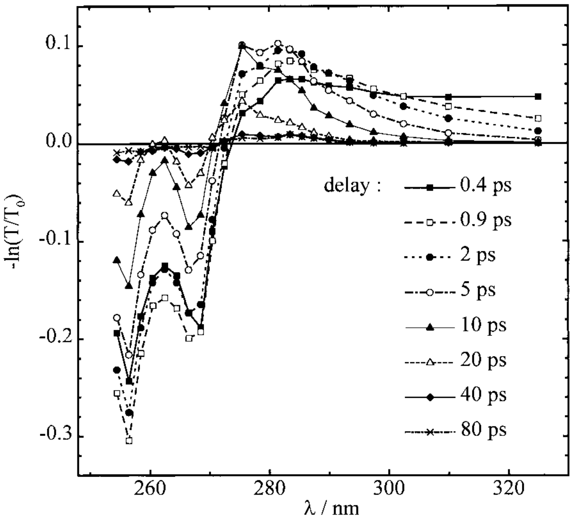

Figure 7. Transient spectra at various delay times after excitation of *tZt*-hexatriene dissolved in ethanol.

The procedure could suffer from three possible errors. First, the calculated loss of 1,3-cyclohexadiene has an uncertainty of 10% (see previous section). Second, it is assumed that the hot 1,3-cyclohexadiene molecules, which have undergone internal conversion, show an absorption spectrum which is very similar to that of the cold molecules (see above) and therefore do not contribute significantly to the transient spectra. Third, the effect of isomerizations on the long wavelength tail is not taken into account. To estimate the influence of these errors on the temperature analysis, the procedure was also carried out with transient spectra which were not corrected for the loss of cyclohexadiene. This results in $\tau_{\text{cool}} = 7.5$ ps and an initial temperature T_0 of 2900 K. So, T_0 critically depends on the actual slopes of the spectral wings, whereas τ_{cool} is obviously rather insensitive to such systematic errors. Therefore we conclude that the temperature of the arising *Z*-hexatriene exponentially decreases from T_0 to room temperature with a time constant $\tau_{\text{cool}} = 7 \pm 1$ ps. The time constant is in good agreement with that of other molecules dissolved in ethanol, such as, for example, with that of sulforhodamine B with a cooling time of 8 ps.[40]

T_0 can also be calculated by distributing the released electronic energy (=photon energy − reaction energy) over all vibrational degrees of freedom. Theoretical calculations yield an energy difference between the ground-state minima of *cZc*-hexatriene and 1,3-cyclohexadiene of 1.16 eV.[26] Therefrom $T_0 = 2050$ K is calculated, in qualitative agreement with the value derived from the analysis of the long-wavelength wings. Due to the large uncertainty of the experimental value, the calculated T_0 is used for further discussion.

3.2.4. Transient Spectra after Excitation of tZt-Hexatriene. The transient spectra of *tZt*-hexatriene are shown for various delay times in Figure 7. They were deduced from the time-dependent measurements presented in section 3.1. Since excited *tZt*-hexatriene mainly undergoes internal conversion and only 3.4% isomerize to *tEt*-hexatriene,[8] the spectra primarily reflect the bleaching and, later on, the recovery of the cold ground-state *tZt*-hexatriene. The additional absorption at longer wavelengths with respect to the original spectrum is caused by hot molecules and may be caused to some extent by higher energy conformers (see below). Since the electronically excited molecules have a lifetime of only 470 fs (section 3.1.2), they contribute only to very early spectra. The change of absorption remaining at long delay times is caused by the slightly higher temperature of the molecules, as well as by the small quantity of tEt-hexatriene produced, but mainly by a residual population of the unstable conformers of *Z*-hexatriene. These results are in complete agreement with the behavior of the transient spectra of *tZt*-hexatriene dissolved in cyclohexane.[14]

To obtain the spectra of the hot molecules, the absorption change caused by the loss of cold *tZt*-hexatriene has to be added to the transient spectra. The probability for excitation was calculated as outlined in section 3.2.2 resulting in a value of 0.4 ±0.05. Since the absorption of *tZt*-hexatriene is rather strong and structured, the correction for the loss of cold *tZt*-hexatriene and the associated error lead to a large uncertainty of the hot spectra. Nevertheless we analyzed the long-wavelength tails in the same way as we did in the case of 1,3-cyclohexadiene. The value of 6.3 ps for the cooling time is in good agreement with that deduced from the transient spectra of the cyclohexadiene solution. The temperature extrapolated to immediately after the internal conversion would be $T_0 = 4200$ K. This is too large by a factor of 2, indicating that the correction was done with insufficient accuracy. Calculating T_0 from the excitation energy yields a value of 2400 K. In the following, as in the preceding section, it is assumed that the temperature of the hot hexatriene molecules exponentially decays with a time constant of 7 ps to room temperature.

3.2.5. A Rate-Equation Model for the Single-Bond Isomerizations. After a delay time of 80 ps, the transient spectra in the case of 1,3-cyclohexadiene indicate that nearly all product molecules exist as *tZt*-hexatriene, although they were produced originally as *cZc* conformers (see section 3.2.2). This requires two single-bond isomerization steps. In a similar way as Pullen et al.,[14] we modeled the isomerizations by kinetic equations with thermal rates *k* for each isomerization path. (In counting these paths, it should be noted that *cZc*-hexatriene has only two possibilities to isomerize to the *cZt* conformer, since steric hindrance of the terminal methylene groups prevents rotation of the two single bonds in opposite sense.) In one model (different from ref 14), the rates *k* of the isomerizations were calculated according to the Arrhenius equation:[41]

$$k = \nu\kappa \exp\left(\frac{-B}{k_B T}\right) \tag{3.2}$$

where ν is the frequency of the vibrations along the isomerization coordinate, *B* the energetic height of the barrier, k_B the Boltzmann constant, and *T* the temperature of the molecule. Equation 3.2 contains a transmission coefficient κ which accounts for the influence of the solvent.[42] In the gas phase, $\kappa = 1$, whereas in the presence of friction $\kappa < 1$. In the alternative model, we determined the rates *k* from RRKM theory.[43] The calculation was the same as in ref 14, except that we took instead of ab initio vibrational frequencies the experimental values of *tZt*-hexatriene given in ref 44, using them also for all conformers and the transition states as well.

For both models we assumed that the vibration with the lowest wavenumber (100 cm^{-1}), which is an antisymmetric single-bond torsional mode,[44] corresponds to the isomerization coordinate. For ν in eq 3.2 and in the RRKM calculations, we used a frequency reduced by 10% to account for the anharmonicity of this mode; with this choice, our results match the more detailed RRKM calculations of ref 14, in particular at high energies. For the energy differences between the conformers and for the barrier heights, we took the ab initio values of Pullen et al.[14] (Table 1). They well agree with previous calculations.[45,46] Slightly higher values were found in very recent density-functional calculations.[47]

TABLE 1: Energies of the Less Stable Conformers and Transition States (TS) (see Figure 3) Relative to the Ground State of *tZt*-Hexatriene as Calculated by Pullen et al.[14] The Barrier Heights Are Not far from Those in Butadiene[48] and Octatetraene[49]

	cZc-HT	TS between *cZc* and *cZt*	*cZt*-HT	TS between *cZt* and *tZt*	*tZt*-HT
energy/cm^{-1}	2956	3370	1088	1809	0

TABLE 2: Isomerization Rates in ps^{-1} at Various Vibrational Energies Calculated by Means of RRKM Theory and at the Corresponding Temperatures by Means of Equation 3.2. Quoted for Comparison Are the Results of S. Pullen et al.[14]

	vibrational energy/cm^{-1} (T/K)					
	30000 (1966)	25000 (1739)	20000 (1504)	15000 (1258)	10000 (991)	5000 (682)
tZt→*cZt*						
RRKM	2.98	2.54	2.04	1.48	0.87	0.26
eq 3.2	2.87	2.42	1.91	1.36	0.78	0.24
S. Pullen et al.	2.86	2.43	1.94	1.42	0.859	0.313
cZt→*tZt*						
RRKM	3.26	3.08	2.83	2.52	2.06	1.28
eq 3.2	3.14	2.92	2.64	2.23	1.77	0.963
S. Pullen et al.	1.98	1.85	1.69	1.49	1.22	0.792
cZt→*cZc*						
RRKM	1.01	0.808	0.593	0.373	0.165	0.018
eq 3.2	0.973	0.772	0.562	0.351	0.157	0.023
S. Pullen et al.	1.22	0.980	0.725	0.469	0.230	0.045
cZc→*cZt*						
RRKM	4.05	3.92	3.75	3.51	3.12	2.08
eq 3.2	3.90	3.72	3.48	3.15	2.60	1.40
S. Pullen et al.	3.27	3.11	2.89	2.58	2.10	0.976

The rates calculated in this way by RRKM theory and by eq 3.2 very well agree with those of Pullen et al. (Table 2). Only at the lowest energies, a difference becomes noticeable. Deviations between our RRKM and Arrhenius values are even smaller. So we can conclude that the simple eq 3.2 is fully adequate for the rates, and a microcanonical (RRKM) calculation is not needed.

To model the relative concentrations of the conformers in dependence of the delay time, the rates were calculated via eq 3.2 and the rate equations numerically integrated. At first we focus on results obtained by transient ionization spectroscopy of 1,3-cyclohexadiene in gas phase. There a duration of 200 fs for the complete ring opening was found.[13] In addition there exists a signal on a time scale of a few hundred femtoseconds which was attributed to single-bond isomerizations of the arising *Z*-hexatriene.[13] It consists of an increasing and a decreasing component and was fitted to eq 3.3 yielding a time constant $\tau = 580 \pm 60$ fs:[50]

$$\text{Signal} = A(0.13 \exp(-t/\tau) + (1 - \exp(-t/\tau))) \quad (3.3)$$

To simulate the signal, we assume that the increasing component originates from *tZt*-hexatriene, while the other conformers contribute to the decreasing component. The calculated data points were then fitted by eq 3.3 resulting in a time constant $\tau = 480 \pm 50$ fs. This is in good agreement with the experimental value, especially as additional delays due to the necessary vibrational redistribution were not taken into account. This shows that the proposed model works well under gas-phase conditions as well as at high vibrational excess energies and that the parameters of the model have been well chosen.

3.2.6. Integrated Spectra and the Isomerizations in Solution. To analyze the influence of single-bond isomerizations on the transient spectra, we focus on the time dependence of the *integrated* spectra for several reasons. First, there exists only a rough estimate for the spectrum of *cZt*-hexatriene,[14] and the spectrum of *cZc*-hexatriene is unknown. Second, the spectra vary with temperature, whereas their integral does not. Third, the transition dipole moment increases from the *cZc* via the *cZt* to the *tZt* conformer due to the increasing length of the molecule. An estimate of the transition moment between the highest occupied and lowest unoccupied molecular orbital by means of the simple Hückel theory[51] shows that *tZt*- should absorb twice as strongly as *cZt*- and several times more strongly than *cZc*-hexatriene, depending sensitively on the nonplanarity of the *cZc* conformer. Ab initio calculations predict ratios of around 4:2:1 for the oscillator strengths for the three conformers.[11] Therefore, the time dependence of the integrated spectra should reflect the evolution of the relative conformer concentrations.

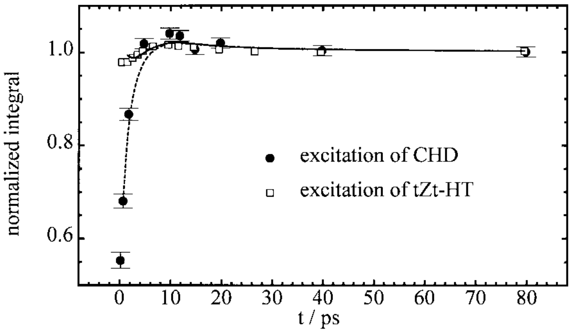

Figure 8. The integrated spectra of the molecules which have performed ring opening of 1,3-cyclohexadiene (circles) or the internal conversion in the case of exciting *tZt*-hexatriene (squares). The dashed and the solid curve are simulations for the ring opening and the internal conversion, respectively. Details are given in the text.

For a rough evaluation of the time-dependent absorption strength, the transient spectra were divided by the wavelength and then integrated from 255 to 350 nm. The long-wavelength limit is chosen in such a way as to cover the complete long-wavelength wing of the ground-state absorption. The 255-nm limit is given by the shortest probe wavelength available from our laser system. This cutoff may decrease the integral, when the spectrum shifts to shorter wavelengths during cooling of the molecules. To estimate this effect, we calculated hot spectra of *tZt*-hexatriene by the method of Mukamel and co-workers [52,53] using the molecular parameters of Ci and Myers.[25] The integral of these spectra over the range considered varies less than 0.5% with temperature. Therefore, one can neglect the direct influence of the temperature (by a shift beyond the cutoff), and the time dependence of the integral will reflect the isomerization processes.

For comparison with the simulations, the integrals of the transient spectra were normalized to the integral of pure *tZt*-hexatriene. In case of the *tZt*-hexatriene experiment, this was done by dividing the integrals of the transient spectra by the integral of *tZt*-hexatriene, weighted with the excitation probability. To these values 1 was added in order to account for the loss of cold *tZt*-hexatriene and to obtain the integrals of the *excited* molecules, just as in the simulations. The results are shown in Figure 8 (squares) as function of the delay time. The variation of the integral is rather small, indicating that the absorption strength of *cZt*-hexatriene over the considered spectral range is quite similar to that of *tZt*-hexatriene. At long delay times, the value approaches unity and the residual amount of *cZt*-hexatriene does obviously not significantly change the integral in comparison with pure *tZt*-hexatriene. In the case of 1,3-cyclohexadiene, the values were corrected for the loss of the educt and normalized to unity in the limit of long delay times, since the product molecules should then absorb as strongly as *tZt*-hexatriene, according to the results presented above. The normalization factor corresponds to an excitation probability of 0.116, which neatly agrees with the value of 0.12 calculated above (see section 3.2.2). The results for the time-dependent spectral integral of the molecules which have performed the ring opening, are depicted in Figure 8, too (circles). They show a strong increase at early delay times (<3 ps) due to the isomerization of the primarily produced *cZc*-hexatriene to the conformers absorbing more strongly.

To perform a more quantitative analysis, the evolution of the integrated spectra was simulated by means of the model presented above. It was assumed that in the case of ring opening primarily *cZc*-hexatriene is produced, whereas in the case of the internal conversion of *tZt*-hexatriene the molecules return to the electronic ground-state still as *tZt* conformer. To incorporate the influence of the solvent, the transmission coefficient κ in eq 3.2 was no longer set to unity, but varied between 0.1 and 0.5. As discussed in sections 3.2.3 and 3.2.4 it was assumed that the molecules have an initial temperature of 2050 K after the ring opening and of 2400 K after the internal conversion of *tZt*-hexatriene, and the molecular temperature decays exponentially with a time constant of 7 ps to 300 K. The integrated spectrum of cold *tZt*-hexatriene was normalized to unity, just as the experimental values.

Simulation of integrated spectra requires the relative absorption strengths of *cZc*-, *cZt*-, and *tZt*-hexatriene. They were obtained by fitting the simulations to both experimental data sets: for 1,3-cyclohexadiene and for *tZt*-hexatriene. In the fit procedure only data points were included with a minimum delay of 2 ps for the internal conversion and 1 ps for the ring opening, since at earlier times the cross-correlation peak and the absorption of electronically excited states contribute to the experimental values.

Good agreement between experiment and simulation can be achieved for values of κ between 0.25 and 0.3; thereby, the relative absorption strength of *cZc*-hexatriene varies between 0.41 and 0.09 and that of *cZt*-hexatriene between 1.10 and 1.14. (Within limits, the measured change of the spectral integral can be simulated by a faster rate, i.e., larger κ, and smaller difference of oscillator strengths, or vice versa.) The simulated evolution of the integrated spectra with $\kappa = 0.27$ and relative absorption strengths of 0.26 and 1.12, respectively, is shown as a solid and a dashed curve in Figure 8.

The relative absorption strength of *cZt*-hexatriene seems twice as high as expected. This is caused by the fact that the considered spectral region covers only the long-wavelength part of the spectra and that the spectrum of *cZt*- is expected to be red shifted relative to that of the *tZt*-conformer. Assuming the spectrum of *cZt*- has the same shape as that of *tZt*-hexatriene, doubling of the integral would be obtained by a long-wavelength shift of about 3000 cm^{-1}. This is a reasonable value, as the comparison with *trans*-hexatriene shows, in which the cEt-spectrum in an argon matrix is red shifted by 2000 cm^{-1} compared to the tEt-spectrum.[54] Pullen et al. present an estimated *cZt*-spectrum[14] which agrees well with this shift. However, the fitted absorption strength of *cZc*-hexatriene should not be interpreted by a smaller or even no red shift of the *cZc* relative to the *tZt* spectrum, since a long-wavelength feature is observed in the early spectra after ring opening (Figure 5). But probably the oscillator strength is sensitive for the degree of nonplanarity which in turn depends on the temperature. Ab initio calculations found a very high energy for the first electronically excited state of *cZc*-hexatriene,[26] probably due to nonplanarity.

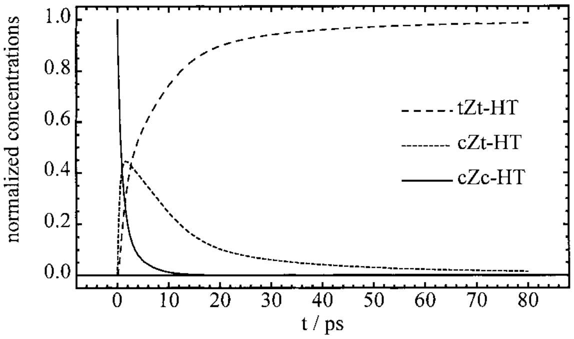

Figure 9. The time-dependent concentrations of the three conformers of *Z*-hexatriene, after ring opening of 1,3-cyclohexadiene at $t = 0$, as calculated by means of the rate equation model discussed in the text. The sum of the concentrations is normalized to one.

The transmission coefficient κ in eq 3.2 can be derived by Kramers' theory from the mass and radius of the moving molecular moiety, the curvature of the potential in the transition state, and the viscosity of the solvent.[41] In the limit of high friction, which is true for ethanol,[55,56] and using methylene as the moving part and the potential data of Table 1, we found $\kappa \approx 0.15$, in very satisfactory agreement with the result of 0.25−0.3 found by the analysis above. Therefore we conclude that the influence of the solvent on single-bond isomerizations of hot molecules in the electronic ground state can be well characterized just by cooling and friction. However, in the case of double-bond isomerizations, in which excited electronic states are always involved, the solvent may also affect the barrier height.[57]

To give an impression of the evolution of the hexatriene conformers, Figure 9 shows their simulated concentrations in the case of the ring opening for $\kappa = 0.27$. *Z*-hexatriene generated by the ring opening of 1,3-cyclohexadiene arises as *cZc* conformer. Since this is an extreme nonequilibrium distribution even at temperatures of 2000 K, most of the *cZc*-hexatriene isomerizes on a time scale of about 3 ps and disappears completely within 14 ps.

Correspondingly, the concentrations of both other conformers increase very rapidly at early delay times. The concentration of *cZt*-hexatriene reaches its maximum already in less than 2 ps and then decays on a time scale of 10 ps more or less in parallel with the temperature, indicating that the concentrations follow roughly the equilibrium distribution. At about 20 ps the decrease slows down and at 80 ps there are still a few percent of residual *cZt*-hexatriene. This behavior is caused by the energy barrier between the *cZt*- and the *tZt* conformer, which strongly reduces the transition rate at low temperatures and leads on this time scale to a trapping of the high-energy conformer in its potential well. The small residual concentration of *cZt*-hexatriene of only a few percent justifies why we could assume, for the determination of the cooling time (sections 3.2.3 and 3.2.4), that the absorption of the product molecules corresponds within experimental accuracy to pure *tZt*-hexatriene at large delay times. As discussed, the isomerization to *tZt*-hexatriene is rather slow at room temperature, but according to our model still sufficient to lead to a complete disappearance of the *cZt*-conformer clearly below the nanosecond time scale. Ohta et al. report about a slow component of the bleach recovery in *E*-hexatriene which they ascribe to *cEt* → *tEt* isomerization.[17] This is consistent with the 15 ps time constant for *cZt* → *tZt* predicted on the bases of two-dimensional surfaces calculated by density-functional theory.[47] Recent time-resolved investigations by means of IR spectroscopy only found an upper bound for this time: It showed that *Z*-hexatriene produced by the ring opening of 1,3-cyclohexadiene isomerizes completely to the *tZt* conformer in less than 20 ns.[58]

In the case of exciting *tZt*-hexatriene, the high temperature of the molecules after the internal conversion leads to an increase of the concentrations of the high-energy conformers during the first 2.5 ps. The thermal equilibrium is completely established within 4 ps, and the further evolution of *Z*-hexatriene is identical with that in the case of the ring opening ignoring small deviations due to the slightly different temperatures. This is in agreement with the experimental values of the integrated spectra (see Figure 8) which show after 5 ps a very similar evolution for both cases. The model proposed by Pullen et al.[14] predicts a rather similar evolution of the conformer concentrations after the internal conversion of *tZt*-hexatriene dissolved in cyclohexane; however, since the comparison with the experiment was less direct, numbers such as the cooling time (14 ps in cyclohexane[14]), the friction by the solvent and thus the time scale of the evolution are less certain.

4. Concluding Remarks

In summary, the analysis of the transient absorption in the wavelength range between 255 and 450 nm, generated by photoexcitation of 1,3-cyclohexadiene and *tZt*-hexatriene dissolved in ethanol, leads to the following conclusions. According to the experimental results in the near-ultraviolet and blue spectral region, the electronic relaxation of *tZt*-hexatriene and 1,3-cyclohexadiene (i.e., the internal conversion and in the case of 1,3-cyclohexadiene also the ring opening) occurs in 470 fs and in less than 300 fs, respectively. This strongly supports the idea that the electronic relaxation follows a continuous pathway through two conical intersections, the first between the primarily excited $1B_2$ and the $2A_1$ state and the second between this state and the electronic ground state.[5,27] In the case of 1,3-cyclohexadiene, the path of the relaxation is direct (i.e., the acceleration by the potential energy surfaces guides the molecule straight to the conical intersections).[13]

Although the data sets have been measured and evaluated by different methods, it may be interesting to compare the times for electronic relaxation in the gas phase and different solvents. For cyclohexadiene there seems to be nearly no change between the gas phase (200 fs[13]), cyclohexane ($\approx$ 250 fs[15]), and ethanol ($<$300 fs, this work). Slightly more variation seems to occur in *tZt*-hexatriene: In the gas phase, the S_1 lifetime varies between 5 ps to 730 fs depending on the excess energy,[34] in ethanol it is 470 fs (this and our previous work[18]), in cyclohexane it is 200 fs[14] or $\approx$ 500 fs,[17] and in acetonitrile it is between 450 and $<$ 200 fs.[17] But these differences are probably not significant, since in the solution there was always enough energy in excess of the S_1 zero-vibrational state. This solvent insensitivity is in contrast to the specific solvent–solute interactions in the case of *E*-stilbene (see, for example, ref 59). This molecule has a barrier arising from the crossing of two different excited states. If the energies of these states are differently affected by the solvent, the activation energy will change accordingly.

From the long-wavelength tail of the ground-state spectra it was deduced that in ethanol the arising hot *Z*-hexatriene cools to the solvent temperature with a time constant of 7 ps. Besides this, the transient absorption in the UV reflects the single-bond isomerizations and the time-dependent concentrations of the three conformers of *Z*-hexatriene. The evolution of the conformer concentrations was simulated by integrating the rate equations using a temperature-dependent rate which obeys the Arrhenius law and takes the friction of the solvent into account by a transmission factor. The model suffers to some extent from the fact that the barriers and reaction energies employed are based on ab initio calculations and hence are of limited accuracy. However, the simulated conformer concentrations of *Z*-hexatriene cannot very significantly differ from the actual ones, since the agreement with the integrated spectra was good. Furthermore, changing the energies will not affect the principal behavior, namely the establishing of a conformer equilibrium in just a few picoseconds, the shift of the equilibrium according to the decreasing molecular temperature during the first 10–20 ps and then a trapping of a few percent of *cZt*-hexatriene in its potential well on a time scale of 100 ps.

It was stated in section 3.2.5 that the isomerization model quite well reproduces the results of the gas-phase experiments,[13] too. But furthermore it allows a consistent interpretation of the Stokes signals which Reid et al. obtained by means of time-resolved resonance–Raman spectroscopy after excitation of 1,3-cyclohexadiene in cyclohexane.[9,10,60] They found in the region of the C=C stretch vibrations one component which bleaches during the excitation, as well as one which exponentially increases with a time constant of 6 ps. The bleaching component was attributed to 1,3-cyclohexadiene. It recovers completely within their time resolution of 1.8 ps, which is consistent with the upper limit of 300 fs deduced in section 3.1.1 from the transient absorption. The increasing component was believed to monitor the appearance of the photoproduct *Z*-hexatriene. Hence ring opening would happen on a time scale of 6 ps, in contradiction to the transient-absorption measurements. But in refs 9, 10, and 60, the differences of the transition dipole moments μ of the three conformers of *Z*-hexatriene were neglected. We simulated the time dependence of the Raman signal by assuming that this signal depends linearly on the concentration of each conformer multiplied by μ^4. According to section 3.2.6, a ratio of $2{:}\sqrt{2}{:}1$ was chosen for the individual μ's. To convert the transmission factor κ in (3.2) from ethanol to cyclohexane, it was assumed to be inversely proportional to the viscosity. As in ref 9, the temperature immediately after ring opening was set to 2100 K and the cooling time in cyclohexane to 15 ps. Fitting an exponential increase to the signal simulated this way results in a rise time of 4 ps. This is in qualitative agreement with the observed time constant and indicates that the increase of the Raman signal is mainly caused by the isomerizations from the weakly scattering *cZc* to the strongly scattering *tZt* conformer. The fact that the agreement is only qualitative is not surprising, since we neglected the dependence of the Raman cross-section on the distance from resonance, which varies with the conformer and with the molecular temperature. A combination of the two effects probably gave rise to the long time constant observed in the Raman experiments; so this time reflects conformer isomerization and cooling. A third contribution is difficult to estimate at present: If one of the conformers has a longer 1B lifetime, its Raman scattering would also be more efficient.

A more detailed analysis of the increasing component by Reid et al. showed that it consists of two peaks, one at 1625 cm^{-1}, which increases with a time constant of 7 ps, and one at 1610 cm^{-1}, which reaches a maximum after a delay time of 6 ps and then disappears on a time scale of 20 ps.[9] Whereas the peak at 1625 cm^{-1} was initially attributed to *cZt*-hexatriene, we suggest that it be assigned it to the *tZt* conformer due to the good agreement with its ethylenic stretch vibration at 1630 cm^{-1}.[25]

Assuming that the corresponding Raman intensity is proportional to the concentration of *tZt*-hexatriene, we fitted an exponential increase to its simulated time-dependent concentration and found a time constant of 7.5 ps, in very good agreement with the experimental value. Since the Raman signal at 1610 cm^{-1} disappears on the same time scale as that of the *cZt* conformer, we tend to attribute it to this conformer, although this signal reaches its maximum a few picoseconds after that of the *cZt* concentration. In general, the simulated initial rise of the *cZt* and *tZt* concentrations is faster by about 20% than the rise of the corresponding Raman signals. This may be caused by the inaccurate barrier heights of the model or by the fact that the Raman cross-section depends on the molecular temperature and tends to increase with decreasing temperature.[61] Nevertheless the increase of the Raman signals correlates with the production of *tZt*-hexatriene and monitors rather the single-bond isomerizations of *Z*-hexatriene than the ring opening of 1,3-cyclohexadiene.

It is worth noting that the single-bond isomerization from *cZc*- to *tZt*-hexatriene proceeds at the high initial temperatures (2000 K) within a few hundred femtoseconds (i.e., much faster than the cooling (7 ps)). This fact may shine new light on the primary steps of the process of vision. The chromophore of rhodopsin is the protonated Schiff-base of 11-*cis*-retinal, which is photoisomerized in the primary event to the all-trans form.[62−64] Since the simplest course of this isomerization, a pure rotation around the $C^{11}C^{12}$ double bond, would require a space-demanding motion of a large part of the molecule in the protein matrix, the observed ultrashort time (200 fs[65]) for product formation would be difficult to understand. Two different space-saving pathways have been postulated: a “bicycle-pedal” isomerization characterized by a simultaneous rotation around neighboring double bonds[66] and a “Hula-twist” isomerization involving simultaneous rotation around a double and an adjacent single bond.[67,68] (A Hula-twist isomerization was recently observed in a triene.[69]) However, the first photoproduct isolated at cryogenic temperature (“bathorhodopsin”) has the chromophore in its all-trans form,[70] whereas a different conformer would be expected from a two-bond isomerization. On the other hand, in transient spectra evidence was found for an intermediate “photorhodopsin” which was supposed to convert by conformational relaxation further to bathorhodopsin.[71] In fact, our results support the view that conformational relaxation of a very hot primary photoproduct cannot be frozen by contact with the cold environment, because it is faster than the cooling rate.

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