210 *J. Phys. Chem. A* **2008,** *112,* 210−214

Ultrafast Ring-Closure Reaction of Photochromic Indolylfulgimides Studied with UV-Pump−IR-Probe Spectroscopy

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Received: May 9, 2007; In Final Form: October 19, 2007

The ring-opening and ring-closure reactions of a photochromic indolylfulgimide are investigated with femtosecond vibrational spectroscopy. Spectral signatures due to excited-state decay and vibrational cooling are seen in the mid-IR region. For the ring-opening reaction triggered with visible pulses, a lifetime of the excited electronic state of 4 ps was obtained in polar solution. In a nonpolar solvent, this time constant is reduced to 2 ps. The ring-closure reaction induced with UV pulses displays an excited-state lifetime and thus a building of the photoproduct of roughly 0.5 ps. For all processes, the subsequent cooling occurs on a 15-ps time scale lasting up to ∼50 ps. The time-resolved IR measurements do not support the existence of any long-living intermediate states.

Introduction

Organic photochromism can be simply defined[1] as the “light-induced reversible change of color”. The thermodynamically stable form A of a molecule is transferred into form B by the action of light. The typical structural dynamics involved in photochromism are, e.g., ring-opening/closure reactions, trans−cis isomerism, or proton transfer. In accordance with the IUPAC definition,[1] photochromism of Type P occurs when the respective ground states of the molecule are converted into each other photochemically by optical excitation excluding a thermal reaction path. Such photochromic molecular switches, with thermally stable ground states, are interesting building blocks with applications in molecular electronics, quantum control, or molecular data storage.[2−8]

Indolylfulgimides exhibit three thermally stable ground state isomers, the E, Z, and C forms, which react according to photochromism type P.[4,9−12] The reaction scheme for the different forms of the indolylfulgimide is shown in Scheme 1. The ring-closed C form can be switched to the ring-opened E form by irradiation of light in the visible spectral range via a pericyclic photoreaction according to Woodward−Hoffmann rules.[13] The E form undergoes isomerization to the Z-form photoproduct by irradiation in the UV. The respective back reactions Z to E and E to C are also induced by UV light. Depending on the chemical substitution of a fulgide, the appearance of the Z isomer can be suppressed.[14]

It was shown in many studies[4,11,12,14−16] that the photochemical properties of these molecules can be designed over a large range. Important photochromic parameters like reaction yields, photochemical degradation, or well-separated absorption spectra for the different isomers are tailored by chemical modification of side groups and choice of the surrounding medium. Because of these advances fulgides and fulgimides have developed an important class of molecular switches featuring several properties that are indispensable for molecular memory applications: they exhibit thermally stable ground state isomers,[4] ultrafast reaction times in the solid state,[17] and several concepts of optical nondestructive readout (not influencing the conformational state) have been demonstrated.[5,18,19]

Recently we reported the ultrafast ring-opening reaction of an indolylfulgimide dissolved in the nonpolar solvent tetrachloroethylene (dielectric constant 2.5), investigated with vis-pump−broadband mid-IR-probe spectroscopy.[20,21] It was found that the photoreaction proceeds from the excited electronic state with a lifetime of 2.1 ps and a reaction yield of 11%. Cooling signatures on the 15−20-ps time scale were observed without further dynamics due to long-lived intermediate states. A comprehensive normal-mode analysis for the relevant modes in the mid-IR for the ground state was performed, and also a qualitative description of the vibrational modes in the excited-state based on the time-resolved transient absorption spectrum was given.

For the back reaction, the ring closure from the E form to the C form, several experimental studies on fulgides in the visible spectral range are reported.[3,17,22,23] In a PMMA matrix, e.g., the ring-closure reaction of an furylfulgimide occurred within about 2 ps, whereas in the solution phase the reaction seemed to take place on a time scale one or two decades slower.[3,17] This was explained by the population of an intermediate state that would be suppressed in the PMMA matrix.

Here we present time-resolved mid-IR measurements, which indicate a very fast ring-closure reaction of an indolylfulgimide dissolved in polar deuterated acetonitrile (dielectric constant 36). The photoreaction is triggered by femtosecond UV pulses at 350 nm. For comparison we also show pump−probe data for the ring-opening reaction of the molecule in the same solvent.

Materials and Methods

The synthesis of N-methyl indolylfulgimide is published elsewhere.[24] For all experiments N-methyl indolylfulgimide was dissolved in deuterated acetonitrile (Aldrich, No. 151807-10G,

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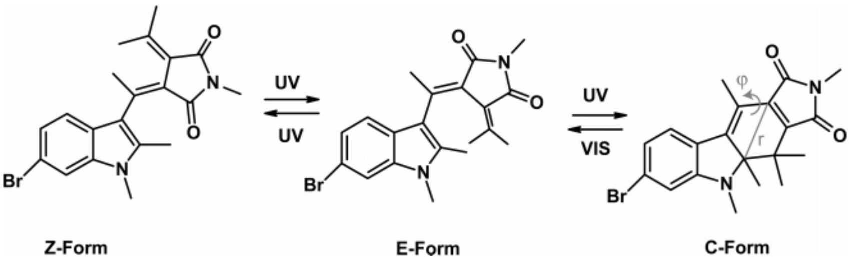
10.1021/jp073545p CCC: $40.75

SCHEME 1: Schematic Structures of Indolylfulgimide Z, E, and C Isomers[a]



[a] The isomers are reversible photoswitchable by UV and visible light as indicated by the arrows. The relevant reaction coordinates according to Geppert et al.[8] are indicated in the sketch of the C isomer.

deuteration grade 99.8%, used as delivered) with concentrations of about 8 mM. Exchange of D atoms to the indolylfulgimide or traces of water in the sample were not observed. Steady-state illumination (according to Koller et al.[20]) of the sample in the UV spectral range using a HgXe short-arc lamp (365 nm) leads to an enrichment of C-form molecules, and the so-called photostationary state PSS-365 is obtained. Illumination of the sample in PSS-365 in the visible spectral range using a cold light source (maximum at 550 nm) leads to a complete conversion of C-form molecules to the E form. In the resulting sample, called PSS-550, the E-form concentration is strongly enhanced, but the Z-form concentration is not affected. Pure C-form samples were obtained by high-performance liquid chromatography (HPLC) of an isomeric mixture. Pure E-form samples were obtained by illumination in the visible spectral range of pure C-form samples until all C-form molecules were converted to the E form due to the ring-opening reaction. For the time-resolved measurements, a PSS-550 sample (for the laser-triggered ring-closure reaction) and a PSS-365 sample (ring-opening reaction) were used.

The samples were handled in CaF_2 cuvettes (window thickness of 2 mm) with an optical path length of 160 μm. For steady-state characterization in the UV/vis spectral range a Perkin-Elmer Lambda 19, in the mid-IR spectral range an IFS66 FT-IR spectrometer from Bruker were used.

The time-resolved pump−probe experiment was based on a home-built 1-kHz Ti:sapphire oscillator-regenerative amplifier system, supplying 90-fs pulses at 800 nm. In brief (for more details, see Schrader et al.[25]): the tunable mid-IR probe pulses were generated by multistage (noncollinear) optical parametric amplifier stages (NOPA, OPA, and difference-frequency generation). At the sample location the probe pulses (pulse energy of 50 nJ) were focused to a diameter of 90 μm.

The ring-opening reaction was optically induced by the output of a NOPA[26,27] stage (pulse energy of 1.3 μJ) tuned to 570 nm and focused to a diameter of 150 μm. The ring-closure reaction was triggered by UV pulses, generated by sum-frequency mixing of the fundamental at 800 nm with NOPA pulses at 620 nm.[28] The resulting pulses (pulse energy of 350 nJ at 350 nm) were focused to a diameter of 150 μm.

The pump pulses were chopped at 500 Hz, and the sample was completely exchanged between two consecutive laser shots by a peristaltic pump. After passing the sample, the probe pulses were spectrally dispersed and detected with mercury−cadmium−telluride arrays (32 elements, Infrared Associates). Absorbance changes of about 50 μOD were resolved by averaging over typically 3000 probe pulses. The time resolution of the experiments was better than 300 fs as determined by cross correlation of the UV/vis pulses with the mid-IR pulses in Germanium.

During the time-resolved experiments, the sample-reservoir was permanently illuminated under the same conditions as in the steady-state experiments to avoid enrichment of an isomer due to the laser-induced photoreaction.

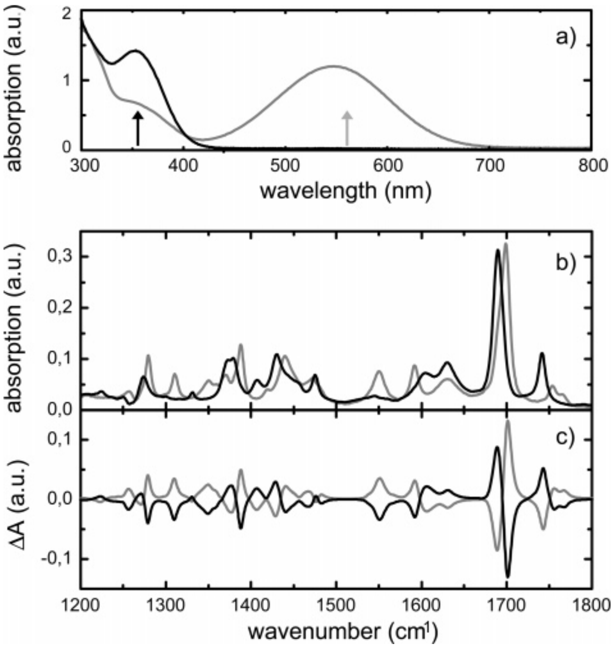


Figure 1. (a) UV/vis absorption spectra of pure C-isomer (gray) and pure E-isomer (black) samples. Arrows indicate the excitation wavelength for the optical experiments: 350 nm for ring-closure reaction and 570 nm for ring-opening reaction. (b) Steady-state absorption spectra in the mid-IR region for pure C-isomer (gray) and pure E-isomer (black) molecules. The time-resolved measurements presented here cover the spectral region of the C═O stretch vibrational modes between 1660 and 1790 cm^{-1}. (c) Steady-state difference spectra between the photostationary states PSS-365 and PSS-550 due to ring-closure (gray) and ring-opening (black) reactions. Strong spectral changes occur in the C═O stretch region around 1700 cm^{-1}. For several illumination cycles between PSS-365 and PSS-550, the respective difference spectra remain unchanged in shape and amplitude.

Results

The absorption spectra of E- and C-form isomers are shown in Figure 1a. The spectral positions of the pump pulses used in the time-resolved studies are marked with arrows. The ring-opened E-form exhibits a strong absorption band in the UV spectral range at 355 nm. The ring-closed C form shows a strong absorption at 360 nm and a broad absorption band at 550 nm in the visible spectral range, where the E and Z isomers of the fulgimide are transparent. Therefore the ring-closed C form can be completely converted to the E form by steady-state illumination in the visible spectral range.

In Figure 1b an overview of the absorption spectra in the mid-IR region of E- and C-form isomers dissolved in acetonitrile is given. Figure 1c shows the light-triggered absorbance changes

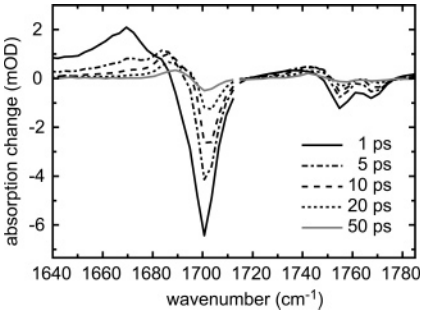


Figure 2. Transient spectra monitoring the ring-opening reaction of indolylfulgimide in acetonitrile in the vibrational C═O stretch region at different delay times. The 50-ps spectrum (gray line) resembles the steady-state difference spectrum (see Figure 1c).

due to the ring-opening reaction (induced at 570 nm) on a sample in the PSS-365 and ring-closure reaction (induced at around 350 nm) on a sample in the PSS-550. Starting from the PSS-365, the respective difference absorption spectra between the photostationary states PSS-365 and PSS-550 are mirror symmetric to each other. This indicates that the concentration of the Z-form isomer is not influenced under these illumination conditions. After complete conversion of C isomer molecules to the E form by illumination in the visible spectral range of the sample in the PSS-550, the ratio of the E- to Z-isomer concentration is about 5, as concluded from ^{1}H NMR and HPLC experiments. Therefore the involvement of the Z isomer in the time-resolved measurements for the ring closure can be neglected furthermore.

Dynamics of Ring-Opening in a Polar Solvent. The dynamics of the ring-opening reaction is studied in the spectral region of the C═O stretch vibrational modes around 1700 cm^{-1} (see transient spectra in Figure 2). Effects due to the pure solvent acetonitrile are only observed in the cross-phase modulation signal around time zero within the temporal resolution of the experiment.

At 1702 (asymmetric C═O stretch mode) and 1756 cm^{-1} (symmetric C═O stretch mode), strong bleach signals are observed stemming from the C-form ground state. The bleach signals partially recover with time-constants of 4 and 10−15 ps. From the remaining offset amplitude the quantum yield is estimated to be ca. 6%, which is in accordance with steady-state experiments in the visible spectral range. Product bands of the E-isomer ground state rise at 1691 and 1744 cm^{-1}, matching the steady-state difference spectra of Figure 1c. At early delay times the spectral signature of these product bands is partially covered by induced hot absorption bands of the bleached educt modes. These absorption bands also decay with 10 to 15 ps, accompanied by a spectral blue shift, indicating a cooling process. Around 1670 cm^{-1}, a broad induced absorption occurs that decays without pronounced spectral shift and a time constant of 4 ps to a zero offset.

For delay times longer than 50 ps, no further changes in the transient signal are observed, and the transient spectrum is identical to the steady-state difference spectrum (Figure 1c). This indicates that the structural dynamics are completed.

Ring-Closure Reaction. A two-dimensional representation of the transient absorption signals due to the ring-closure reaction is given in Figure 3b. Here we also concentrate on the C═O stretch region around 1700 cm^{-1}. Transient signal contributions due to the pure solvent acetonitrile are negligible (beyond 100 μOD) and only observed at delay time zero within the experimental temporal resolution.

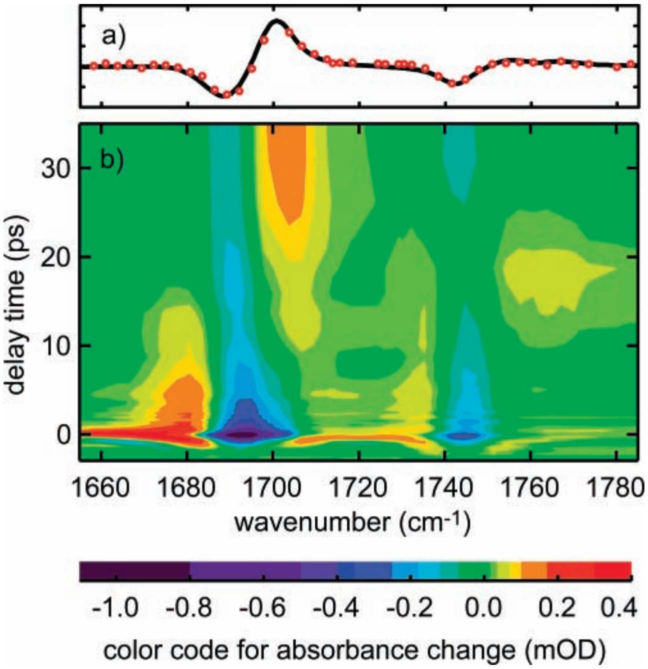


Figure 3. Transient absorption data in the mid-IR spectral range in the vibrational C═O stretch region monitoring the ring-closure reaction of indolylfulgimide: (a) comparison of the transient spectrum at a delay time of 50 ps (red circles) with the steady-state difference spectrum from Figure 1c (black line). (b) Two-dimensional representation of the complete time-resolved data set in the C═O stretch region. Amplitudes of the transient absorption signal are given in a color code.

Around and before delay time zero, well-known effects such as perturbed free induction decay[29,30] (PFID) and cross-phase modulation[31] (XPM) dominate the transient signal. The influence of these effects after time-zero has clearly been vanished within the temporal resolution of the experiment. At the latest after 300 fs signal contributions due to the solvent, PFID, or XPM are negligible. Instantaneous strong bleach signals at 1691 and 1744 cm^{-1} are observed within the temporal resolution of the experiment. The bleach recovery takes place on a 10-ps time scale. From the amplitude of the bleach recovery, the quantum yield for the ring-closure reaction is estimated to be 20%. On the low-frequency wings of the bleached bands the typical induced absorption signals due to hot vibrational modes occur, which decay within 20 ps. A strong product band rises at 1702 cm^{-1} and remains constant for later delay times (in accordance with the steady-state difference spectrum). For short delay times, this band is partially covered by the bleach signal around 1691 cm^{-1} but is clearly observed after 10 ps. The very weak product band around 1760 cm^{-1} (expected from the steady-state difference spectrum in Figure 1c) is also observed by closer inspection of the data set. When signal contributions due to XPM and PFID have vanished, short-lived induced absorption signals around 1660 cm^{-1} and less pronounced at 1720 cm^{-1} are observed. These signals decay with a time constant of 0.5 ps to a zero offset. Such a behavior is expected for vibrational modes in the excited electronic state and is also found for the ring-opening reaction in this spectral range.

For delay times longer than 50 ps, the transient absorption spectra resemble the steady-state difference spectrum (Figure 3a), indicating that the structural relaxation is completed.

Discussion

Solvent Dependency of the Ring-Opening Reaction. For an overview of the parameters describing the ring-opening

TABLE 1: Overview of the Solvent-Dependent Reaction Dynamics

reaction	ring-opening	ring-opening	ring-closure
solvent	tetrachloroethylene	acetonitrile	acetonitrile
dielectric constant	2.5	36	36
excited-state lifetime	2 ps	4 ps	0.5 ps
cooling time	15−20 ps	10−15 ps	∼10 ps
quantum yield	∼11%	∼6%	∼20%

reaction in acetonitrile (dielectric constant $\epsilon_r = 36$) and tetrachloroethylene (dielectric constant $\epsilon_r = 2.5$), see Table 1. Aside from a small red shift of ∼5 cm^{-1} for the C═O stretch modes, the spectral signature of the absorption spectra in the mid-IR spectral range for each isomer are similar in both solvents. In analogy to the studies on the ring-opening reaction in tetracholoroethylene,[20,21] the fast-decaying induced absorption around 1670 cm^{-1} is assigned to the decay of the electronic excited state. The excited-state lifetime is prolonged by a factor of 2 from 2 to 4 ps in acetonitrile (Figure 4c). Recent studies on the dynamics in the excited-state of indolylfulgimide dissolved in acetonitrile by time-resolved fluorescence reveal that fast relaxation processes on the excited-state potential energy surface occur in the time range below 100 fs. These fast processes, which would also lead to spectral shifts in the mid-IR region, are beyond the temporal resolution of this mid-IR transient absorption experiment (better than 300 fs) and only information on the relaxed excited-state is obtained. The quantum yield is reduced by a factor of 2 from 11 to 6% for the indolylfulgimide dissolved in tetrachloroethylene and acetonitrile, respectively. The typical times for the cooling processes (Figure 4d) are comparable.

The observed dependence of the reaction time for the ring-opening reaction on the dielectric constant of the solvent (acetonitrile = 4 ps and tetrachloroethylene = 2 ps) could be related to a changed activation energy in the excited electronic state. It is known from temperature-dependent studies that fulgides in acetonitrile exhibit an increased activation energy for the ring-opening reaction in comparison to nonpolar solvents.[32] This would also explain the reduced reaction yield found in this study (acetonitrile = 6% and tetrachloroethylene = 11%).

Ultrafast Ring-Closure Reaction. For the ring-closure reaction in fulgide systems an intermediate state was introduced by several studies[3,19] to explain the experimental results. As pointed out by Renth et al.[33] background signals due to the used solvent may obscure details of the transient data in the UV/vis spectral range, and the intermediate state was absent in later experiments[17] of fulgides in the PMMA matrix.

In contrast to those studies, direct and fast structural dynamics are observed for the indolylfulgimide when dissolved in acetonitrile as investigated by mid-IR probing in this work. Judging from the time-resolved mid-IR data, there are no indications for any long-lived intermediate state. Aside from the cooling process that lies well in the temporal range of several tens of picoseconds expected for a molecule as indolylfulgimide in solution, no further slow dynamics is observed. In a recent study monitoring the time-resolved spontaneous fluorescence of the indolylfulgimide E isomer, the lifetime of the electronic excited-state was shown to be 0.4 ps.[34] A similar short decay time of 0.5 ps is also seen in the transient data at 1660 and 1720 cm^{-1} presented in this work. Both in the depletion of the vibrational bands of the excited state (see Figure 4a) and the recovery of the bleached vibrational bands of the nonreacted educt molecules, the same time constant of ∼0.5 ps can be extracted (see Figure 4b). Therefore it can be concluded that the ring-closure reaction is essentially completed after roughly 1 ps with the decay of the excited electronic state. Further dynamics can be explained completely by cooling of the hot ground-state modes (see also Figure 4b). A similar picture was found also for the ring-opening reaction of the same molecule in polar (this study, see parts c and d of Figure 4) and nonpolar[20,21] surrounding media.

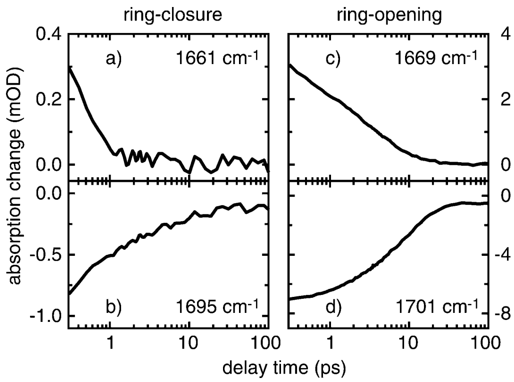


Figure 4. Transient traces at distinct vibrational frequencies displaying typical times involved in the dynamics of the pericyclic photoreactions (note the logarithmic time scale). Ring-closure reaction: (a) decay (0.5 ps) of the excited-state signal at 1661 cm^{-1}; (b) initial recovery of the bleach signal (0.5 ps) at 1695 cm^{-1} followed by cooling (about 10 ps). Ring-opening reaction: (c) decay (4 ps) of the excited-state signal at 1669 cm^{-1}; (d) initial recovery of the bleach signal (4 ps) at 1701 cm^{-1} followed by cooling (10−15 ps).

The ring closure is observed to occur faster than the ring-opening reaction. For several fulgides, the fast reaction time of the ring closure was explained on the basis that this reaction does not require activation energy on the electronically excited-state surface.[4,35] In contrast to this, activation energies in the excited-state were found for the ring-opening reaction on fulgides.[36] This results in a reduced reaction probability and increased lifetime of the excited-state for the ring-opening compared to the ring-closure.

The photochromic motif of fulgides is the 1,3-cyclohexadiene/1,3,5-hexatriene ring, which can be regarded as a prototype example for pericyclic reactions. The ultrafast photochemistry of the ring-opening reaction is well investigated for this system by experimental and theoretical studies.[37−43] It is found that the ring-opening reaction occurs via a barrierless reaction coordinate in less than a picosecond in the solution[39] and gas phases.[40] Resonance Raman and picosecond-time-resolved Raman studies give insight in the initial motion out of the Franck−Condon region along a conrotatory reaction coordinate and the formation of photoproducts.[37−39,44] In contrast to these results on 1,3-cyclohexadiene an activated behavior is found for the much larger fulgimides for the ring-opening reaction with a time constant of several picoseconds.[32,36] Therefore the reaction is expected to occur from a relaxed excited-state geometry. However, the ring-closure reaction of fulgides/fulgimides is a barrierless process[36] and occurs in the sub-picosecond time range as shown in this work.

Theoretical studies describe the pericyclic reaction of fulgide systems in analogy to the cyclohexadiene molecule.[7] Here, three reaction coordinates r, φ, and ϑ are analyzed, which are mainly responsible for the geometry of the ring system, and according to Geppert et al.,[7,8] the reaction coordinate φ is responsible for the planarity of the photochromic ring (see Scheme 1). According to the normal-mode analysis for the investigated indolylfulgimide,[20] the respective promoting normal modes modulating the planarity of the indolylfulgimide are expected in the frequency range of 50 cm^{-1}. It should be pointed out that these low-frequency vibrations correspond to an oscillation period of 600 fs. Therefore the promoting modes responsible for the pericyclic reaction obtained by DFT calculations and the experimentally determined time for the ring-closure reaction of 0.5 ps are in close agreement. This suggests that this ring-closure reaction should be better treated in the framework of wavepacket dynamics and relaxation via conical intersections instead of describing it with simple exponential kinetics.

Conclusion

The polar solvent acetonitrile slows down the reaction dynamics for the ring-opening reaction and also reduces the reaction yield. The ring-closure reaction can be successfully triggered with UV light at 350 nm. The structural dynamics of the ring-closure reaction monitored in the mid-IR region occurs with a time constant of 0.5 ps. Dynamics in the transient absorption signal are completed latest after 50 ps, which is determined by cooling of the hot educt and product ground states. The cooling occurs on a 10−15-ps time scale. Therefore both the ring-opening and ring-closure reactions show ultrafast dynamics. The ring-closure reaction occurs even faster than the ring-opening reaction. Long-lived intermediate states are not observed. The sub-picosecond reaction time found for the ring-closure reaction points to a driven process on the excited-state potential energy surface.

Acknowledgment. We thank W. Zinth for fruitful discussion. This work was supported by Deutsche Forschungsgemeinschaft through the DFG-Cluster of Excellence Munich-Centre for Advanced Photonics and the SFB 749.

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