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Ultrafast UV-mid-IR Investigation of the Ring Opening Reaction of a Photochromic Spiropyran

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Abstract: We present a femtosecond UV-mid-IR pump−probe study of the photochemical ring-opening reaction of the spiropyran 1′,3′,3′,-trimethylspiro-[-2H-1-benzopyran-2,2′-indoline] (also known as BIPS) in tetrachloroethene, using 70 fs UV excitation pulses and probing with 100 fs mid-IR pulses. The time evolution of the transient IR absorption spectrum was monitored over the first 100 ps after UV excitation. We conclude that the merocyanine product is formed with a 28 ps time constant, contrasting with a 0.9 ps time constant obtained in previous investigations where the rise of absorption bands at visible wavelengths were associated with product formation. We deduce from the observed strong recovery of the spiropyran IR absorption bleaches that, in tetrachloroethene, the main decay channel for the S_1 excited state of the spiropyran BIPS, is internal conversion to the spiropyran S_0 state with a quantum yield of ≥ 0.9. This puts an upper limit of 0.1 to the quantum yield of the photochemical ring-opening reaction.

Introduction

Photochromic compounds have the property of color change after the absorption of light of specific wavelengths. In addition, for a compound to be photochromic, it is necessary that this color change can also be reversed by exposure to light, yielding again the original substance. Photochromism continues to generate much scientific interest.[1−16] Applications that are envisaged for photochromism include optical data storage[2] and optically controlled molecular switching,[3] that ultimately may drive developments in molecular nanotechnology.[3] From a scientific and technological standpoint, it is relevant to map reaction pathways and efficiencies, and to identify intermediates involved in the switching between the different photochromic isomers. Time-resolved spectroscopy provides excellent tools to shed light on the dynamics of photochromism. The majority of time-resolved investigations of photochromism, from femtosecond to millisecond time scales, so far focuses on the evolution of the absorption bands responsible for the color changes. Although such investigations have been paramount to the advancement of our understanding of reaction mechanisms in general, and photochromic reactions in particular, complications may occur if the complexity of the reaction increases, due to formation of several different isomers and involvement of numerous electronic states. In these situations, electronic absorption bands of different species may significantly overlap, or go unnoticeable if the oscillator strength of electronic transitions in different species differs considerably. Femtosecond time-resolved vibrational studies open a new window on the dynamics from a different perspective: the evolution of the vibrational absorption spectrum. Vibrational IR absorption lines are typically very narrow, and thereby increase the chances of finding regions where different lines do not overlap. Moreover, certain IR absorption regions are known to correspond to specific structural molecular features and therefore monitoring the time depencence of the vibrational spectrum offers better chances for obtaining detailed information on changes in the spatial structure of the molecule.

In this article, we present an investigation with ∼130 fs time resolution of one of the most studied photochromic reactions: [1−16] the spiropyran−merocyanine chemical ring opening /closure (see Figure 1). The photochemical ring opening reaction of a spiropyran molecule is initiated by 70 fs UV pump pulses, and the time-evolution of the vibrational absorption spectrum toward the formation of merocyanine product species is directly followed by probing with ∼100 fs tunable mid-IR pulses. Given

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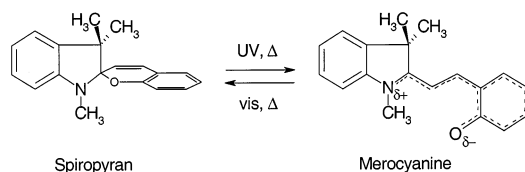
Figure 1. Reactant and product structures for the photochromic reaction of BIPS.
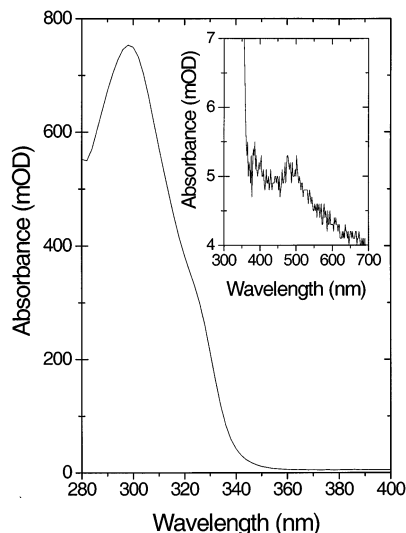
Figure 2. Absorption spectrum of 1 mM BIPS in tetrachloroethene. The insert illustrates the nearly complete absence of merocyanine absorption around 540 nm.

the enormous research effort on these systems it is remarkable that up to now only a handful of studies have been performed with subnanosecond time-resolution.[5–11] The molecule we investigated is 1′,3′,3′,-trimethylspiro-[-2H-1-benzopyran-2,2′-indoline], commonly referred to as BIPS, dissolved in tetrachloroethene. The spiropyran compound can to first approximation be regarded as two nearly independent orthogonal halves:[12] a chromene and an indoline. The BIPS molecule does not absorb in the visible (cf. Figure 2). Upon absorption of a UV photon a ring opening and cis–trans isomerizations take place, resulting in a more or less planar molecule with a strong broad absorption around 540 nm. The huge shift in absorption wavelength can easily be understood from the fact that now the delocalized π-system extends over the entire molecule. In the literature, it has been concluded that if the chromene part contains an NO_2 substituent, then the ring opening reaction of spiropyrans will (at least to some extent) involve triplet states.[13] For spiropyran compounds without this NO_2 substituent, such as the one we investigate here, it has been stated[6] that the reaction involves only singlet states. In principle, eight isomers can be formed of the merocyanine compound, due to cis–trans configurations at the three double bonds of the bridge segment. Theoretical calculations have indicated, however, that due to steric hindrance only isomers with a trans configuration around the second bond are stable.[7]

Femtosecond UV-pump/white-light probe experiments have been performed at room temperature on BIPS in ethanol[5] and *n*-pentane,[6–7] and on the naphthopyran analogue[6–7] naphtho-BIPS and 6-nitro-BIPS[6] in *n*-pentane. These data demonstrated the appearance after about a picosecond of a broad nearly featureless absorption, covering the entire probing range of 380–

680 nm. At the wavelengths of the merocyanine product absorption band, the rise time[6] in *n*-pentane was 0.9 ps for BIPS (at 540 nm) and 1.4 ps for naphtho-BIPS (at 520 nm). During the following 6 ps, the absorption at the maximum did not change drastically; however, the featureless initial spectrum did evolve toward sharper spectral features that more closely resemble the product spectra observed on μs time-scales.[6–7] The broad initial absorption and subsequent sharpening was ascribed to transitions from the spiropyran excited state to higher electronic states, and to transitions from vibrationally hot merocyanine in the electronic ground state.[6] For the 6-nitro-BIPS compound the initial spectrum was similar. However, at later times, two absorption bands, at 430 and 575 nm, increased in intensity with a 20 ps time constant.[6] Room-temperature experiments with femtosecond UV-pump and probing at diverse wavelengths in the visible have been performed on 6-hydroxy-BIPS in 1-propanol, methanol, and 1-hexanol.[8] Pumping at 310 nm and probing at 620 nm an exponential rise of the signal with ≤2 ps was identified in 1-propanol. The general conclusion from these experiments seems therefore that the merocyanine product is formed with a 1–2 ps time constant in the compounds without a nitro-group, and with a 20 ps time constant for 6-nitro-BIPS.

The nearly featureless absorption after 1 ps, covering at least the range of 380–680 nm,[6] motivated us to undertake the present UV pump-mid-IR probe studies. Electronic transitions of molecules in solutions are typically significantly broadened by optical dephasing and inhomogeneity effects. Therefore, at every wavelength, several different vibronic and/or electronic states contribute to the absorption, resulting in smooth broad spectral features. Consequently, the question can be raised if UV–vis investigations are ideal for unravelling the details of such a complex chemical reaction. In contrast, vibrational IR absorption lines are typically very narrow and without much inhomogeneous broadening. Although the large number of vibrations for larger molecules can also be complicating, there are still good chances of finding regions with relatively few IR absorption lines. In addition, no time-resolved *single* color UV experiment has yet been reported to directly determine whether any recovery of the spiropyran (closed form) absorption occurs. Such a measurement is essential for obtaining quantitative information on the quantum yield of this photochemical reaction. In the present study, we will extract this information from the time evolution of bleaches related to the IR vibrational absorption spectrum of the spiropyran compound. We believe therefore that the present method of investigation can increase the insight into the possible existence and structure of reaction intermediates, the time scale(s) of product formation, and whether different isomers are being formed on femtosecond and picosecond time scales. The FT-IR spectrum of BIPS in tetrachloroethene, and existing resonance Raman spectra on the photoproducts of BIPS in different solvents,[16] taken 200 ns after UV excitation, are used to support the analysis.

Experimental Section

The absorption spectrum of 1 mM BIPS in a 1 mm quartz cuvette was recorded in a Perkin-Elmer UV–vis spectrometer. Below 280 nm strong absorption from tetrachloroethene (C_2Cl_4) prevents an accurate determination of the absorption spectrum. Steady-state FT-IR spectra were recorded with 2 cm^{-1} resolution, using a Biorad FT-IR spectrometer. The 50 mM
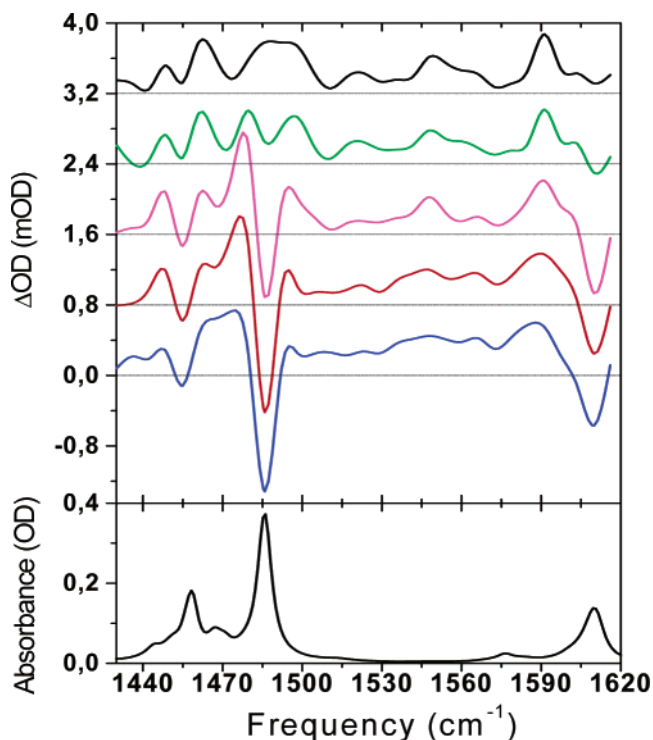
sample of BIPS in C_2Cl_4 was injected in a home-built cell with CaF_2 windows and a spacer of approximately 100 μm. For the femtosecond pump−probe experiments, 400 ml solution of 21 mM BIPS in C_2Cl_4 was made, and pumped through a free streaming jet with a nominal thickness of 100 μm. No noticeable degradation of the solution was observed after the measurements.

The near-UV pulses for electronic excitation were generated by sum frequency mixing of the fundamental of a home-built 1-kHz amplified Ti:sapphire laser and visible pulses obtained by a noncollinear optical parametric amplifier, as described elsewhere.[17] The excitation wavelength was tuned to 316 nm, the pulse energy was 2.5 μJ and the pulse duration around 70 fs. The pump pulses could be variably delayed and were focused with a concave mirror on the sample with a spot diameter of approximately 150 μm. The mid-infrared probe pulses were generated using double-pass collinear optical parametric amplification, followed by difference frequency mixing of signal and idler, as described in detail in ref 18. The center frequency was tuned to 1530 cm^{-1} and the output energy was about 700 nJ. Probe and reference pulses were formed using reflections from a BaF_2 wedge, and were both focused in the sample with off-axis parabolic mirrors (spot size 100 μm). The entire pump−probe setup was purged with nitrogen gas to prevent spectral and temporal reshaping of the mid-IR pulse by absorption of water vapor in air. Probe and reference pulses were dispersed in a grating spectrometer after passing the sample, and complete spectra were recorded simultaneously for each shot using a liquid nitrogen cooled 2 × 31 HgCdTe detector array. Normalization of probe and reference signal on a single shot basis provided highly reliable transient absorption spectra: allowing at best the detection of absorption changes ΔOD as small as 0.10 mOD, with an accuracy of ±0.05 mOD. The experimental curves presented here are the average of 15−25 time delay scans, with each scan averaging 400 shots per data point. The time-resolution (fwhm ≈ 130 fs) and the zero time delay point were determined by a cross-correlation experiment performed in a polished ZnSe window.

Results and Discussion

Transient Changes in the IR Absorption Spectrum. The spectral evolution of the transient changes in optical density (OD) of the IR absorptions between 1430 and 1620 cm^{-1} during the first 100 ps after excitation of BIPS at 316 nm is illustrated in the upper panel of Figure 3. For comparison the IR absorption spectrum of BIPS in the electronic ground state, at a concentration of 50 mM in tetrachloroethene, is depicted in the lower panel of Figure 3 over the same frequency range. We have investigated the entire spectral range from 1200 to 1800 cm^{-1}. The other ranges did not provide additional information. The presented range contains the strongest IR band, as well as the most isolated IR band. Note furthermore that the merocyanine compound does not exhibit a true carbonyl stretching mode in the range 1600−1800 cm^{-1}, probably because it is part of the delocalized π-system.

The spectrum after 2 ps is dominated by strong bleaches of the ground-state IR absorption bands at 1458, 1486, and 1610 cm^{-1}. For the data in Figure 3 each detector pixel integrates

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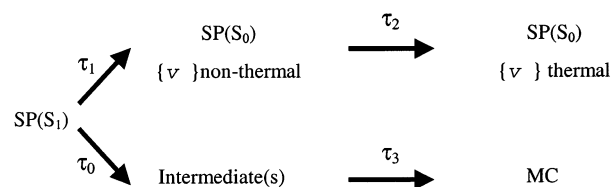(18) Hamm, P.; Kaindl, R. A.; Stenger, J. *Opt. Lett.* **2000**, *25*, 1798.

Figure 3. Upper panel: Transient changes in the IR absorption spectrum between 1430 and 1620 cm^{-1} at, from bottom to top, 2, 10, 20, 51, and 100 ps after UV excitation at 316 nm. For representation purposes the signals are displayed with the offset at consecutive delay times increased in steps of 0.8 mOD. The dashed lines indicate the zero signal level for the different traces. Lower panel: Steady-state IR spectrum of 50 mM BIPS (closed form) in tetrachloroethene.

signal over a range of 6 cm^{-1}. This implies that for vibrational bands broader than 6 cm^{-1} the peak position of bands can be determined within ~4 cm^{-1}. The calibration of the grating spectrometer was checked by comparing the positions of the bleaches to those observed in the steady-state FT-IR spectrum. In addition, weak transient (increased) absorption is seen at most other frequencies. Between 1535 and 1585 cm^{-1} most of this absorption (amplitude ranging from 0.1 to 0.4 mOD) disappears with time constants ranging from 2 to 22 ps, leaving a residual change in absorbance (ΔOD) varying between 0.06 and 0.20 mOD (accuracy ±0.05 mOD). The height of this residual offset was found to depend clearly on the pulse duration of the UV pulse and is ascribed to minor undesirable multiphoton contributions from BIPS molecules and the solvent. After 100 ps, the strong bleaches have nearly entirely recovered, indicating that the majority (≥90%) of the BIPS molecules have by that time returned to the vibrational and electronic ground state of the closed spiropyran form. At this time delay, product vibrational absorption bands can clearly be identified at 1461 cm^{-1} (0.6 mOD),1489 cm^{-1} (0.6 mOD), and 1591 cm^{-1} (0.6 mOD).

Kinetic Scheme for Analysis of the Time-Resolved Data. The following kinetic scheme is used for the data analysis. The assignments are defined in the discussion below.

This scheme assumes the following: the initial species generated by UV photoexcitation is the excited singlet state of spiropyran, $SP(S_1)$. This either decays through internal conversion to form hot spiropyran in the electronic ground state, ($\{v\}$ designates the vibrational manifold), or decays to other intermediate states which eventually may lead to merocyanine product formation. The $SP(S_1)$ decays with time t according to

$$A \cdot e^{-t(1/\tau_0 + 1/\tau_1)} \tag{1}$$

where A is the amplitude at delay time $t = 0$.

The time constant τ_1 does not represent the true internal conversion time constant in our analysis. A complete characterization of the cooling process from the initial hot vibrational distribution to the thermally equilibrated vibrational distribution in the electronic ground state, requires knowledge about many more parameters than the data give access to. Therefore, we have chosen to fit the data related to vibrational cooling using an effective description involving only two time constants: τ_1, which characterizes the average arrival time at the vibrational levels within the frequency interval covered by the relevant detection diode, and the time constant τ_2, which characterizes the effective average departure time from this frequency interval. Note that the signals are the nett difference between (increased) absorption from $v \rightarrow v + 1$ and stimulated emission from $v + 1 \rightarrow v$. The signals related to transient passage of vibrational levels other than $v = 0$, are now described by

$$B \cdot \left(\frac{\tau_2}{\tau_2 - \tau_1}\right) \cdot (e^{-t/\tau_2} - e^{-t/\tau_1}) \tag{2}$$

The recovery of the thermally equilibrated electronic ground state, using the effective parameters τ_1 and τ_2, as evidenced by the refilling of the bleached IR absorptions, is described by

$$C \cdot \left[\left(\frac{\tau_1}{\tau_2 - \tau_1}\right) \cdot e^{-t/\tau_1} - \left(\frac{\tau_2}{\tau_2 - \tau_1}\right) \cdot e^{-t/\tau_2}\right] \tag{3}$$

Amplitude C divided by the amplitude of the bleach at $t = 0$, in principle equals the internal conversion quantum yield (disregarding solvent and multiphoton contributions).

The rise of the main product absorption bands can be described by

$$D \cdot (1 - e^{-t/\tau_3}) \tag{4}$$

This equation is valid if formation of intermediates from the $SP(S_1)$ state, governed by $(1/\tau_0 + 1/\tau_1)^{-1}$, is very fast compared to the time constant τ_3 that governs formation of merocyanine product from these intermediates. The amplitude D gives the final signal strength of the product band.

Kinetic Behavior at Vibrational Frequencies of the (Closed) Spiropyran Form of BIPS. We first address the recovery of the bleaches in more detail. Figure 4 shows kinetic traces measured at the IR absorption maxima at 1486 and 1610 cm^{-1}, and, in both cases, at slightly lower frequencies. The observed kinetics is consistent with rapid internal conversion followed by vibrational cooling. Note that during the first 20 ps the recovery of the bleaches occurs clearly at a slower pace than in the following 80 ps. This can easily be understood because the relaxation from the excited state created by the UV pulse passes through other intermediate vibronic states with $v > 0$ before
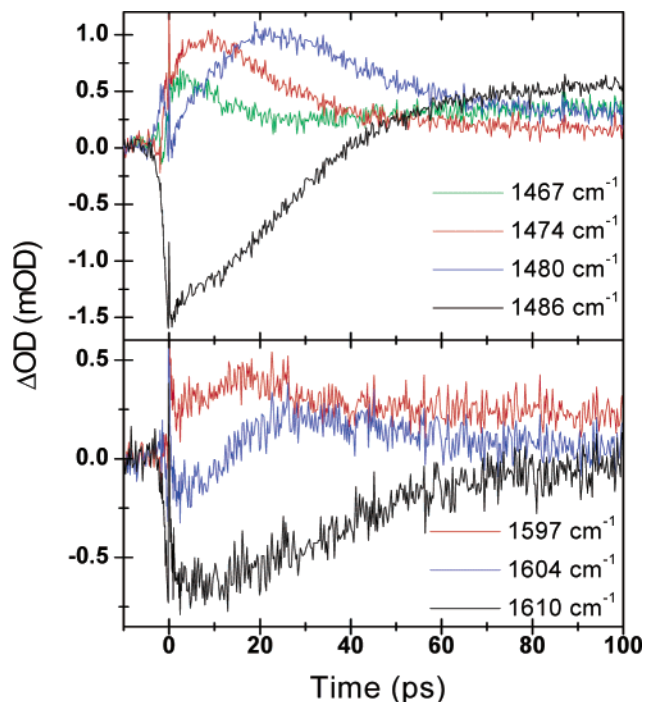
Figure 4. Kinetics at and below the 1486 cm^{-1} (upper panel) and 1610 cm^{-1} (lower panel) IR absorption fundamental frequencies of the closed form of BIPS.

Table 1. Fit Results for the Data Displayed in Figures 4–6

| ν (cm^{-1})	constant (mOD)	B (mOD)	τ_1 (ps)	τ_2 (ps)	- C (mOD)	D (mOD)	τ_3 (ps)
1461	0.41					0.26	85
1467	0.18	0.62	1	8		0.38	150
1474	0.15	1.16	3	21			
1480	−0.09	2.41	19	19		0.31	28 (F)
1486			17	17	−1.51	0.64	28 (F)
1492	0.02					0.56	28
1498	0.13					0.46	28
1591	0.47					0.13	13
1597	0.22	0.40	14	14			
1604		1.01	24	24	−0.29		
1610	0.05		25	25	−0.71		

returning to the vibrational and electronic ground state ($v = 0$). Stimulated emission from $v = 1 \rightarrow v = 0$ presents an additional reason for an initially slower recovery of the bleaches at the fundamental frequencies. Due to anharmonicity, lower frequencies correspond to IR transitions between increasingly higher consecutive levels v of the vibrational ladder. Signals at frequencies below the fundamental frequencies are the difference between (increased) absorption from $v \rightarrow v + 1$ and stimulated emission from $v + 1 \rightarrow v$. Nett increased absorption can be taken as an indication that the wave function amplitude for the level v is larger than for the level with $v + 1$. After internal conversion from the S_1 electronic state to the S_0 electronic state, the initial distribution is expected to be dominated by states with relatively high vibrational quantum numbers v. Note that the 316 nm light contains sufficient energy for about 20 quanta of the 1486 or the 1610 cm^{-1} mode (disregarding anharmonicity). The rapid rise of the signal at 1467 cm^{-1} immediately after the spike (see Figure 4 and Table 1) therefore indicates that the internal conversion probably occurs on a subpicosecond time-scale. In accordance with a stepwise downward relaxation on the vibrational ladder,[19] the increased absorption rises slower the

nearer the frequency is to that of the $v = 0 \rightarrow v = 1$ transition, as is clearly illustrated in Figure 4. Finally the red-shifted increased absorption of the higher-lying vibrational quantum levels v disappears, while simultaneaously the bleach of the ground-state vibration is filled up.

Fit results for the displayed transients based on eqs 1−4, are summarized in Table 1. It appears that fits with expressions 2 and 3 have a strong tendency to make τ_1 and τ_2 nearly equal if they do not differ very much (naturally the numbers cannot be exactly equal since this would make the factor $1/(\tau_2 - \tau_1)$ infinite). Only for the data at 1467 and 1474 cm^{-1} this does not occur. A single-exponential fit for the 1486 cm^{-1} data resulted in a value of 37 ps for the bleach recovery, comparable to the sum of τ_1 and τ_2 (both 17 ps) obtained from fitting with eq 3. The values for τ_1 and τ_2 obtained at 1610 cm^{-1} are slightly longer than at 1486 cm^{-1}, i.e., both 25 ps instead of 17 ps. In principle, there is no reason the recovery should not be very different for different vibrational modes. First of all, the internal conversion may favor specific vibrational modes for the conversion of electronic to vibrational energy. Second, the quantum number v of the levels populated by the internal conversion can vary considerably (differences in anharmonicity, fundamental frequency, and population of combinatorial bands). Third and last, the relaxation rates along different vibrational ladders may strongly depend on the capacity of the solvent to accept vibrational energy quanta of different frequencies, and on the efficiency of intramolecular vibrational redistribution (IVR) to other modes with lower fundamental frequencies.

Although at 1610 cm^{-1}, the signal is only related to the bleached spiropyran IR absorption, at 1486 cm^{-1} the bleach appears to overlap with the IR band at 1489 cm^{-1} of a merocyanine product (open form), and therefore, eventually, the bleach turns into an increased absorption. The kinetics at both of these bands indicate that the dominating fraction that underwent internal conversion contributes very little to the signals after 100 ps. Because, as illustrated by the data in Figures 3 and 4, the bleach of the 1610 cm^{-1} IR absorption band has already recovered by 90% after 100 ps, the quantum yield for the internal conversion has to be $\geq$ 0.9. Consequently, the quantum yield for the photochemical conversion can maximally be 0.1. This value compares well to a photocoloration quantum yield of 0.055 mole/einstein at -120 °C in a 1-propanol/2-propanol mixture reported[1,15] for BIPS irradiated at 313 nm.

Kinetics at Vibrational Frequencies of the Merocyanine Product. As mentioned before we identify the peaks in the spectrum after 100 ps at 1461, 1489, and 1591 cm^{-1} as product bands. Because the open merocyanine form fairly quickly converts back to the spiropyran form (within seconds, because no coloration of the streaming solution was noticed), steady-state IR spectra of the merocyanine compound are not available. Further support for the assignment can however be derived from published time-resolved resonance Raman data,[16] generated 200 ns after UV irradiation, in a variety of solvents. Unfortunately, tetrachloroethene is not one of the solvents used in those studies. We propose that the data in benzene should be closest in comparison, since tetrachloroethene and benzene both do not form hydrogen bonds, are without a permanent dipole moment but slightly polarizable, and have the same dielectric constant

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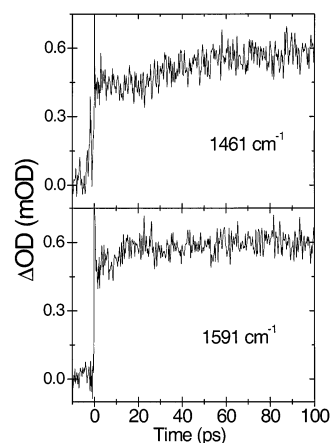
Figure 5. Transient signal behavior at the 1461 and 1591 cm^{-1} product bands.
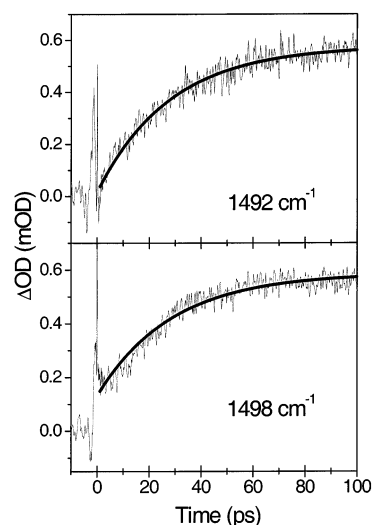
Figure 6. Product formation kinetics of the 1489 cm^{-1} IR absorption band, together with fits indicating a rise time of 28 ps.

($\epsilon_r = 2.28$). Naturally, vibrational modes that are Raman active need not be active in IR absorption, and vice versa. Many modes are nevertheless active in both and should then appear at the same frequencies, albeit with probably very different peak intensity patterns. The 1461, 1489, and 1591 cm^{-1} bands obtained from our data correspond reasonably well with the lines at 1447, 1493, and 1577 cm^{-1}, observed in the resonance Raman spectrum of merocyanine species.[16] The difference in these numbers could very well be accounted for by the resolution and signal/noise in both measurements. Note in ref 16 that the resonance Raman signals do not drop to zero inbetween the vibrational peaks, perhaps due to nonresonant Raman contributions.

Figures 5 and 6 show the time dependent behavior during the first 100 ps at frequencies we identify as product related. In Figure 5, it is shown that the signals at both 1461 and 1591 cm^{-1} jump within a few hundred femtoseconds to about 0.4−0.5 mOD, to be followed by a modest increase to about 0.6 mOD in the next 100 ps. Only on the high frequency side of the fairly broad product band at 1489 cm^{-1} clear product formation transients, well exceeding the noise level (about ±0.05 mOD) are observed. We postulate that the rise time extracted from the data in Figure 6 best characterizes the formation rate

of merocyanine product(s). A look at the IR absorption spectrum of the closed form in Figure 3b illustrates that both at 1461 and 1591 cm^{-1} we should expect complication of the dynamical behavior due to transient signals related to vibrational cooling of the large fraction of spiropyran molecules that underwent the internal conversion $S_1 \rightarrow S_0$. In addition, at 1461 cm^{-1} recovery of bleached spiropyran vibrational absorptions will also contribute to the signals. On the other hand the traces in Figure 6 at 1492 and 1498 cm^{-1} are fairly free of such contributions, since the first vibrational mode which could noticeable contribute through hot band absorption has its fundamental frequency more than 100 cm^{-1} higher at 1610 cm^{-1}. Only a minor bleach recovery contribution from the tail of the bleached IR absorption at 1486 cm^{-1} can complicate these signals. We therefore conclude that only at 1492 and 1498 cm^{-1} interpretation of the data results in a reliable product formation time constant. We extract a product formation time constant of 28 ps from these data (see Table 1). This is drastically slower than the 0.9 ps time constant previously concluded from UV-pump/white-light probe measurements on BIPS in *n*-pentane.[6] Can these vastly different numbers be reconciled with each other?

In our opinion, the 0.9 ps rise time of the broad absorption band peaking at 540 nm after UV irradiation of BIPS does not characterize the merocyanine product formation rate, but instead is an indication of how fast the $S_1 \rightarrow S_0$ internal conversion rate is for the spiropyran form. The additional absorption, which makes the spectrum after 1 ps nearly featureless between 380 and 680 nm, was assigned by Ernsting and Arthen-Engeland[6] to absorption from the S_1 excited state of the spiropyran form to higher electronic states of the closed form and absorption from vibrationally hot merocyanine products. In view of the rapid and efficient internal conversion indicated by the data in Figure 4, we prefer to assign this featureless spectrum to absorption from a mixture of vibationally hot levels of the spiropyran S_0 state to vibrational levels of the spiropyran S_1 state. The sharpening of the 540 nm band between 1.1 and 7.5 ps, accompanied by about 50% increase in increased absorption, as reported by Ernsting and Arthen-Engeland, would then be the result of a gradual replacement of absorption from vibrationally hot spiropyran, which disappears due to vibrational cooling, by merocyanine absorption which is formed with a 28 ps time constant according to our data. Unfortunately, the published UV pump/white-light probe transients for BIPS do not extend beyond 8 ps, and as mentioned previously, no single color UV pump–probe measurements have been reported yet that could confirm the nearly complete ground-state recovery of the closed spiropyran form. Further support for our interpretation can be derived from combining quantum yield information for photocoloration of BIPS and 6-nitro-BIPS, with the UV/white-light pump–probe data for these two compounds. At −120 °C in a 1-propanol/2-propanol mixture a photocoloration quantum yield of 0.055 mole/einstein has been reported for BIPS, whereas for 6-nitro-BIPS this yield is 0.3 mole/einstein, both with irradiation at 313 nm.[1,15] The generally much higher photocoloration quantum yield for 6-nitro-BIPS compared to BIPS is well established and has been brought in connection with involvement of triplet states[13,14] in the photochemical reaction route for 6-nitro-BIPS. In addition, preliminary results of measurements performed by us on 6-nitro-BIPS in tetrachloroethene indicate a much higher quantum yield for

photochemistry and a lower yield for internal conversion. Although based on the above numbers the photocoloration quantum yield for 6-nitro-BIPS is expected to be about 5 times higher than for BIPS, the UV-white light pump–probe data[6] show spectra with comparable peak intensities during the first 7.5 ps, and even after 70 ps the 6-nitro-BIPS signal is only about twice that of BIPS after 7.5 ps. Notice that for 6-nitro-BIPS a 20 ps merocyanine formation time constant has been reported.[6] Clearly, the difference in visible absorption at the product wavelength is less than the quantum yield data suggest, but this could be accounted for by additional absorption for BIPS from vibrationally hot molecules formed by internal conversion. As mentioned above, the energy of the 316 nm radiation is equivalent to about 20 quanta of the fundamental frequency of the 1486 or 1610 cm^{-1} modes. Absorption at 680 nm could, for instance, correspond to transitions for these from $v \geq 10 \rightarrow v' = 0$, and at 380 nm to transitions $v \cong 3 \rightarrow v' = 0$ (the accent indicates vibrational levels of the electronic excited state).

Intermediate States to Product Formation and Different Isomers. Given the fact that we could determine the product formation rate undisputably only at the 1489 cm^{-1} IR absorption band, it is clear that we cannot make any statements about the possibility of formation of several different isomers for the merocyanine form of BIPS. Because the ring opening and closing reactions can both occur thermally as well as photochemically, it seems worth to raise the question whether the product is formed from the vibrationally hot states created by internal conversion, or from other intermediates (not involving the spiropyran S_0 state). In any case, it is clear that the product is not directly formed from the S_1 state of spiropyran. Direct competition between the internal conversion process and the ring-opening reaction from the S_1 state of spiropyran should lead to a subpicosecond product formation rate, which is clearly not observed.

The perhaps somewhat puzzling aspect is the absence of a clear distinct signature of an intermediate species/state that itself is decaying with a 28 ps time constant. Ways to explain this rely on the proposal that there are many intermediates rather than a single one. This still leaves two possibilities:

(1) A large number of intermediates (spiropyran-like, merocyanine-like, and/or neither), each with distinct vibrational signatures, could be involved. This could simply lead to a diffuse background absorption in the transient IR spectrum, similar to the signal we assigned to multiphoton and solvent effects. (2) If photochemistry takes place from vibrationally hot S_0 states, a distribution over several vibronic levels of the vibrational manifold (including combinatorial bands), would make absorption of the transient species diffuse. Our preference lies with the first scenario, since it seems highly likely that in the last scenario the photochemistry efficiency would strongly depend on the vibrational quantum number v. This should lead to nonexponentiality in the formation dynamics, which was not observed here. Also the formation time is then expected to be considerably faster than the bleach recovery time, whereas the observed 28 ps is still fairly close to the 37 ps single-exponential fit result for the bleach recovery at 1486 cm^{-1}. The signals in Figure 6 strongly suggest that the intermediate(s) are formed in less than a picosecond, without any additional feeding occurring at later times.

Conclusions

We studied the photochemical ring-opening reaction of the spiropyran BIPS in tetrachloroethene, by probing the evolution of the transient IR absorption spectrum with a time resolution of 130 fs. The merocyanine product is probably formed from intermediates other than the initially created excited state of the spiropyran, which are populated on a subpicosecond time-scale in competition with a very efficient and rapid internal conversion process. From these intermediates a single exponential formation of a merocyanine form with a 28 ps time constant is concluded, which is in sharp contrast to previous conclusions of a 0.9 ps formation time constant, derived from femtosecond UV pump/ white-light probe measurements. This illustrates that care has to be taken with conclusions based on optical pump−probe spectroscopy only. From the recovery of the spiropyran IR absorption bleaches we conclude that the main decay channel for the spiropyran S_1 excited state is internal conversion to the spiropyran S_0 state with a yield of 90% or more. The quantum yield for the photochemical reaction is therefore ≤ 0.1. The present results demonstrate the usefulness of direct femtosecond IR probing as an alternative means of obtaining information on photochemical reactions.

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