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Femtosecond UV/mid-IR study of photochromism of the spiropyran 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro-[2H-1-benzopyran-2,2′-(2H)-indole] in solution

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Abstract

The ring-opening reaction of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] is investigated in two solvents, by probing the evolution of the vibrational absorption spectrum with 130 fs time-resolution. Competition between internal conversion and photochemistry is found to depend on the solvent. The internal conversion quantum yield is determined to be 0.63 in perdeuterated acetonitrile and 0.34 in tetrachloroethene. Based on spectral features and biexponential kinetics, the formation of an additional merocyanine isomer in tetrachloroethene is concluded.

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1. Introduction

Photochromism is the property that a substance can undergo reversible colour changes by exposure to light of specific wavelengths. Photochromism has met with a longstanding scientific and industrial interest [1–17], with visions of applying this phenomenon in optical data storage [2], and optically controlled molecular switching [3]. Here, we investigate the spiropyran–merocyanine photochemical ring opening/closure (Fig. 1) of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (6-nitroBIPS) in two solvents: tetrachloroethene (TCE) and perdeuterated acetonitrile (ACN-d_3).

Scientifically this simple reaction already presents a rather complex puzzle. Not only is there the issue whether singlet and triplet states both are involved [4–7], but also the product can appear as eight different *cis–trans* isomers [8–13]. On top of that the merocyanine product can aggregate [14]. A wide range of experiments has been performed on 6-nitroBIPS, including low temperature absorption [8], triplet sensitization [6], femto- [12,15] and nanosecond [7] time-resolved UV–vis pump–probe spectroscopy, and time-resolved resonance

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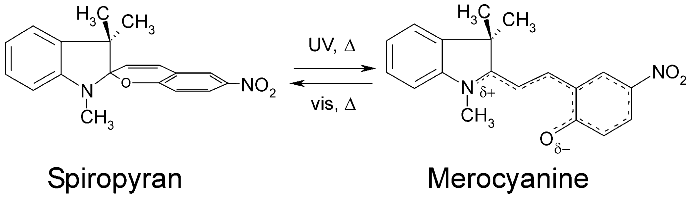

Fig. 1. Reaction scheme for 6-nitroBIPS.

Raman spectroscopy [9,10]. Nevertheless, the number of investigations on the femto- and picosecond timescale is still relatively limited.

Recently, we started femtosecond UV/mid-IR investigations on photochromism of spiropyrans, focussing on the time evolution of the vibrational absorption spectrum. In a first publication [16] on the compound 1′,3′-dihydro-1′,3′,3′-trimethyl-spiro[2H-1-benzopyran-2,2′-(2H)-indole] (BIPS) in TCE, we concluded that the photochemistry quantum yield was maximally 0.1 due to a very fast and efficient internal conversion process. Moreover, appearance of the merocyanine product seemed to involve a 28 ps time constant, much slower than the 0.9 ps rise time concluded from UV–vis experiments [12]. Here, we extend our investigations to 6-nitroBIPS. We find that internal conversion competes with the photochemical conversion pathways, although less efficient than for BIPS. In addition, the efficiency of this process appears to be solvent dependent. Data acquired over a wider frequency range are presented and comparisons are made to results from investigations on 6-nitroBIPS with other techniques [7–13].

2. Experimental

Tetrachloroethene (TCE) and 6-nitroBIPS were purchased from Sigma–Aldrich. Perdeuterated acetonitrile (ACN-d_3; deuteration grade 99.8%) was purchased from Deutero GmbH. The compounds were used without further purification. These solvents have limited IR absorption in the investigated frequency range. Steady-state FT-IR spectra of 6-nitroBIPS in TCE and ACN-d_3 were recorded with 1 cm^{-1} resolution, using a Bio-Rad FT-IR spectrometer. Time-resolved measurements were performed on 20 mM solutions of 6-nitroBIPS in TCE and ACN-d_3. The photochromic reaction was initiated by 70 fs pulses at 330 nm (2 μJ/pulse), and the evolution of the vibrational absorption spectrum was probed with 100 fs IR pulses (~20 nJ/pulse), with the centre frequency varying from 1260 to 1600 cm^{-1}. In each measurement the detector covers 100–200 cm^{-1}, with a spectral resolution of 4–7 cm^{-1}. More extensive experimental details can be found in [16].

3. Results

Fig. 2 shows the steady-state IR absorption spectra of 6-nitroBIPS in ACN-d_3 and TCE at room temperature, corrected for solvent contributions, in the range probed in our time-resolved measurements. Electronic absorption spectra (not shown) indicate that the compound is almost exclusively in the closed spiropyran form in both solutions. We estimate that at most 1% is in a merocyanine form in ACN-d_3 and 0.01% in TCE. The IR spectra in Fig. 2 clearly illustrate that the peak intensities of IR absorption bands can vary quite considerably in different solvents. For instance, the ratio of the peak intensities at ~1342 cm^{-1} divided by that at ~1524 cm^{-1} differs by 40% for these two solvents. Solvent dependence of IR

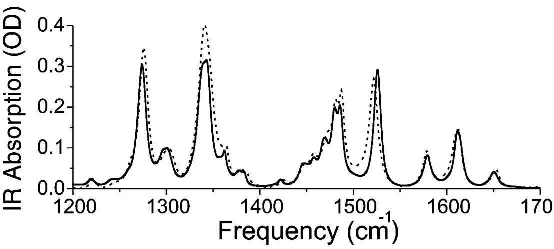

Fig. 2. Steady-state IR absorption spectra for 6-nitroBIPS in ACN-d_3 (– –, 51 mM) and in TCE (——, 42 mM).

absorption intensities and frequencies is a known effect [18].

Fig. 3 demonstrates overall transient differential spectra created from our data for 6-nitroBIPS in TCE (Fig. 3, upper panel) and ACN-d_3 (Fig. 3, lower panel), 2 ps after UV excitation, and at long delay. For comparison with the bleaches at early delays the steady-state IR absorption spectrum is also plotted. The initial spectra resemble the steady-state IR spectra well, indicating removal of ground state (closed) spiropyran species by the femtosecond UV excitation pulse. Note further that in TCE not a single sharp increased absorption feature is found at early times. In ACN-d_3 the initial spectrum shows a few positive features (marked *), that we assign to vibrational hot bands of the spiropyran species in the electronic ground state formed after internal conversion. The kinetics in ACN-d_3 at 1264 cm^{-1} depicted in Fig. 4c, illustrate the vibrational cooling dynamics for hot spiropyran [16].

Spectra at long delay times show for both solvents (residual) bleaches as well as a number of peaks related to photoproducts. First we point out that in TCE the bleaches have recovered by ~34% in TCE after 150 ps, and ~63% in ACN-d_3 after 60 ps. Note also the strong lines at 1297 and 1519 cm^{-1} (marked O) in TCE, which appear nearly absent in ACN-d_3. These lines we associate with the formation of an additional merocyanine isomer in TCE.

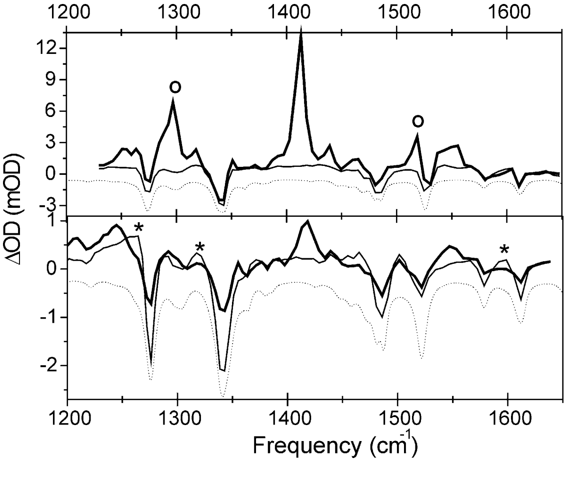

Fig. 3. Transient IR-spectra between ~1200 and ~1650 cm^{-1}, for 6-nitroBIPS in TCE (upper panel) and in ACN-d_3 (lower panel), 2 ps after UV-excitation (thin solid lines), and at 150 and 60 ps, for TCE and ACN-d_3, respectively (thick solid lines). For comparison, the inverted steady-state IR spectra of 6-nitroBIPS in the respective solvents are also depicted (dotted lines), roughly scaled to the bleaches at early times, with an offset of −0.25 mOD for ACN-d3, and −0.5 mOD for TCE.

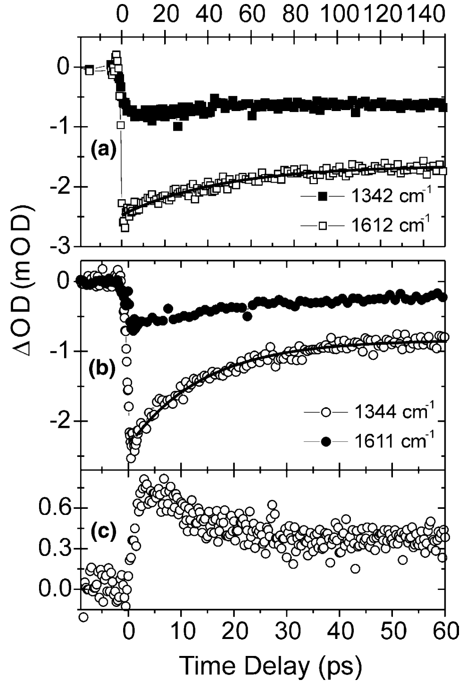

Fig. 4. (a–b) Bleach recovery at two vibrational frequencies of 6-nitroBIPS (in the spiropyran form) in TCE (a) and in ACN-d_3 (b). The numbers correspond to the central frequency associated with the diode pixels. The solid lines are fits corresponding to decay times of 47 ps in TCE, and 14 ps in in ACN-d_3. (c) Kinetics related to the spiropyran vibrational hot band at 1264 cm^{-1} in ACN-d_3. The time scale at the bottom applies to both panels b and c.

4. Discussion

4.1. Bleach recovery and internal conversion

The kinetic behaviour related to the spiropyran form of 6-nitroBIPS is illustrated in Fig. 4 at two bleached vibrational absorption bands: at 1342 and 1612 cm^{-1}. These data show that both in TCE (Fig. 4a) and in ACN-d_3 (Fig. 4b) the bleaches partially recover. This recovery has to be due to regeneration of the spiropyran ground state, and therefore indicates the occurrence of internal conversion. The data demonstrate that the quantum yield for internal conversion is solvent dependent: about 34% in TCE, and 63% in ACN-d_3 (error margin: 5%). Previous investigations had not identified this apparently rather influential decay channel. It may well be that the efficiency of internal conversion is a key factor in determining the overall photochemistry quantum yield. Given the observed bleach recovery the maximum quantum yield for photochemistry of 6-nitroBIPS is 0.66 in TCE, and 0.37 in ACN-d_3. (Absolute [1,17] and relative [4,5] photochemistry quantum yields have been reported for 6-nitroBIPS in various solvents.) The refill rate of the bleach, after internal conversion and subsequent vibrational cooling, is also different for these two solvents: 47 (± 10) ps in TCE, and 14 (± 2) ps in ACN-d_3.

4.2. Existence of different merocyanine isomers

Based on the spectra at long delays shown in Fig. 3, combined with observed kinetics at different frequencies, we identify with certainty product bands in ACN-d_3 around 1245, 1299, 1355, 1417 and 1551 cm^{-1}. In TCE bands are identified at the similar frequencies 1251, 1297, 1351, 1413 cm^{-1} and in the range 1537–1556 cm^{-1}. In addition, in TCE we observe bands at 1263, 1318, 1439, 1463 and 1519 cm^{-1}. Note that, in general, the signals in TCE are much stronger than in ACN-d_3. Therefore some of the weaker bands in TCE could be below the detection threshold in ACN-d_3. The bands at 1297, 1413 and 1519 cm^{-1} are much more intense in TCE than in ACN-d_3 (about an order of magnitude or more). As the difference in internal conversion efficiency can only justify a factor two in photochemistry quantum yield, we conclude that these three peaks constitute reliable evidence for the existence of an additional different merocyanine isomer in TCE, that is not present in ACN-d_3. Because all product bands in ACN-d_3 are also observed in TCE, the isomer that is formed in ACN-d_3 is likely to be present in TCE as well. These conclusions are further supported by the product formation kinetics discussed below.

Takahashi and co-workers have concluded the existence of five isomeric species [9] from time-resolved Raman spectra of 6-nitroBIPS, taken from 200 ns to 2 ms after UV excitation in three different solvents. These assignments were mainly based on intensity variations with solvent of different Raman lines, and analogy to a similar study on the parent compound BIPS [11]. Two species were brought in connection with only a single Raman line. As we demonstrated for spiropyran in Fig. 2, IR absorption intensities of the same species can already vary considerably from solvent to solvent. Clearly, moderate intensity variations alone are a poor basis for the identification of different isomeric species. In a later investigation on 6-nitroBIPS in cyclohexane, they followed the time evolution of the Raman spectrum between 20 ns and 100 μs after UV excitation [10]. This time only three transient species were invoked in the interpretation. The species identified at earliest times was ascribed to a merocyanine triplet state. A convincing correlation between the decay of the 1409 cm^{-1} Raman intensity (0.33 μs time constant), and the increase of the 1525 cm^{-1} Raman intensity, led to assignment of the second species as ground state merocyanine. On the microsecond timescale a third species is identified as a dimeric species. As none of these re-assignments require the existence of different isomers, the previous claim of five existing isomers should at least be reduced to maximally three. Several other inconsistencies can be noted in their Raman assignments. For example, the 20 ns data in [10] clearly illustrate that assigning both the 1550 and 1523 cm^{-1} lines to the same 'initial cisoid 1523 cm^{-1} species' in [9] was incorrect.

About half of the observed resonance Raman peaks correspond to lines we observe in IR absorption: for 6-nitroBIPS in ACN (after 2 ms, [9]) these are at 1358 and 1411 cm^{-1}. Data in TCE are probably best compared to the 20 ns Raman data in cyclohexane [10], that show related peaks at 1297, 1350, 1409 and 1552 cm^{-1}. Recall that Raman and IR absorption yield complementary information.

Recently, density-functional-theory calculations on the spiropyran form of 6-nitroBIPS and the four most stable merocyanine isomers were presented, and compared to IR absorption spectra in an argon matrix at 8 K [13]. Reasonable agreement was obtained between experiment and calculations, although insufficient to unequivocally identify the isomers. More specific, we point at the intense experimental line at 1529 cm^{-1}, which corresponds to a calculated line at 1551 cm^{-1}. This experimental 1529 cm^{-1} line could be associated with the extra isomer in our TCE data, whereas the calculated 1551 cm^{-1} line agrees with both isomers observed by us.

Altogether we are convinced that existing experimental results provide insufficient evidence for claiming formation of five isomers. It seems therefore prudent to limit our conclusion to strong indications for existence of a second isomeric species in TCE, not formed in ACN-d_3.

4.3. Product formation kinetics

Kinetics at selected wavelengths is depicted in Fig. 5. In Fig. 5b the product formation kinetics in ACN-d_3 are shown at 1418 (●) and 1551 cm^{-1} (○). Single exponential fits of these two traces indicate a single exponential formation time of 9.5 ± 1.5 ps. No further change in product absorption was observed between 30 and 100 ps. However, there seems to be some variation in rise time over the bands; e.g., at 1413 cm^{-1} we obtain 7.1 ps. This behaviour is observed even more clearly in TCE, where the overall product formation in TCE is considerably slower. As an illustration Fig. 5a shows the product related signals at 1551 (□) and 1556 cm^{-1} (■). Clearly the signal rises much faster at 1551 cm^{-1} during the first 50 ps. Single exponential fits at different product bands produce rise times in the range of 35 to 60 ps for 6-nitroBIPS in TCE. As indicated by the data in Fig. 5b the kinetics require at least a biexponential fitting approach. For the strongest band (around 1413 cm^{-1}) this procedure resulted in a faster component increasing from about 5 ps at 1397 cm^{-1} to 28 ps at 1413 and 1418 cm^{-1}, and a second component typically >100 ps. Because the data are only up to 150 ps, the time constant of the slow component cannot be extracted reliably. The most likely source for the observed frequency dependence of the faster component is vibrational cooling dynamics of the merocyanine products.

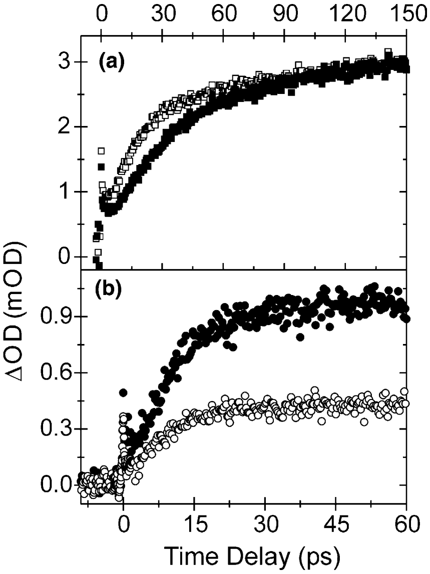

Fig. 5. (a) Merocyanine product formation kinetics for 6-nitroBIPS in TCE at 1551 (□) and 1556 cm^{-1} (■). (b) Product formation kinetics for 6-nitroBIPS in ACN-d_3 at 1418 (●) and 1551 cm^{-1} (○).

Absorption change studies on 6-nitroBIPS in hexane and acetonitrile by Lenoble and Becker [7], with 1 ns time resolution, indicated that in acetonitrile the rise of the 570 nm product related band was complete within 1 ns. Our measurements lower the upper limit for the product formation time in (perdeuterated) acetonitrile to about 9.5 ps. The fast component in TCE (~5–28 ps), and the time constant in ACN-d_3 (~7–10 ps), are in line with a 20 ps time constant found by Ernsting and Arthen-Engeland [12] in a femtosecond UV/white-light investigation of 6-nitroBIPS in *n*-pentane. Based on solvent polarity one may suspect that the kinetic behaviour in hexane, *n*-pentane, and tetrachloroethene should be rather similar. This seems true for our measurements compared to those of Ernsting and Arthen-Engeland [12]. However, in hexane the fastest rise time identified by Lenoble and Becker was 4 ns at 430 nm [7]. Whether the slow >100 ps component in TCE can be reconciled with their nanosecond result in hexane remains an open question.

The biexponentiality of the product formation in TCE, versus single exponential kinetics in ACN-d_3, clearly corroborates the conclusion drawn above on formation of a second isomeric species in TCE. This biexponentiality also implies that these species cannot be formed in direct competition from a mutual precursor state, since this would lead to the same formation constant for both. Note that published conclusions on different isomers was based on data obtained 20 ns or more after UV irradiation of a sample. These data therefore constitute the first time-resolved evidence that a second isomer already appears within 100 ps.

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