Photochemistry with thermal versus optical excess energy: Ultrafast cycloreversion of indolylfulgides and indolylfulgimides

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ABSTRACT

The dependence of the pericyclic ring-opening reaction of indolylfulgides and indolylfulgimides on excess energy is investigated by quantum efficiency measurements and by ultrafast spectroscopy. The ring-opening reaction shows a pronounced improvement of reaction efficiency up to a factor of 6, when excess energy is available either by increasing the temperature or by exciting the molecules above the 0–0-transition. Ultrafast spectroscopy allows to deduce time constants for the ring-opening reaction and leads to a theoretical model, where the redistribution of excess energy among different vibrational modes is considered. The analysis shows that excess energy supplied by optical excitation accelerates the ring-opening reaction less efficiently than thermal energy. Apparently vibrational relaxation from highly excited modes to modes promoting the ring-opening reaction is not completed within the $\sim$10 ps duration of the ring-opening reaction.

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1. Introduction

Fulgides and the associated fulgimides undergo light induced isomerisation, ring-closure and ring-opening reactions [1,2]. These reactions are related to the photochromism of these molecules, which is associated with the three photoisomers *C*, *E*, and *Z* (see Scheme 1) featuring different optical absorption spectra. It was shown in a number of previous investigations that physical properties, reaction quantum yields, and absorption characteristics of the isomers can be tailored by chemical substitution [3–9]. It was also reported that indolyl substituted fulgides/fulgimides may be thermally stable in the electronic ground state and that these molecules show a high resistance against photochemical fatigue [6,10]. This makes them interesting candidates for different applications as optical switches or memory elements [4–7,10–13]. The attachment of photochromic switches on surfaces explores a new class of materials with photoswitchable properties [14–20]. Photoswitches with thermally stable ground state isomers and different fluorescence properties are also excellent candidates for newly emerging

microscopy techniques summarised by the acronym reversible saturable optical fluorescence transitions (RESOLFT) [21–24]. In the context of potential applications in photoswitching microscopy the fluorescence properties and switching capabilities (durability, quantum efficiency) of photochromic molecules are relevant [25]. The fluorescence dynamics of indolylfulgide photoisomers was investigated recently [26]. Indirect switching of attached molecular probes with high fluorescence yield was demonstrated [27].

In former studies we investigated in detail the ring-opening reaction of indolylfulgimides and -fulgides in different solvents with various ultrafast methods in the UV, VIS, and mid-IR [26,28–32]. A reaction scheme for the ring-opening reaction of the indolylfulgide and the indolylfulgimide is depicted in Fig. 1 [26,28]. After excitation from the electronic ground state (S_0) into the Franck-Condon (FC) region of the first electronically excited state (S_1), the system relaxes towards the minimum of the S_1 potential energy surface. From here the molecule converts back to the ground state S_0 after passing a barrier with an activation energy E_a. This internal conversion process may proceed via a conical intersection (CI) between ground and excited state and may reach the electronic ground state of either the ring-opened product *E* or the reactant *C*. Vibrational cooling of the hot molecules in the ground states (reactant and product) was found to occur on the 10 ps time scale [28,29]. It was shown that the ring-opening proceeds also directly from higher excited states with increased reaction yield [33]. This implies a violation of Kasha's rule [34] which was

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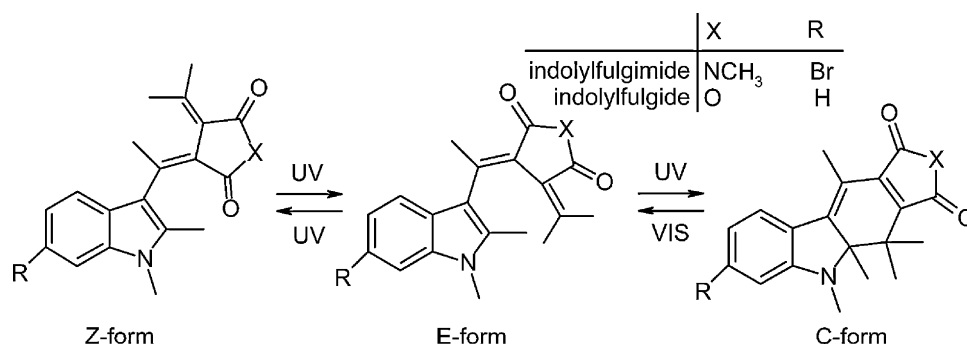
Scheme 1. The isomers (*Z*, *E*, and *C*) of the investigated indolylfulgide (R = H, X = O) and indolylfulgimide (R = Br, X = NCH$_3$). Arrows denote the possible photoreactions.

originally formulated for the fluorescence properties of molecules, but is extended meanwhile also to photoreactions [35]. Similarly the Kasha–Vavilov rule [36–38] states that the yield of fluorescence (photoreactions) is independent of the wavelength of exciting radiation [35].

The experimental observations show that typical times for cooling processes to the surrounding solvent are in the same temporal regime or even slower than the reaction time for ring-opening. Therefore, it can be assumed that the ring-opening in the electronically excited state may occur prior to thermal equilibration with the solvent. As a consequence optical excess energy in the electronically excited S$_1$ state, brought in by exciting the molecules far above the 0–0-transition, is not dumped to the surroundings before the photoreaction occurs. The related non-equilibrium may influence the reaction yield and dynamics of the ring-opening reaction, i.e. the ring-opening reaction may depend on the excitation wavelength and may violate the Kasha–Vavilov rule [36–38]. Reports in the literature on such a behaviour are rare [39–44].

In this study we present results from steady-state and femtosecond time-resolved absorption spectroscopy of the ring-opening reaction of an indolyl substituted fulgimide and fulgide in the visible spectral range. The quantum yield η of the ring-opening

reaction is investigated as a function of temperature and optical excess energy in two different solvents. Time-resolved absorption experiments provide supplementary information on the reaction dynamics. A model is developed to account for the redistribution of optical excess energy and to describe the dependence of the ring-opening reaction on the excess energy.

2. Materials and methods

2.1. Sample preparation

The ring-opening reaction of two different optical switches is investigated (molecular structures see Scheme 1): an indolylfulgide (R = H; X = O) and the associated indolylfulgimide (R = Br; X = NCH$_3$). Via a substitution of the bromide at position R and the NCH$_3$ group at position X the indolylfulgimide can be covalently incorporated into complex switching systems. The synthesis of these molecular switches is published in Ref. [45]. For the experiments in the visible spectral range the molecules were dissolved either in toluene (Uvasol) purchased from Merck KGaA or acetonitrile from Sigma–Aldrich Chemie GmbH used without further purification. The solvents represent surroundings with strongly different dielectric constants (toluene: $\varepsilon = 2.379$ and acetonitrile: $\varepsilon = 35.94$). The *C*-isomers of both indolylfulgide/imide were photochemically prepared by steady-state illumination at 365 nm (10 mW) with a Hg(Xe) lamp (Hamamatsu, 8251) and an optical filter UG1 (Schott) until the photostationary state (PSS-365) was reached with a constant fraction of isomers in the *C*-, *E*-, and *Z*-form. All presented experiments were performed on samples in PSS-365. The PSS-550, containing a high concentration of the molecules in the *E*-form is obtained by visible illumination (Schott, KLC 2500 with optical filter OG550) of a PSS-365 sample, where all *C*-form molecules are converted to the *E*-form.

In the visible only the closed *C*-isomers of the indolyl substituted fulgimide and fulgide (see Scheme 1 and Fig. 2) show characteristic absorption bands at around 550 nm, while the *E*- and *Z*-isomers do not absorb here. As a consequence, photoexcitation of an isomeric mixture by light in the visible spectral range addresses the ring-opening reaction $C \rightarrow E$ exclusively. Therefore the *Z*-form content remains unchanged.

2.2. Stationary spectroscopy

Absorption spectra in the visible spectral range were measured using a spectrophotometer (PerkinElmer, Lambda19). For the measurements of the quantum efficiency of the ring-opening, the $C \rightarrow E$ reaction was initiated by illumination either at a fixed wavelength by a cw Nd:YAG laser at 532 nm (1 mW, LCM-T-11, Laser-compact Plus) or spectrally tunable by a system of XBO arc lamp and monochromator. For determination of the reaction yield η as a function of excitation wavelength the power of the excitation light
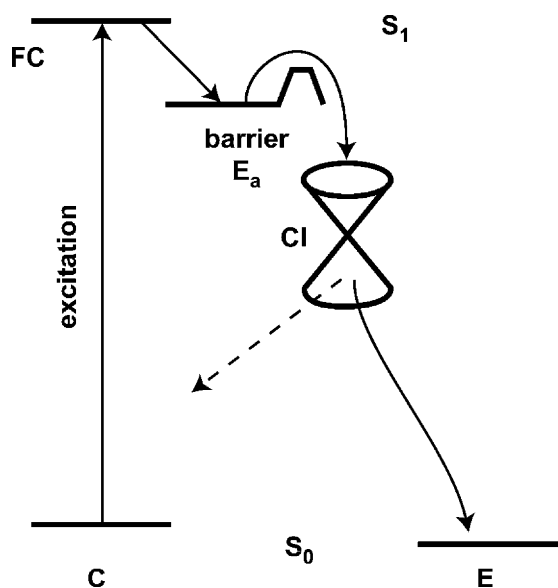
Fig. 1. Scheme of the ring-opening reaction of the indolylfulgimide and the indolylfulgide. After excitation from the electronic ground state S$_0$ of the *C*-form the molecule reaches the Franck-Condon (FC) region of the excited state S$_1$, which has low radiative coupling to the electronic ground state. Then it relaxes towards the minimum of the S$_1$ potential energy surface. From here the molecule converts back to the ground state S$_0$ over a barrier with an activation energy E_a by internal conversion (e.g. via a conical intersection CI).
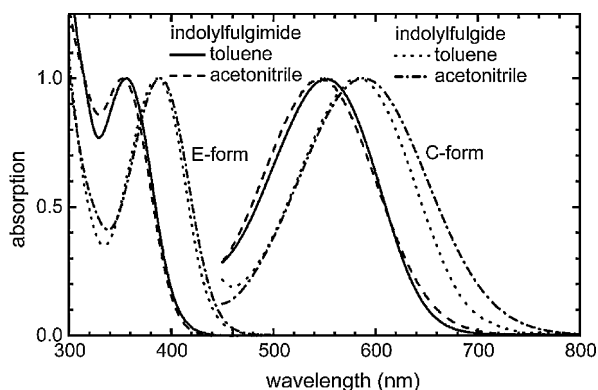
Fig. 2. Normalised optical absorption spectra of the *E*-isomer (PSS-550) in the range between 300 nm and 500 nm and of the C-isomer (PSS-365) between 450 nm and 800 nm of the four investigated samples (indolylfulgimide in toluene, indolylfulgimide in acetonitrile, indolylfulgide in toluene, and indolylfulgide in acetonitrile). Both *E*- and *C*-isomers of the indolylfulgimide are about 35 nm blue-shifted compared to the indolylfulgide. The absorption maxima of the *E*- and *C*-forms (see Table 1) of indolylfulgimide and indolylfulgide are not sensitive to the polarity of the solvent. From the absorption data the energy of the 0–0-transition E_{0-0} is estimated (see Table 1).

was measured by a calibrated Si-photodiode PD-9304-1/SN 10532 (Gigahertz-Optik) with a relative uncertainty of ±2%. The temperature of the sample was adjusted in the range between 255 K and 313 K with a precision of ±1 K. The reaction yield η was determined from the change of the optical density of the absorption band of the *C*-isomer in the visible spectral range after illumination [32]. The temperature and wavelength dependent data was fitted according to Eqs. (1) and (2) using data analysis software Origin 6.1 (OriginLab Corporation).

2.3. Ultrafast spectroscopy

For the time-resolved pump-probe experiments a home-built Ti:sapphire based laser spectrometer (repetition rate 1 kHz) was used, which is described in detail in Ref. [46]. Pump pulses centred at 530 nm with a band width of 20 nm (FWHM) and broad-band probe pulses in the visible spectral range (510–740 nm) were generated via two non-collinear optical parametric amplifiers (NOPA) [47,48]. These pulses were compressed in prism compressors. Probe pulses in the UV spectral range at 395 nm were produced by frequency doubling the fundamental of the laser pulses. The time delay between pump and probe pulse was adjusted by a delay stage. The polarisation between pump and probe pulse was parallel for the experiment with broad-band probe pulses and perpendicular for the UV probe pulse. The time-resolution of the experiment (FWHM of the cross-correlation trace) was better than 50 fs for the broad-band probe pulse in the visible spectral range and about 120 fs for the UV probe pulse.

About 3 ml of the sample (kept in PSS-365 by continuous illumination) was pumped in a closed circuit with a fused silica flow-cuvette (200 µm optical path length, Hellma) at a temperature of 300 K. The sample concentration was adjusted to an optical transmission of about 10% at the maximum of the absorption band of the *C*-form in the visible spectral range. The excited sample volume was completely exchanged from shot to shot by a peristaltic pump (Ismatec). The detection set-up (monochromator, 42-channel photodiode array and ADC) [49] allowed single-pulse detection with a repetition rate of 1 kHz. Transient absorption data was fitted by a global fitting procedure including two exponentials and an offset.

3. Experimental results and spectroscopic analysis

The investigated ring-opening reaction $C \rightarrow E$ is initiated by visible light between 480 nm and 700 nm, i.e. in a spectral range, where only molecules in the *C*-form are excited. This is evident from the absorption spectra of the investigated molecules (see Figs. 2 and 4a), which show that only the *C*-form of the investigated molecules absorbs at $\lambda > 480$ nm. Possible photoproducts reached after excitation of the *C*-isomer at $\lambda > 480$ nm are *E*-form molecules with a yield of η and *C*-form molecules with a yield of $(1 - \eta)$. Immediately after internal conversion to the ground state the molecules are vibrationally excited and these hot molecules relax and cool down on the 10 ps time scale. Two general remarks should be added: in all experiments presented here only the *C*-form is excited and no reaction to the *Z*-form occurs [8]. Therefore the *Z*-isomer must not be considered in the further discussion. It has been shown recently that the investigated indolylfulgide and indolylfulgimide have a very low fluorescence yield of <1% [29].

### 3.1. Stationary absorption spectroscopy

In Fig. 2 the absorption spectra of *E*- and *C*-isomers of the investigated molecules in the two solvents toluene ($\varepsilon = 2.379$) and acetonitrile ($\varepsilon = 35.94$) are shown. The *E*-isomer exhibits an absorption band in the UV spectral range, whereas a broad absorption band related to the S_0–S_1 absorption of the *C*-isomer is seen peaking around 550 nm (indolylfulgimide in toluene). The positions of the absorption maxima for the four samples are given in Table 1. The absorption band of the indolylfulgide is about 35 nm red-shifted with respect to the indolylfulgimide. The influence of the solvent on the absorption peak is low. In acetonitrile, the absorption band is slightly blue-shifted for the indolylfulgimide while it is red-shifted for the indolylfulgide. For both molecules the polar solvent acetonitrile leads to weak broadening of the absorption band. These observations indicate that the S_0 and S_1 potential energy surfaces of both molecules react in a similar way to the changed polarity of the solvent.

The determination of the energy of the 0–0-transition E_{0-0} between S_1 and S_0 state of the investigated *C*-form molecules caused serious problems since no reliable fluorescence emission spectra could be recorded for the investigated *C*-form samples by standard steady-state fluorescence set-ups. However a rough estimate was obtained by the following procedure. From literature data in Ref. [29] E_{0-0} was estimated as the intersection of the normalised absorption $\alpha(\nu)$ and emission spectra $I_{fl}(\nu)/\nu^2$ for the indolylfulgimide in tetrachloroethylene. These emission spectra were recorded using a highly sensitive and optimised fluorescence spectrometer with the capability of Kerr-shutter gated experiments [26]. Here the wavelength of the 0–0-transition was found to be at 631 nm and the peak of the absorption spectrum at 549 nm. For the four investigated samples we assumed, that the same shifts occur for the absorption peaks as for the 0–0-transitions, which leads to the values of E_{0-0} given in Table 1. It should be noted that the values of E_{0-0} are only used for the analysis of the influence of the optical excess energy on the reaction yield. In the fitting procedure

Table 1

Spectroscopic parameters of indolylfulgimide and indolylfulgide (*C*-isomer) at 300 K: maximum of the visible *C*-form absorption band λ_{max}, 0–0 transition E_{0-0}, quantum yield of the ring-opening reaction η excited at 532 nm (at 293 K), and life time of the electronically excited state τ_2.

	λ_{max} (nm)	E_{0-0} (nm)	η (%)	τ_2 (ps)
Indolylfulgimide in toluene	551	640	11.5	2
Indolylfulgimide in acetonitrile	547	640	5.5	3
Indolylfulgide in toluene	583	685	6.3	8
Indolylfulgide in acetonitrile	588	690	0.7	12
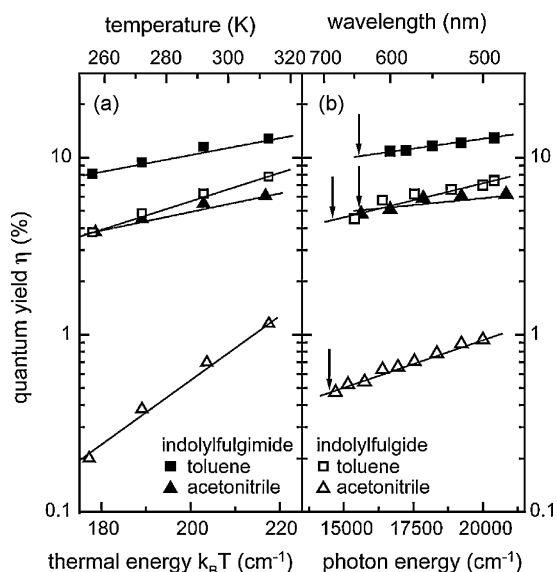
Fig. 3. Quantum yield η of the $C \rightarrow E$ photoreaction for indolylfulgimide and indolyl-fulgide dissolved in toluene and acetonitrile shown as a function of temperature and photon energy. (a) The yield of the $C \rightarrow E$ photoreaction induced by illumination at 532 nm plotted on a logarithmic scale against thermal energy (temperature). (b) Reaction yield at room temperature (300 K) displayed versus photon energy (wavelength) of the excitation light. The lines are a guide to the eye. For all four investigated samples an increase of the yield is observed with increasing temperature and with increasing photon energy. In general the indolylfulgimide shows a higher reaction yield compared to the indolylfulgide and a polar surrounding (acetonitrile) reduces the yield. The arrows denote the estimated energies of the 0–0-transition (see Table 1).

described below (see Eq. (2) and Fig. 6) the slope of the data points essentially determines the results; the exact value of E_{0-0} is of minor importance.

3.2. Quantum efficiencies of the ring-opening reaction

In Fig. 3a the quantum efficiency η of the ring-opening reaction of the investigated samples is plotted versus thermal energy. In all four samples the reaction yield rises with increasing temperature. At a distinct temperature, e.g. at 293 K it is evident that the quantum efficiency η strongly depends on the specific sample.

Values between 11.5% for the indolylfulgimide in toluene and 0.7% for the indolylfulgide in acetonitrile are observed (see Table 1). In the same solvent the efficiency is higher for the indolylfulgimide than for the indolylfulgide. For the same molecule the efficiency is increased in toluene as compared to acetonitrile. In the investigated temperature range (256–313 K) the quantum efficiency of the indolylfulgimide rises by a factor of about 1.6 in both solvents. The indolylfulgide shows a stronger rise of the quantum efficiency with temperature. In toluene the factor is about 2, while a sixfold increase of the ring-opening efficiency is found in acetonitrile. The strong enhancement of the quantum efficiencies with temperature indicates that the ring-opening reaction of both species is thermally activated.

The yield of the ring-opening reaction can also be influenced by the wavelength of the excitation light [42]. In Fig. 3b the results of an experiment performed at constant temperature (300 K) is shown, where the illumination wavelength has been varied over the long-wavelength absorption band of the C-isomers. The quantum efficiency η is plotted versus the wavelength (top scale) and the photon energy ν/c of the excitation light. Here again a distinct variation of quantum efficiency η with excitation frequency ν/c is observed. The rise of quantum efficiency with optical excitation frequency or photon energy can be modelled, for the logarithmic plot used here, by a linear function. The different samples show the same trend as observed in Fig. 3a the indolylfulgide in acetonitrile shows the steepest slope. In the investigated wavelength range the quantum yield rises by a factor of about 1.2 for the indolylfulgimide in both solvents, for the indolylfulgide the increase is about 1.6 for toluene and about 2 for acetonitrile.

Both experiments show that the efficiency of the ring-opening reaction is increased when more excess energy is available for the molecules in the excited electronic state. This energy may be supplied either from the thermal bath and increases with the temperature of the sample or by the optical excitation, where the energy supplied by the photons in excess to the 0–0-transition energy can be used.

3.3. Time-resolved spectroscopy

For the determination of the rates of the ring-opening reaction, time-resolved transient absorption experiments were performed in the UV and visible spectral range for all four samples in PSS-365 at a
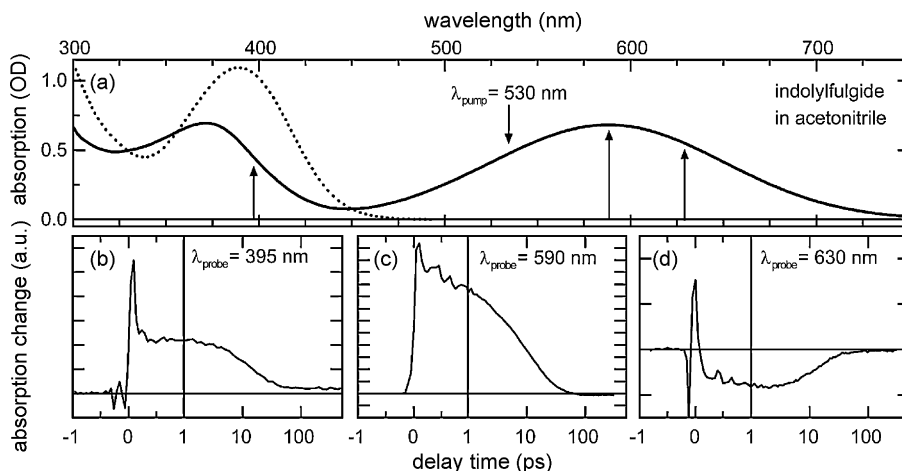
Fig. 4. Steady-state and transient absorption spectra of the indolylfulgide dissolved in acetonitrile at 300 K. (a) Steady-state absorption spectra of the PSS-365 (mainly C-isomer, solid line) and PSS-550 (mainly E-isomer, dotted line) of the indolylfulgide. A broad absorption band in the visible (wavelength > 450 nm) is characteristic for the C-form. The maximum of the E-form absorption is located at about 390 nm. The wavelength of the pump pulse (530 nm) and three different probe wavelength (395 nm, 590 nm, and 630 nm), where the transient data is shown in b–d, are indicated with arrows. (b–d) The transient absorption signal probed at 395 nm (b), 590 nm (c), and 630 nm (d). Please note that the time scale is linear up to 1 ps and logarithmic at longer delay times. All signals show at early times ground state bleaching and excited state absorption and decay with a time constant of about 12 ps to offset values related to product formation.

temperature of 300 K. As an example we present experimental data recorded for the indolylfulgide dissolved in acetonitrile (see Fig. 4). The steady-state absorption spectra of this sample in the PSS-365 (solid line) and after visible illumination to the PSS-550 (dashed line) is shown in Fig. 4a. The open form (*E*-isomer) present in PSS-550 shows the long-wavelength absorption band at 389 nm and negligible absorption at wavelengths longer than 475 nm, where the closed form shows its S_0–S_1 absorption band. The wavelength positions used in the time-resolved experiment are indicated by arrows.

In Fig. 4b–d the transient absorption change of the ring-opening reaction is plotted as a function of time delay between excitation and probe pulse. A linear axis is used for delay times between −1.0 ps and 1.0 ps and a logarithmic one for longer delay times.

Fig. 4b shows the transient absorption changes recorded with an UV probe pulse at 395 nm, where the open *E*-isomers (product of the ring-opening reaction) show an absorption band. Around time zero the signal displays strong modulations from the coherent artifact [50]. Subsequently weaker modulations are found which are superimposed to a strongly increased absorption, which is attributed to excited state absorption (ESA). Finally an exponential decay with a time constant of about 12 ps leads to a weak positive absorption offset observed at longer delay times. This offset is related to the newly formed *E*-isomer.

Fig. 4c and d shows data from the probe wavelengths 590 nm and 630 nm where the closed form absorbs. At both probing wavelengths a coherent artifact around delay time zero is followed by oscillatory features. These modulations indicate that distinct vibrational modes are excited by the pump pulse and will not be discussed in this paper. At the probe wavelength of 590 nm a positive signal is observed at early delay times which can be attributed to ESA. The negative signal observed in the same time domain at the probe wavelength of 630 nm (Fig. 4d) may be due to ground state bleach (GSB) and stimulated emission. Further time-resolved data have been recorded over the whole spectral range from 575 nm to 631 nm. A global fitting procedure of the complete data set shows that the absorption changes can be modelled by two exponentials with time constants $\tau_1 = 0.7$ ps and $\tau_2 = 12$ ps. The weak negative offset at long delay times displays the decrease in *C*-form molecules and so the newly formed *E*-form molecules due to the ring-opening reaction.

Time-resolved experiments have been performed for the other samples, too. All four samples qualitatively show a very similar behaviour with the same spectral features and somewhat different time constants. An example is given in Fig. 5. Here, probing wavelengths were used where the decay of the excited electronic state is clearly visible and where only minor signal contributions due to vibrational cooling are present. In all cases initial wavepacket motion (oscillatory signal component) is observed followed by the decay of the ESA to the long-lived offset absorption signal due to the $C \rightarrow E$ photoreaction. The decay of the excited state population is faster for the indolylfulgimide samples as compared to the indolylfulgide. The polar surrounding (acetonitrile) leads to a slower decay for both compounds. The time constants observed for the different samples are summarised in Table 1.

4. Discussion

4.1. Reaction model

The femtosecond time-resolved measurements on the investigated indolylfulgimide and indolylfulgide (Figs. 4 and 5) are in full agreement with the reaction model described previously for indolylfulgimides [26,28–31]. The dynamics found for the four investigated samples can be assigned as follows: (i) on the time
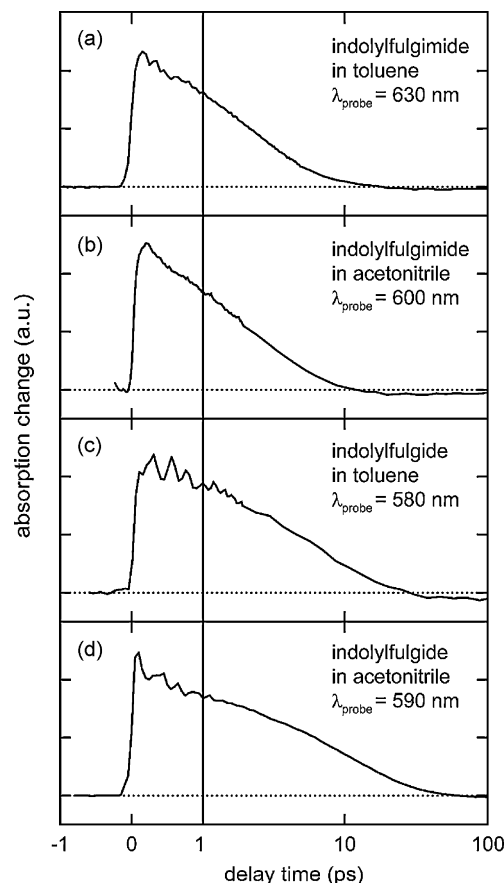
Fig. 5. Comparison of the transient absorption signals of the four investigated samples. All traces exhibit oscillatory components due to wavepacket motion at early times. For later times a small negative absorption offset is found due to disappearance of the *C*-form (reactant) upon ring-opening. (a) Indolylfulgimide in toluene (time constant: 2 ps). (b) Indolylfulgimide in acetonitrile (time constants: 0.6 ps, 3 ps). (c) Indolylfulgide in toluene (time constants: 1.5 ps, 8 ps). (d) Indolylfulgide in acetonitrile (time constants: 0.7 ps, 12 ps).

scale of about 1 ps the system leaves the Franck-Condon state prepared by the optical excitation. Fast wavepacket-like motions in combination with a rearrangement of the surrounding solvent molecules (solvation) lead to a relaxed state on the excited states potential energy surface. (ii) The second relaxation time is essentially connected with the decay of the excited electronic state. This population decay time τ_2 is 2 ps and 3 ps for the indolylfulgimide and 8 ps and 12 ps for the indolylfulgide in non-polar and polar solvent, respectively. With the time constant τ_2 the ring-opening reaction is finished. There are some indications for absorption changes on the 10 ps time scale, related to cooling of hot ground state molecules to the surrounding solvent.

For the *E* and *C* isomer only very weak fluorescence is observed, which may be rationalised by the ultrafast reaction dynamics and the short lifetime of the S_1 state. However, a detection of this fluorescence signals for the investigated isomers was possible by a highly optimised fluorescence spectrometer [26]. Therefore the radiative relaxation pathway can be neglected for the following considerations about the photochemical reaction dynamics.

4.2. Temperature dependence

The temperature dependent steady-state measurements of the reaction yield (illumination at 532 nm) clearly show that the ring-opening reaction is thermally activated. The values of the activation energy $E_a^{(\text{Arrhenius})}$ are determined from the fit of the experimental

data (Fig. 3a) to an Arrhenius behaviour [32]:

$$\eta(T) = A \, \exp\left\{ \frac{-E_a^{(\text{Arrhenius})}}{k_B T} \right\} \tag{1}$$

Activation energies $E_a^{(\text{Arrhenius})}$ are in the range of 451–1625 cm^{-1} (see Table 2). Several arguments indicate that the observed energy barrier is located on the excited state potential energy surface: the ring-opening reaction occurs via the excited electronic state [29,30], no long-lived intermediate state is observed in the electronic ground state and the involved isomers in the ground state are thermally stable [7]. In addition, it was shown for other fulgides that the decay of the excited electronic state is thermally activated [51,52]. At room temperature only low frequency modes have noticeable contribution to the heat capacity. Therefore the increase in quantum yield η for the indolylfulgimide in toluene by a factor of 1.6 during a temperature change of 60 K implies that predominantly low frequency modes are responsible for the increased reaction yield η of the ring-opening.
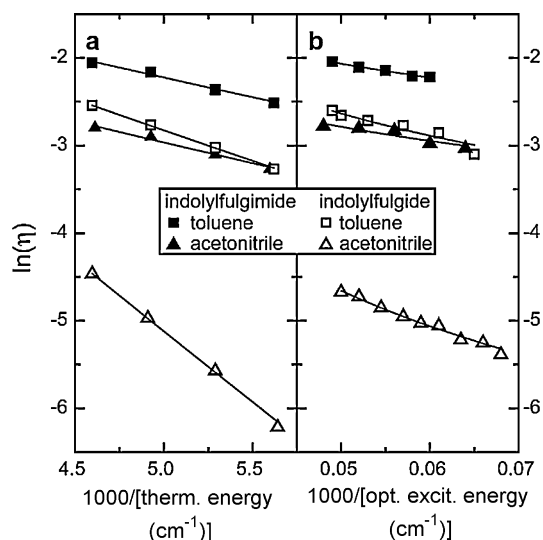
4.3. Optical excess energy

In the following we discuss the question whether equilibrated thermal population of vibrational modes originating from the temperature of the molecules or excess energy supplied initially by the excitation process to specific vibrational modes promotes the reaction yield. This question is directly related to the energy equilibration in the excited electronic state. In the experiment (Fig. 3b) the optical excess energy was varied by tuning the wavelength of the excitation pulse over the long-wavelength absorption band. This tuning changed the excess energy in the range from 0 to up to about 6000 cm^{-1}. The data clearly demonstrate that the quantum yield η of the ring-opening is strongly affected by the optical excess energy, which implies a violation of the Kasha–Vavilov rule [36–38]. The increase of the quantum yield with excess energy indicates that the optical excess energy leads to vibrationally excited (hot) molecules in the excited state which facilitate to overcome the reaction barrier in the excited state. Apparently the excess energy supplied by photoexcitation can only play a significant role in the photoreaction if the modes relevant for the reaction are populated. In other words, intramolecular vibrational redistribution (IVR) should be faster than the lifetime of the excited state, i.e. faster than 2–12 ps, while the relaxation of the vibrational energy to the solvent surroundings should be slower [53–56].

Information on the energy redistribution may be obtained from the quantitative analysis of the dependence of the reaction yield on the optical excess energy. For this purpose we assume that a fraction D of the optical excess energy $(hc/\lambda - E_{0-0})$ is present in the reactive modes during the course of the reaction and can promote the passage over the reaction barrier. Within this model, the quantum yield $\eta(T, \lambda)$ as a function of temperature T and excitation

Fig. 6. Temperature and excitation wavelength dependent quantum efficiency η of the four investigated samples. Lines are the results of the successive fit to the data with the modified Arrhenius equation (Eq. (2)) for each sample. The energy barriers E_a obtained by this fit are listed in Table 2.

wavelength λ follows an Arrhenius-like behaviour:

$$\eta(T, \lambda) = A \, \exp\left\{ \frac{-E_a}{k_B T + D(hc/\lambda - E_{0-0})} \right\} \tag{2}$$

Here E_a is the activation energy, E_{0-0} is the energy of the 0–0-transition for the respective molecule (estimated from absorption data in Fig. 2, given in Table 1) and the parameter D describes the effective conversion of optical excess energy.

Both temperature and wavelength dependent quantum efficiency data were modelled in one successive fitting procedure. In Fig. 6 the experimental data (from Fig. 3) and the resulting fits according to Eq. (2) are shown for the investigated samples. The experimental results for E_a and D_{exp} obtained by the fitting procedure are summarised in Table 2. The values for the activation energy E_a are found to be similar to the results obtained from the classical Arrhenius behaviour $E_a^{(\text{Arrhenius})}$ according to Eq. (1). The values D_{exp} in the range of 0.004 indicate, that only a small fraction of the excess energy has reached the modes promoting the ring-opening reaction.

For the hypothetical case that the optical excess energy is thermalised completely (temperature rise ΔT) between all vibrational modes of the excited electronic state prior to the ring-opening reaction, a value D_{theo} for the parameter D in Eq. (2) may be calculated. For this purpose we assume that the optical excess energy $(hc/\lambda - E_{0-0})$ is completely converted into intramolecular vibrational energy ΔE_{vib} and distributed over the $3N - 6$ vibrational degrees of freedom with normal modes ν_i. The increase ΔT in intramolecular temperature is deduced from:

$$\Delta T = \frac{\Delta E_{vib}}{c_v^{vib}} = \frac{hc/\lambda - E_{0-0}}{c_v^{vib}} \tag{3}$$

The vibrational heat capacity per molecule c_v^{vib} is deduced from the Einstein model [57]:

Table 2

Parameters from the fit of temperature and wavelength dependent quantum yield data. Activation energy $E_a^{(\text{Arrhenius})}$ according to the Arrhenius formula (Eq. (1)), activation energy E_a and conversion parameter D_{exp} according to Eq. (2), upper limit for the conversion parameter D_{theo} (Eq. (5)), and conversion efficiency α of optical excess energy (Eq. (6)).

	$E_a^{(\text{Arrhenius})}$ (cm^{-1})	E_a (cm^{-1})	D_{exp}	D_{theo}	α
Indolylfulgimide in toluene	451	517	0.0044	0.022	0.20
Indolylfulgimide in acetonitrile	475	542	0.0043	0.022	0.19
Indolylfulgide in toluene	701	844	0.0046	0.025	0.18
Indolylfulgide in acetonitrile	1625	1861	0.0033	0.025	0.13

$$c_v^{vib}(T_0) = k_B \sum_{i=1}^{3N-6} \left(\frac{h\nu_i}{k_B T_0} \right)^2 \frac{\exp\{h\nu_i/k_B T_0\}}{(\exp\{h\nu_i/k_B T_0\} - 1)^2} \tag{4}$$

For this situation of complete intramolecular thermalisation the conversion parameter D_{theo} is calculated:

$$k_B(T + \Delta T) = k_B T + k_B \frac{\Delta E_{vib}}{c_v^{vib}} = k_B T + \frac{k_B(hc/\lambda - E_{0-0})}{c_v^{vib}}$$
$$= k_B T + D_{theo}(hc/\lambda - E_{0-0}) \qquad (5)$$
$$D_{theo} = \frac{k_B}{c_v^{vib}}$$

For the investigated indolylfulgimide 132 (indolylfulgide 120) vibrational normal modes ν_i have to be considered, which are determined from ground state DFT calculations (with a scaling factor of 0.92) [30]. This calculation leads at $T_0 = 300\,K$ to values of the conversion efficiency $D_{theo} = 0.022$ for the indolylfulgimide and $D_{theo} = 0.025$ for the indolylfulgide (see Table 2).

The experimental conversion parameters D_{exp} extracted from the fit are smaller than D_{theo} and thus indicate that the relevant vibrations carry only a small excess population. To describe the degree of energy conversion a relative efficiency α may be introduced according to:

$$\alpha = \frac{D_{exp}}{D_{theo}} \qquad (6)$$

For the case of the investigated indolylfulgimide (and indolylfulgide, respectively) this relative conversion efficiency α is in the range between 13% and 20% (see Table 2).

The small value of the conversion efficiency shows convincingly, that (i) the relevant vibrational modes are not directly populated in the optical excitation process, (ii) intramolecular vibrational relaxation is not finished during the short period (few picoseconds) of the excited state lifetime and/or (iii) intermolecular vibrational energy redistribution to the solvent molecules prevents the complete build-up of vibrational excess population. Nevertheless, the observed increase in reaction efficiency with optical excess energy demonstrates that IVR operates on the few picosecond time scale. However IVR is not completed before internal conversion and intermolecular vibrational energy redistribution terminate the ring-opening reaction.

The possibilities to tune the photoreaction yields and dynamics as described in this work are relevant for several applications (RESOLFT or photoswitchable surfaces) of those molecular switches as indicated in the introduction. The overall very low fluorescence yield ensures that disturbing background emission from the switching units is not recorded. The excitation wavelength dependence of the photoreaction can be used to control the efficiency of the switching process, e.g. in non-destructive readout concepts for molecular memory applications.

5. Conclusion

In conclusion, the investigated indolylfulgimides and indolylfulgides show ring-opening reactions on the few picosecond time scale and quantum efficiencies which strongly depend not only on temperature but also on optical excess energy. For the investigated molecules equilibration of vibrational energy is not completed before the ring-opening reaction and intermolecular energy redistribution occurs. The experiments demonstrate that the optical excess energy contributes with 13–20% to the promotion of the ring-opening reaction. This causes the violation of the Kasha–Vavilov rule [36–38] for the investigated indolylfulgimide and indolylfulgide.

Acknowledgements

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