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Reversibility is an important issue that prevents ultrafast studies of chemical reactions in solid state due to product accumulation. Here we present an approach that makes use of spectrally-selected, post-excitation, ultrashort laser pulses to minimise photoproduct build-up, i.e. recover before destroy. We demonstrate that this method enabled us to probe the ultrafast dynamics of the ring opening reaction of spironaphthooxazine thin crystals by means of transient absorption spectroscopy. By extension, this approach should be amenable to other photochromic systems and use with structural probes.

While chemistry happens predominantly in solution, chemical reactions occurring in the solid state can be exploited to fabricate dynamic devices relevant for today’s needs.1 Solid-state reactions can be more selective and more efficient than in solution2 and offer more controllable parameters making solids the preferred medium for some industrial applications. On a more fundamental level, solid-state media presents a unique platform for mechanistic studies of chemical reactions using spectroscopic and diffraction techniques which constitutes an important first step towards their control. Ultrafast spectroscopies3,4 employing pump-probe methods have been at the forefront of the techniques that may not always be trivial or practical. One approach to tackle the reversibility issue is to employ a scheme that uses a dual echelon grating design12 to split the probe pulse into many delayed replicas thereby enabling the dynamics to be covered in a single pump laser shot.13 A limitation of this scheme is that the probe cannot be wavelength-resolved and therefore acquiring data over a broad spectral range requires several experiments to be performed. Despite this limitation, such single-shot experiments should be the choice for completely irreversible samples, i.e. those that are irreparably damaged after a single pump shot. For systems with limited reversibility, multi-shot experiments are possible. But, care must be taken to ensure that no permanent build-up of photoproducts is occurring that may interfere with the transient signal of interest. Jean-Ruel et al.14,15 exploited the bi-directional switching in photochromic systems to present a different approach that made possible ultrafast studies of photochromism in diarylethene crystals. The authors used a

Synchronised photoreversion of spirooxazine ring opening in thin crystals to uncover ultrafast dynamics†

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633 nm continuous wave (CW) helium–neon (HeNe) laser to convert the photoproducts back to their initial condition, returning the system to its original state.

Here we extend this approach and use the ring opening reaction of a spirooxazine (SO) to show that reversibility can be improved by implementation of a non-collinear optical parametric amplifier (NOPA). The role of the NOPA is to revert the system back to its original state (photoreversion). Compared to CW lasers, the use of a NOPA offers several advantages such as broad bandwidths, higher flux, ultrashort pulse durations and the possibility of precisely synchronising the time delay with respect to the pump and probe pulses. The protocols that will be mentioned have been explicitly developed to resolve the structural dynamics of the ring opening reaction using femtosecond electron diffraction and will be reported separately. Information obtained from these experiments would be indispensable in understanding the reaction mechanism in the solid state and would also offer new insights for the design and fabrication of new materials.

Spirooxazines (SOS) and spiropyrans (SPs) have received much attention due to their ability to reversibly switch conformations, and hence their properties, upon absorption of a photon of appropriate wavelength. Such photochromic compounds have potential applications as photoswitches, memory devices and logic gates. A common use of SOS is in ophthalmic lenses for protection against ultraviolet (UV) radiation from the sun. SOs consist of an indoline ring joined to an orthogonal oxazine ring by a sp³ hybridised spiro carbon. A well accepted mechanism of SO photochromism is that upon UV irradiation, the bond between the spiro carbon and the oxygen in the oxazine ring is broken to produce a ring-opened isomer. Isomerisation involves rotation of the oxazine unit by almost 90 degrees relative to its position in the closed-ring form. The resulting planar structure is known as merocyanine (MC). Due to an extended π system and hence electron delocalisation, MC has characteristic absorption in the visible region of the spectrum. MC returns to the SO state either thermally or photochemically (Fig. 1).

Photochemistry of spironaphthooxazine (SNO) has been investigated experimentally in different media and also theoretically. From solution phase studies, it is known that the photochromic reaction of SNO occurs via the excited singlet state manifold leading to a very rapid process in which the so-called intermediate X, having the orthogonal parent geometry, is formed and isomerisation to the trans-merocyanine is completed in less than 10 ps. While the photochromic reaction always takes place in solution and amorphous films, the reaction may not be possible in crystalline form due to spatial confinement and the large structural change associated with the reaction. To explore this, Suzuki and coworkers carried out detailed studies of the photochromic reaction of SNO in microcrystalline state using ultrafast diffuse reflectance spectroscopy. They performed the experiments exciting the sample with 390 nm light and changing the sample position after every 50 pump shots to avoid accumulating artefactual signals from damaged sample areas.

Under low excitation conditions (fluence <1 mJ cm⁻²), they reported rapid C–O bond breaking, but isomerisation leading to the MC form was not observed. Instead, the ring-opened transient returned to the original spiro-form on a nanosecond time scale. However, at higher fluences, they noted the formation of the MC photoproduct. They later proposed a cooperative model to explain this observation in which a high concentration of the ring-opened products was attained by intense femtosecond laser excitation and the interaction between the open form with the excited state consequently created local free volumes within the crystalline environment making it possible for the molecules to undergo isomerisation to MC.

We carried out transient absorption spectroscopy experiments on crystals of SNO with a thickness of 500 nm, in transmission mode, using a home-built spectrometer (see the ESI file for preparation methods and details of the experimental setup). A fraction of the fundamental output of a Ti:Sapphire laser (800 nm, 200 fJ, 40 fs) was frequency-tripled (266 nm, 1.4 mJ cm⁻²) and used as the pump while a single stable filament of white light supercontinuum (380–900 nm) generated by focussing 2 μJ of the 800 nm light in water was used as the probe. The optical path length of the probe with respect to the pump pulse was varied using an optical delay line. For all of the experiments discussed here, the repetition rate of the pump was fixed to 31.25 Hz and 250 Hz for the probe. The pump repetition frequency was chosen to ensure no damage to the sample occurred (thermal or other) while maintaining relatively fast data collection. The spectra obtained with each probe pulse were recorded by a low-noise charge-coupled device (CCD). We performed two separate experiments in order to compare the approach that we introduce with the more conventional one. The following acquisition scheme was adapted for the experiments. For each time delay, 100 pump-probe cycles were acquired. For each pump pulse, 8 spectra were recorded and labelled according to their distance to the

Fig. 1 a) Photochromic reaction of spironaphthooxazine (SNO). b) Steady-state spectra of a 0.5 mM SNO solution in ethanol and merocyanine (MC) produced under UV excitation of the SNO solution.
immediately preceding pump pulse, as shown in Fig. 2. For instance, pulse number 6 corresponded to the spectrum measured 24 ms after the pump. All the pulses with the same label were averaged and the transient absorption spectra were calculated as:

\[
\Delta A(\lambda,t) = A_{ON}(\lambda,t) - A_{OFF}(\lambda,t) = -\log \left[ \frac{I_0(\lambda,t)}{I_7(\lambda,t)} \right]
\]

where \( \lambda \) is the probe wavelength, \( t \) is the time delay of the probe with respect to the pump (\(-1 \text{ ps} \leq t \leq 7 \text{ ps}\)), \( A_{ON} \) is the absorption spectrum of the sample with excitation and \( A_{OFF} \), without excitation, \( I_0(\lambda,t) \) is the background-subtracted transmitted intensity of pulse 0 measured \( t \) ps after the pump and \( I_7(\lambda,t) \) corresponds to that of pulse 7, measured 28 ms + \( t \) ps after the pump. As stated before, identical conditions must be ensured for every pump-probe cycle, i.e. at pulse 7 the sample must be in the same state as before starting the experiment.

To check this, we measured the change in the absorption spectrum between pulse 7 and the pristine sample as a function of the number of pump laser shots used:

\[
\Delta A(\lambda,s) = -\log \left[ \frac{I_s(\lambda,s)}{I_{ref}(\lambda)} \right]
\]

where \( s \) is the number of pump laser shots that hit the sample and \( I_{ref}(\lambda) \) is the background-subtracted transmitted intensity of the sample before UV irradiation.

Plots corresponding to \( \Delta A(\lambda,s) \) for the experiment using only the pump and probe beams are shown in Fig. 3a. It is obvious from these plots that the absorption in the whole probe region grows with the number of excitation shots hitting the sample. The absorption profile after 4000 shots resembles that of the MC absorption in solution (Fig. 1) with the peak slightly red shifted, typical of species in the solid state. This suggests that MC is being formed in the crystal and its concentration increases reaching a steady-state after about 8000 pump pulses. The number of shots leading to a steady-state concentration of species was heavily dependent on the experimental conditions, with the rate of product formation increasing with higher fluences or repetition rates. Indeed, with repetition rates of the pump laser as low as 2.5 Hz, the build-up of MC was still observed albeit with much slower rates. The build-up manifested itself as a bleach band with the maximum at about 600 nm in the transient absorption spectra (see the ESI† file) obtained under these conditions. We interpreted the bleach as the excitation of the trapped MC caused by the 266 nm pump. After the experiment, colouration of the probed region was detectable by eye (see the ESI† file).

It is evident that the accumulation of the photoproducts was preventing us from performing experiments under reversible conditions and a new strategy was needed. Therefore, we carried out a three-beam experiment where we used the output of a NOPA with the wavelength tuned to the maximum of the photoproduct absorption (see Fig. 3a), operating at 1 kHz and delayed by \( \sim 10 \text{ ns} \) with respect to the probe pulse as our third beam to switch the MC produced back to...
the spiro form and thus halt the build-up of the photoproduc-
tent. For this purpose, 32 NOPA pulses (\(\lambda = 600 \pm 25 \text{ nm}, 2.8 \text{ mJ cm}^{-2}\)) hit the sample after each UV excitation pulse as shown in Fig. 2. The results of \(\Delta A(\lambda, s)\) for this experiment are presented in Fig. 3b showing clearly that no significant amount of MC remained even after \(10^5\) UV laser shots. This result indicates that the sample was returning to the original state before each pump-probe sequence. It is also noted that NOPA excitation did not have any adverse effect on SNO by the virtue that the sample is transparent in the region of the NOPA spectrum and the peak intensity used (\(<10 \text{ GW cm}^{-2}\)) was below the multiphoton damage threshold.

Thereafter, we performed transient absorption experiments with the NOPA beam and compared them with the solution-phase photochromic reaction, measured without using the NOPA but by flowing the sample in order to renew it after every pump-probe cycle. For the case of crystals, transient spectra were measured for three different regions on the sample and then averaged. The results are shown in Fig. 4a and b as 2D maps. Spectral traces corresponding to selected time delays are also plotted (Fig. 4c and d). Clearly, MC was formed in the solution, as evidenced by the intense growing absorption band at 550 nm, but the signature for its production was absent from the crystal data for the delay range covered. Instead, a strong decaying absorption feature centered at about 500 nm was observed. These results are similar to the ones from Suzuki et al. with 390 nm pump,\(^{18}\) indicating that excitation with 266 nm light also produces a ring-opened transient species. The ability to overcome the sample damage by exciting with broadband 600 nm light also supports their model for the damage mechanism in SO crystals, whereby a large local free volume in crystal – necessary for spatial reorganisation during isomerisation to planar MC – is created due to the build-up of intermediate species which, once removed via photoreversion, significantly minimises sample degradation.

In summary, we improved the reversibility of SNO photo-
switching in the crystalline state by using a NOPA to revert the photoproducts back to the initial state. Due to the ultra-
short pulse duration of the NOPA and the possibility to syn-
chronise it to the pump pulse, this process can be driven faster than the deformation of the crystal which requires an accumulated propagation of the stress to strain, that takes considerably longer than nanoseconds to manifest itself. This relatively simple approach is expected to be quite generic for photochromic systems and solves the reversibility problem and the need for using one shot data collection methods to follow reaction dynamics in the solid state. It is equally nota-
table that this method also permits the prospect of probing the dynamics of the back reactions thereby developing a complete picture of the bi-directional processes. With this approach, it is possible to get complete information from well-
defined areas of the sample, circumventing the need for translation. Moreover, if the ensemble dynamics from different spots is required, many cycles can be run at each spot increasing the signal-to-noise ratio dramatically, compared to single-shot experiments. This progress in reducing the photo-
degradation in SO also opens up the possibility of applying ultrafast diffraction techniques that would enable direct probing of the transient intermediate structures and aid with the understanding of the degradation mechanism. We hope that this approach will enable a wider class of studies involving solid-state photoreversible systems on ultrafast time scales.

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