

Exploring Higher-Lying Electronic States of a Molecular Switch by Coherent Triggered-Exchange 2D Electronic Spectroscopy

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Abstract. We use pump-repump-probe transient absorption spectroscopy to investigate the role of higher-lying electronic states in the photochemistry of a molecular switch. Moreover, replacing the pump pulse by a pulse-shaper-generated phase-stable double pulse, triggered-exchange two-dimensional (TE2D) electronic spectroscopy is established in the visible regime.

1 Introduction

Many photochromic compounds and their ultrafast dynamics have been studied by means of transient absorption spectroscopy. However, the role of higher-lying excited states has not yet been explored for many of these systems. By exploiting pump-repump-probe transient absorption spectroscopy we can resolve the kinetics happening after excitation to higher-lying electronic states. In the context of coherent two-dimensional (2D) spectroscopy, an additional laser pulse has led to the development of triggered-exchange 2D (TE2D) vibrational spectroscopy [1,2]. Here we introduce TE2D electronic spectroscopy in order to reveal the correlation between the spectral response of photoproducts and their chemical precursors.

2 Results and Discussion

Exemplarily, we investigate 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6,8-dinitro BIPS), a molecular switch present in two conformations (named TTT and TTC) of the merocyanine form (MC) differing in a cis/trans configuration. The photochemical behavior after S_1 excitation is illustrated in Figure 1a. After excitation in the visible, both isomers can undergo a ring closure reaction to the spiropyran form (SP) [3]. Relaxation to the MC ground state of each isomer is also possible, either via an ultrafast radiationless pathway or by fluorescence.

The applied pulse sequence is indicated in Figure 1b. For pump-repump-probe spectra, a single pump pulse (560 nm) excites the molecule to S_1 . The repump pulse (440 nm), delayed by t_{PR} relative to the pump pulse, is resonant with excited-state absorption, and the white-light probe pulse at waiting time T enables the observation of products. For TE2D spectroscopy, the first excitation occurs with a phase-stable pulse pair (separated by the adjustable coherence time τ) generated with a pulse shaper. This allows the recording of absorptive 2D spectra in the presence of the repump pulse.

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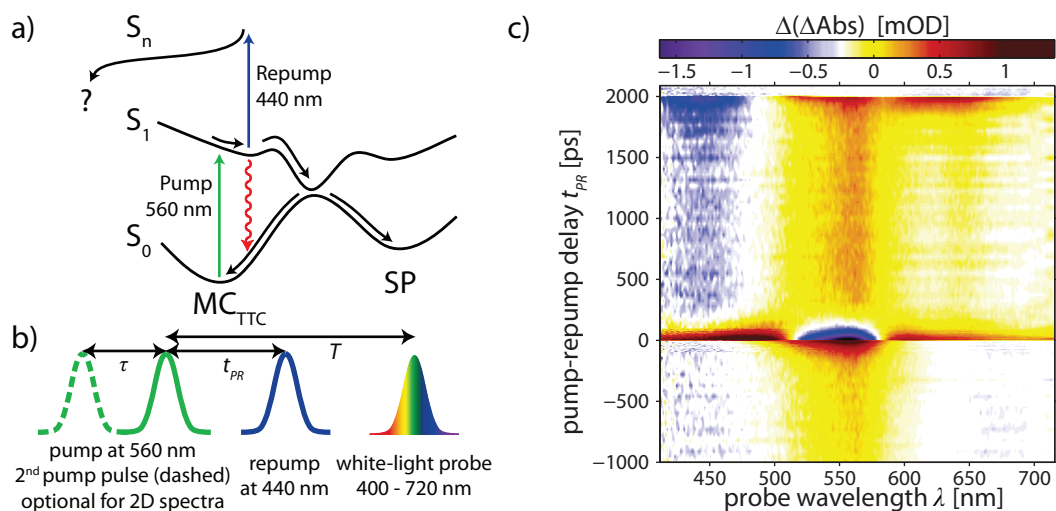


Fig. 1. a) Sketch of the reaction scheme for the TTC isomer of 6,8-dinitro BIPS from the open merocyanine (MC) to the closed spiropyran (SP) form. b) Employed pulse sequence. An optional phase-stable pulse pair can be used to record two-dimensional electronic spectra. c) Change of absorbance induced by the combination of pump and repump pulses as a function of pump-repump delay t_{PR} at a fixed pump-probe delay of $T = 2000$ ps.

2.1 Pump-Repump-Probe Transients

We start with a discussion of pump-repump-probe transient absorption measurements. There, we detect the change of absorption due to the combination of pump and repump pulses. For that purpose both pulses are mechanically chopped such that all four possible combinations of pump and/or repump pulse present or absent together with the white-light probe are achieved [4]. The pump-repump signal is then extracted by subtracting the signals with either only pump or repump from the signal with both of them present. Figure 1c shows the extracted pump-repump signal as a function of probe wavelength and pump-repump delay t_{PR} at a fixed probe delay of $T = 2000$ ps. Thus, only long-living photoproducts are monitored (except for $t_{PR} \approx T$). The most prominent feature in Figure 1c is the strong decrease of absorbance for small t_{PR} in the region of ground-state absorption (~ 560 nm), indicating a reduced concentration of MC. Cuts along the t_{PR} - and λ -axis for selected wavelengths and pump-repump delays are shown in Figs. 2a and b, respectively. Two bands with positive absorption rise around 460 nm and 600 nm, indicating the formation of a new reaction product. All three signatures decay with the S_1 lifetime of the main isomer (TTC, 80 ps, black dashed line in Figure 2a) indicating that the observed pathway is accessible from S_1 only.

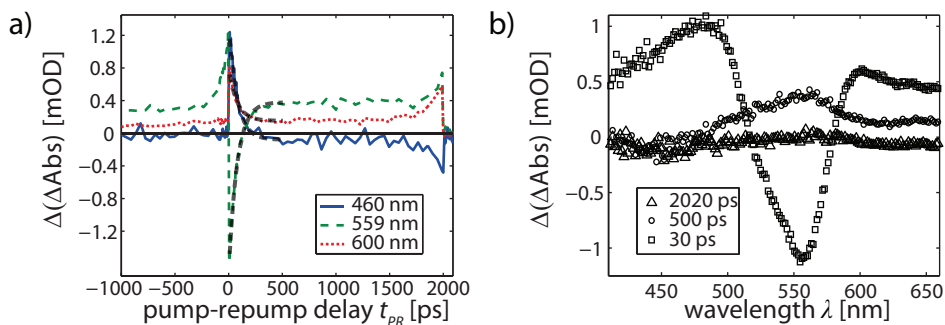


Fig. 2. a) Cuts along the t_{PR} -axis for three selected wavelengths (460 nm: solid, 559 nm: dashed, 600 nm: dotted) together with the result of a global monoexponential fitting routine (black dashed line). b) Difference spectra for $t_{PR} = 30$ ps (squares), 500 ps (circles), and 2020 ps (triangles).

2.2 Triggered-Exchange 2D Spectroscopy

To gain more insight and unambiguously identify the precursor isomer we implemented triggered-exchange 2D electronic spectroscopy by expanding the pulse sequence with a fourth pulse (Figure 1b). We use four-step phase-cycling [5,6] in combination with the above mentioned chopper arrangement (pump pair and repump are blocked either both, one at a time, or none) to extract the 2D data for those molecules interacting with all four pulses. Exemplary time-domain data for $\lambda = 554$ nm are depicted in Figure 3a. The resulting absorptive TE2D spectrum is shown in Figure 3b for $t_{PR} = 500$ fs and $T = 2000$ ps, where positive (negative) contributions resulting from increased (decreased) absorption are marked by solid (dashed) contour lines. It can be considered as the change in the 2D spectrum due to the additional interaction with the repump pulse. From this the S_1 state of TTC is identified as the precursor state of the so far unknown absorptive species absorbing at 400-500 THz (600-750 nm) and 600-750 THz (400-500 nm) as all corresponding features are located on the same vertical dashed line corresponding to TTC excitation. Possible candidates for this species might be triplet states of MC or SP or a product that has been ionized by the repump pulse.

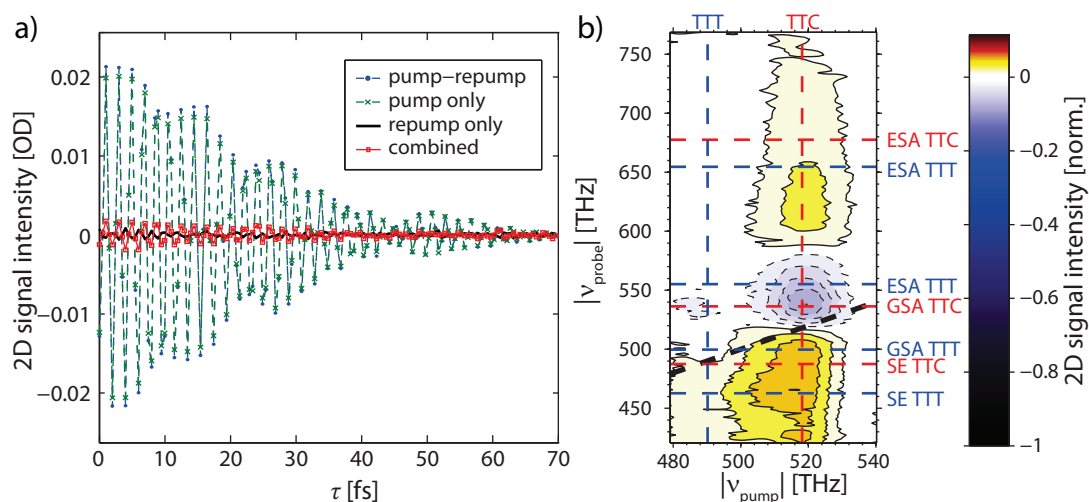


Fig. 3. a) Time domain TE2D data for $\lambda = 554$ nm. b) TE2D spectrum for $t_{PR} = 500$ fs and $T = 2000$ ps.

3 Conclusion

We extended spectrally resolved pump-repump-probe spectroscopy to establish triggered-exchange 2D spectroscopy via pulse shaping for the visible region. This offers a highly sensitive measurement tool for molecular excited states and their photochemical pathways.

References

1. J. Bredenbeck, J. Helbing, R. Behrendt, C. Renner, L. Moroder, J. Wachtveitl, P. Hamm, *J. Phys. Chem. B* **107**, 8654–8660 (2003)
2. C. R. Baiz, M. J. Nee, R. McCanne, K. J. Kubarych, *Opt. Lett.* **33**, 2533–2535 (2008)
3. J. Buback, P. Nuernberger, M. Kullmann, F. Langhojer, R. Schmidt, F. Würthner, T. Brixner, *J. Phys. Chem. A* **115**, 3924–3935 (2011)
4. J. Buback, M. Kullmann, F. Langhojer, P. Nuernberger, R. Schmidt, F. Würthner, T. Brixner, *J. Am. Chem. Soc.* **132**, 16510–16519 (2010)
5. M. Kullmann, S. Ruetzel, J. Buback, P. Nuernberger, T. Brixner, *J. Am. Chem. Soc.* **133**, 13074–13080 (2011)
6. S. Shim, M.T. Zanni, *Phys. Chem. Chem. Phys.* **11**, 748–761 (2009)