5.1 Allgemeine Angaben zum beendeten Teilprojekt B1

5.1.1 Titel:

Femtosekunden-Stimulierte Raman-Spektroskopie (FSRS) von Photoreaktionen in kondensierter Phase mit konischer Durchschneidung

Femtosecond Stimulated Raman Spectroscopy (FSRS) of photoreactions in the condensed phase with conical intersection

5.1.2 Fachgebiete und Arbeitsrichtung:

Ultrakurzzeitspektroskopie, Photochemie

5.1.3 Leiter:

Prof. Nikolaus P. Ernsting, PhD

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5.2 Bericht über die Entwicklung des Teilprojekts

5.2.1 Bericht

UP I: **Photoisomerisation in solution**

was studied for molecules where the minimum-energy path can be calculated quantum-chemically. Of the three target systems in the application, two were studied as planned: *2,2′-Pyridocyanin* (PC, **1**) and *Benzo-Indenylidene-Dihydropyridin* (BIDP, **2**). Instead of the third system, a spiropyran, *Stilbene* was examined. A setup for Femtosecond Stimulated Raman Scattering (FSRS) was built and transient Raman spectra were obtained for PC. Entire fluorescence bands can be routinely time gated (80 fs in the visible, 200 fs in the UV).

Stilbene

We addressed a textbook question: what is the lifetime of the perpendicular excited state **p*** at the global minimum of the S_1 state? Since this work has been published [KDI10, SDG10], only the main observations are presented here.

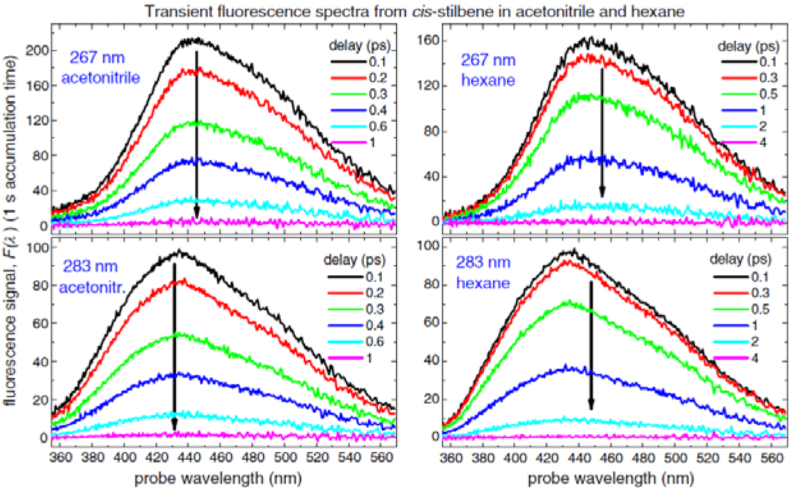


Fig. 1 (*left*) shows transient fluorescence spectra from *cis-* or *c*-stilbene in solution, recorded by a Kerr-shutter after excitation at 283 and 267 nm. (0.24 ps time resolution).

The fluorescence decay shows no dependence on the excitation wavelength. No spectral shift or distortion of the fluorescence band is observed during the decay

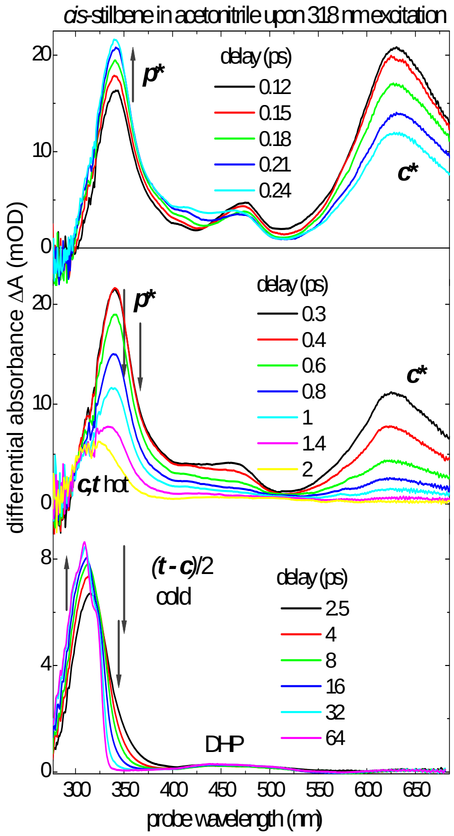
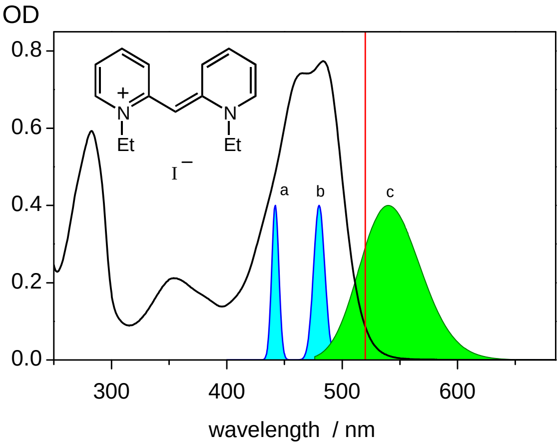


Fig. 2 (*left*) shows transient absorption spectra of *c*-stilbene in acetonitrile upon 318 nm excitation. A decay at 630 nm (c^*) and a rise at 340 nm (p^*) correspond to the $c^*\rightarrow p^*$ transition (*top*). Further decay reflects internal conversion $p^*\rightarrow p\rightarrow(c/2, t/2)$ resulting in hot products (*middle*, yellow spectrum at 2 ps). Ground-state vibrational cooling is evidenced by narrowing and blue shift of the difference spectrum (t–c)/2, which is the same (but inverted) spectrum of *t*-stilbene at 300 ps (*bottom*). The rise conforms with the decay of the *c* fluorescence of the previous figure. From the fall of the p^* absorption, the p^* lifetime is derived to be τ_{p*}=0.4 ps in acetonitrile and 0.3 ps in hexane. In summary, the optical transitions and properties of the important p^* state have been charted.

2,2'-Pyridocyanin (PC)



has not been synthesized since 1952 and is almost unknown. We prepared and studied 2,2´-Pyridocyanin because it can be considered a "Parent Cyanine"; a corresponding publication is in preparation. Briefly, the photoisomerisation reaction path was characterized by fs transient absorption (N. Ernsting in Berlin, G. Cerullo in Milan) , transient stimulated Raman (Ernsting), and computational chemistry (F. Santoro in Pisa). **Fig. 3** (*top right*) shows the stationary absorption spectrum of 2,2'-Pyridoyyanin in methanol and the excitation bands used (*a* for survey transient absorption, *b* "actinic excitation" for photoinduced Raman spectroscopy, and *c* for 10 fs excitation).

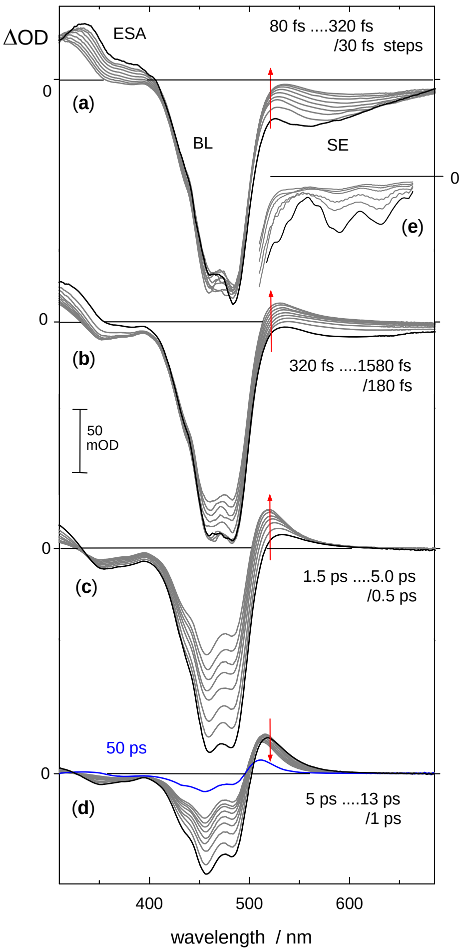


Fig. 4a-d (*left*) shows transient absorption spectra of PC in methanol after excitation at 442 nm. The time resolution was 86 fs in this case. BL – bleached absorption $S_1 \leftarrow S_0$, SE – stimulated emission $S_1 \rightarrow S_0$, ESA – excited-state absorption $S_n \leftarrow S_1$. *(e):* evolution upon 10 fs red-edge excitation (G. Cerullo, Milan). Shown are spectra at 0.1, 0.2, 0.3, 0.5, 1.2 ps. Arrows indicate the spectral evolution, and also the wavelength of the Raman pump in transient Raman experiments (see below).

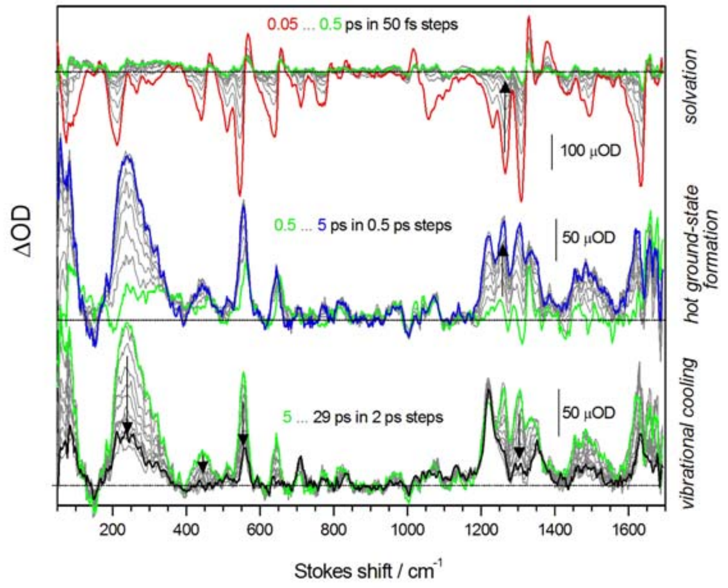
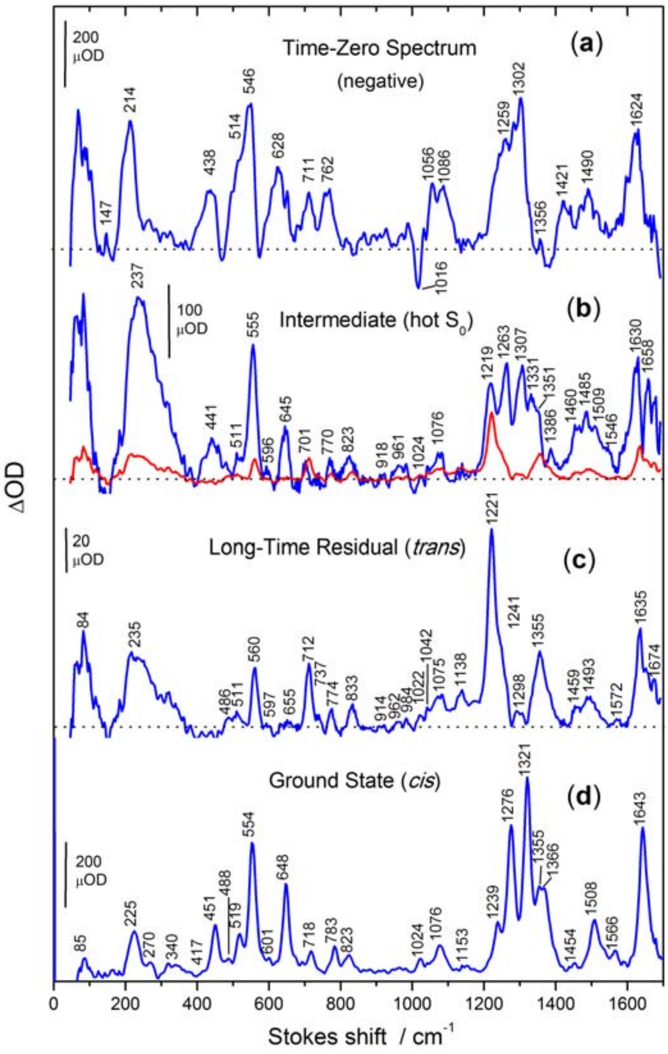


Fig. 5 *(upper left)* shows the time evolution of the induced transient Raman spectrum (*i.e.* after bleach has been removed) of PC in methanol, after actinic excitation at 482 nm.

Fig. 6 (lower *left*) shows Species-Associated-Spectra from a global analysis. The spectrum at t=0 (*a*) disappears with 90 fs time constant. An intermediate spectrum (*b*), attributed to a hot S_0 state, rises with 2.2 ps. It decays with 11 ps to (*c*) which can be assigned to the *trans*-conformer, having a marker band at 1221 cm^{-1}. For comparison, (*d*) shows the ground-state stimulated Raman spectrum of the *cis* form. A contribution of (*c*) in (*b*) is shown by a red line. The spectra of the intermediate and long-term species could be assigned quantitatively. The earliest transient Raman spectra should correspond to the broad plateau region which was mentioned earlier. Its quantitative understanding requires further experiments with a red-shifted Raman pump (at 600-700 nm) which are presently in progress.



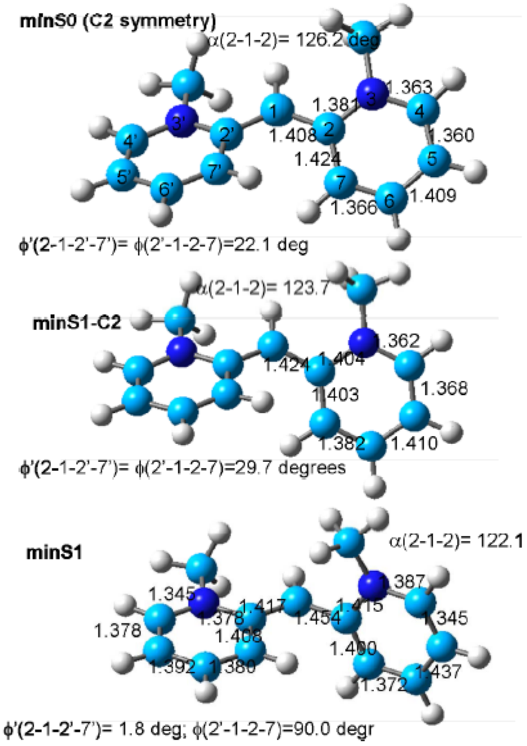


Fig. 7 (*left*) shows results from quantum-chemical calculations (TD-DFT). The S_1 Franck-Condon state first relaxes into a broad plateau on the S_1 potential-energy surface which has C_2 molecular symmetry (minS1-C2). Then, by asymmetrisation, a global S_1 minimum is reached which has intramolecular charge-transfer character. From here internal conversion to the electronic ground state proceeds.

Butyl-Indenylidene-Dihydro-Pyridine (BIDP)

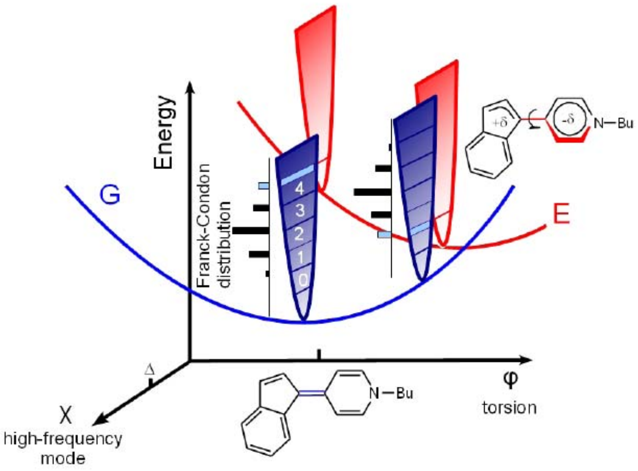


Fig. 8 (*left*) shows as inset the structure of 1-Butyl-4-(1H-inden-1-ylidene)-1,4-dihydropyridine (BIDP). Potential energy surfaces of ground (G, blue) and first-excited states (E, red) are represented along two coordinates: inter-ring double bond stretch Δ and torsion ϕ. Quantum-chemical calculations predict a planar minimum for the ground electronic state and a surface crossing for the perpendicular conformation. Because both modes are displaced, the Franck-Condon distributions associated to each of them span several vibrational levels. Ultrafast population transfer from the photoexcited level E to the ground state G demands strong coupling $V = V_{el} \times f_{ij}$, where V_{el} is the electronic coupling and f_{ij} is the Franck-Condon factor. Since the energy gap between E and G is large, ≈ 20000 cm^{-1}, only high-frequency modes can show Franck-

Condon distributions with non- negligible overlap integrals between displaced isoenergetic vibronic levels of states G and E (shown in cyan). Low-frequency modes come close this condition for large displacements, which in turn give rise to ample distributions with very small overlap integrals for any pair of neighbour vibronic levels, i.e. to small effective coupling. Therefore, in general and when the energy gap is large, high-frequency modes are responsible for coupling. Vibrational energy is redistributed from excited high-frequency vibrational levels to the molecular bath.

We explored the possibility that relaxation along a low-frequency coordinate modulates coupling strength by switching between different vibrational levels. The change in the relevant Franck-Condon factor alters the effective coupling.

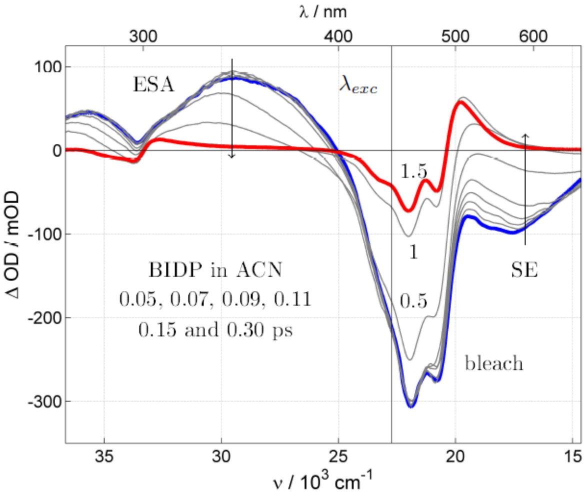


Fig. 9 *(left)* shows transient absorption spectra of BIDP in acetonitrile, with the components bleach, excited-state absorption, and stimulated emission. Such evolutions were recorded for a variety of solvents, thus altering the relative stabilisation of the higher excited state(s).

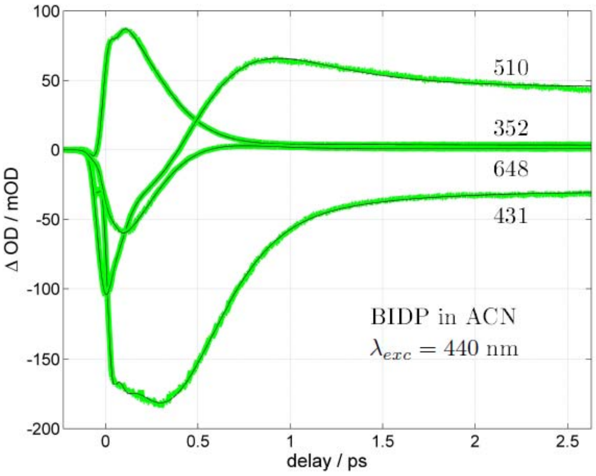


Fig. 10 (*right*) shows time traces at selected observation wavelengths (green lines) together with model fits. We conclude that the transient population funnels to the ground state after 0.5 ps. Population dynamics is non-exponential, depends slightly on solvent polarity and stronger on excess pump energy. Red-edge excitation gives rise to a signal decay which can be described by an exponential and a damped low-frequency cosine oscillation, as expected for direct coupling between the Franck-Condon and the ground state. The oscillation frequency (the Rabi frequency) mirrors the coupling strength, 20 cm^{-1}. On the other hand, excitation with excess of vibrational energy is better modeled with

two exponentials (0.15 and 0.5 ps) and a damped oscillation with significant sine contribution. Quantum dynamics is simulated by solving the master equation for the density matrix in a coupled degenerate two-level system with different preparation schemes. Analytical solutions for constant and time-dependent coupling are obtained. Our analysis suggests that coupling sets in with a characteristic time constant of 150-200 fs and remains on for half a picosecond. This enables coherent population transfer to the ground state, which takes place along the way towards the conical inter-section. Remarkably, the oscillation shows negative chirp, suggesting that the coupling decreases in the neighbourhood of the crossing point. A corresponding paper is in preparation.

UP II: **Lineshapes expected with optical $\chi^{(3)}$ and $\chi^{(5)}$ spectroscopy**.

In [DE08] the molecular vibrational coherence from impulsive stimulated Raman (SR) scattering, as observed by broadband transient absorption spectroscopy, was treated within the third-order perturbation formalism. Shaped femtosecond optical pulses are used for the pump and supercontinuum probe fields. Dephasing is assumed to be homogeneous in the Bloch approximation. A key step requires three-fold time integration over reponse functions and electric fields. For well-separated pulses the triple integral can be solved analytically, resulting in lineshape functions. These allow to describe the SR signal through absorption/emission/dispersion profiles which are associated with the inherent contributions. A clear physical interpretation of the amplitude and phase of oscillatory signal is thereby obtained, and a direct connection with the vibronic structure of the molecular system is provided.

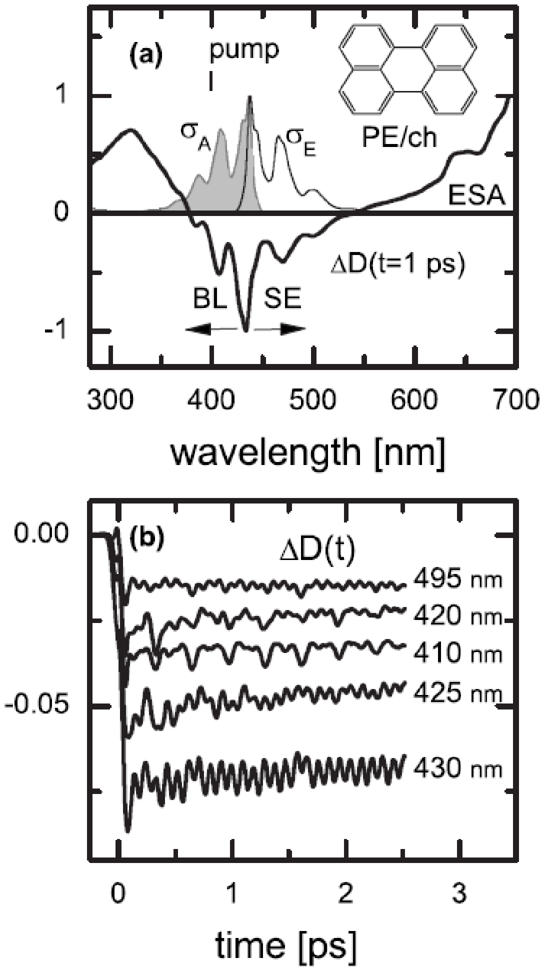


Fig. 11 *(right)* Example used in [DE08]. Top: Perylene in cyclohexane, measured 1 ps after excitation at 400 nm, bottom: kinetic traces at selected wavelengths.

In [DLK08] we examined the vibronic structure which is observed while pump and probe pulses overlap, superimposed on bands which broaden and shift on several time scales. Third-order perturbation theory was again used to simulate and understand such spectra under experimental conditions, i.e., with chirped pump pulses and 40–80 fs pump/probe correlation time. The electronic system is coupled to a solvent bath whose fluctuations enter through a lineshape function g(t). This approach has two advantages compared to the Bloch model: (i) In the general case when g(t) is modelled realistically it provides a distinction of coherent and sequential contributions to early transient spectra. The time-zero stimulated emission band can be extracted, giving access to the relaxation function for the emission frequency. (ii) For limiting forms of g(t) corresponding to the Bloch approximation and to inhomogeneous broadening the threefold time integrals underlying the theory reduce to a single integral. In such cases the lineshape formulation of transient absorption spectra can be used for data fitting. As an example, transient absorption spectra of Coumarin 153 in alcoholic solvents were studied.

UP III: Cooperations

In [RSS09] we examine the red flavylium cation of anthocyanins, which forms ground-state charge-transfer complexes with several naturally occurring electron donor copigments. Excitation of such a complex results in ultrafast (240 fs) internal conversion to the ground state by way of a low-lying charge transfer state. Thus, both uncomplexed anthocyanins, whose excited state decays by fast (5-20 ps) excited state proton transfer, and anthocyanin:copigment complexes have highly efficient mechanisms for deactivation that are consistent with the proposed protective role of anthocyanins against excess solar radiation in vegetative tissues of plants.

In [DKS08] the TICT compound 4-cyano-N-phenyl pyrrol is compared to a rigidized derivative. A broad study of fluorescence, lifetimes, quantum yields, and solvent dependence was carried out by K. Zacahriasse and coworker. We contributed insight into the S_1 relaxation directly after optical excitation, by monitoring excited-state absorption and stimulated emission spectra.

In [LKK08] the photoreduction of cytochrome c (Cyt c) was reinvestigated using femtosecond-to-nanosecond transient absorption and stationary spectroscopy. Femtosecond spectra of oxidized Cyt c, recorded in the probe range 270–1000 nm, demonstrate similar evolution upon UV or blue excitation: an ultrafast 0.3 ps internal conversion followed by a 4 ps vibrational cooling. Late transient spectra after 20 ps, from the cold ground-state chromophore, reveal a small but measurable signal from reduced Cyt c. The yield for $Fe^{3+} \rightarrow Fe^{2+}$ photoreduction allows a guess of the barrier for thermal ground-state electron transfer (ET). In summary, our results point to ultrafast internal conversion of oxidized Cyt c upon UV or visible excitation, followed by Fe-porphyrin reduction due to thermal ground-state ET as the prevailing mechanism.

5.2.2 Liste der aus dem Teilprojekt seit der letzten Antragstellung entstandenen Publikationen

[KDI10]	*Evidence for the phantom state in photoinduced cis-trans isomerization of stilbene*, S. A. Kovalenko, A.L. Dobryakov, I. Ioffe, N.P. Ernsting, Chemical Physics Letters **493**, 255 (2010)
[SDG10]	*Time-resolved fluorescence spectra of cis-stilbene in hexane and acetonitrile*, M. Sajadi, A. L. Dobryakov, E. Garbin, N. P. Ernsting, and S. A. Kovalenko, Chem. Phys. Lett., **489**, 44-47 (2010)
[RSS09]	*Ultrafast Internal Conversion in a Model Anthocyanin-Polyphenol Complex: Implications for the Biological Role of Anthocyanins in Vegetative Tissues of Plant*, R.F Rodrigues , P.F da Silva , K. Shimizu , A.A Freitas , S.A. Kovalenko , N.P.Ernsting , F.H Quina, A. Macanita, Chemistry European Journal, **15**, 1397 (2009).
[DKS08]	*Intramolecular Charge Transfer with the Planarized 4-Cyanofluorazene and Its Flexible Counterpart 4-Cyano-N-phenylpyrrole. Picosecond Fluorescence Decays and Femtosecond Excited-State Absorption*, S. I. Druzhinin, S. A. Kovalenko, T. A. Senyushkina, A. Demeter, R. Machinek, M. Noltemeyer, K. A. Zachariasse, J. Phys. Chem. A **112**, 8238 (2008)
[LKK08]	*Transient and Stationary Spectroscopy of Cytochrome c:Ultrafast Internal Conversion Controls Photoreduction*, D. Löwenich, K. Kleinermanns, V. Karunakaran, S. A. Kovalenko, J. Photochem. Photobiol **84**, 193 (2008)
[DE08]	*Lineshapes for Resonant Impulsive Stimulated Raman Scattering with Chirped Pump and Supercontinuum Probe Pulses*, A. L. Dobryakov and N. P. Ernsting, J. Chem. Phys. **129**, 184504 (2008)
[DLK08]	*Femtosecond Transient Absorption with Chirped Pump and Supercontinuum Probe: Perturbative Calculation of Transient Spectra with General Lineshape Functions, and Simplifications* A. Dobryakov, L. P. Lustres, S.A. Kovalenko, N. P. Ernsting, Chem. Physics **347**, 127 (2008)

5.3 Bewilligte Mittel für die laufende Förderperiode

Das Teilprojekt wurde im Sonderforschungsbereich von 01/1998 bis 06/2010 gefördert.

Haushalts-jahr	Personalmittel	Sachmittel	Investitionsmittel	Gesamt
2007/2	46.0	3.1	0	49.1
2008	92.0	5.9	35.6	133.5
2009	92.0	6.1	0	98.1
2010/1	49.0	3.2	0	52.2
Summe	279.0	18.3	35.6	332.9

(Alle Angaben in Tausend EUR)

5.3.1 Personal im Teilprojekt

	Name, akad. Grad, Dienststellung	engeres Fach des Mitarbeiters	Institut der Hochschule oder der außeruniv. Einrichtung	im SFB tätig von (Monat / Jahr) bis (Monat / Jahr)	Entgelt-gruppe
Grundausstattung					
wissenschaftl. Personal (einschl. Hilfskräfte)	1. Ernsting, Nikolaus, Prof. Dr.	Physikalische Chemie	HU Berlin	07/1998 – 06/2010	
	2. Kovalenko, Sergey, Dr.	Physikalische Chemie	HU Berlin	07/1998 – 06/2010	
nichtwissen-schaftl. Personal	3. Steingräber, Heiderose		HU Berlin	07/1998 – 06/2010	
Ergänzungsausstattung					
wissenschaftl. Personal (einschl. Hilfskräfte)	4. Seynushkin, Tamara Doktorandin	Physikalische Chemie	HU Berlin	01/2007 – 06/2007	BAT IIa1/2O
	5. Pérez Lustres, Luis, Dr.	Physikalische Chemie	HU Berlin	01/2007 – 06/2007	BAT IIa1/1O
	6. Dobryakov, Alexander, Dr.	Physikalische Chemie	HU Berlin	07/2007 – 06/2010	BAT IIa1/1O
	7. Sajadi-Hezaveh, Mohsen, Doktorand	Physikalische Chemie	HU Berlin	09/2007 – 06/2010	BAT IIa1/2O