

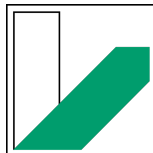
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PPD

Transient Absorption Spectroscopy

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Group 1



Information

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1 Introduction

Transient absorption spectroscopy is a powerful technique used in various scientific fields to investigate the dynamic behavior of molecules and materials. By probing the absorption properties of a sample in an excited state, transient absorption spectroscopy gives insight into details of photoinduced phenomena, such as energy transfer, charge carrier dynamics, and molecular structural changes. It enables researchers to explore fundamental processes and devise strategies for improving a wide range of technologies.

In this lab practice, we explore this method with the material ZnTPP (zinc tetraphenylporphyrin), ZnOEP (zinc octaethylporphyrin) and P3HT (poly(3-hexylthiophene)). Goal of this experiment is to get a deeper insight into the decay rate and lifetime of triplet states and to investigate the possible influences in those properties. Additionally, UV-VIS spectroscopy will be performed to explain the phenomenas observed in the transient absorption.

2 Theoretical background

2.1 Singlet and Triplet Excited States

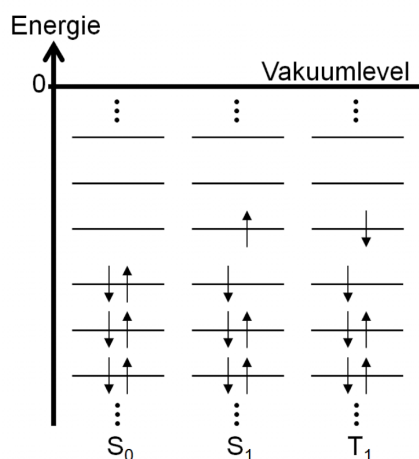


Figure 2.1: Orbital diagram of the dominant orbital occupations of the singlet states S_0 , S_1 and the triplet state T_1 .³

In this section we want to discuss the relevant aspects of electronic processes in organic molecules. The energy levels of these systems can be described by molecular orbitals. Molecular orbitals can be obtained through the usage of the **LCAO** method, which combines multiple atomic orbitals to a molecular orbital. A concrete occupation of these orbitals is called state, which has two specific states called **HOMO** (Highest Occupied Molecular Orbital) and **LOMO** (Lowest unOccupied Molecular Orbital). In addition to that distinction is made between singlet and triplet state with the following properties

- Triplet State T_i : Total spin (sum of all electron spins) is ± 1 ,
- Singlet State S_i : Total spin is 0.

Figure 2.1 shows a simplified representation (only the largest contribution) of electronic states in molecules.

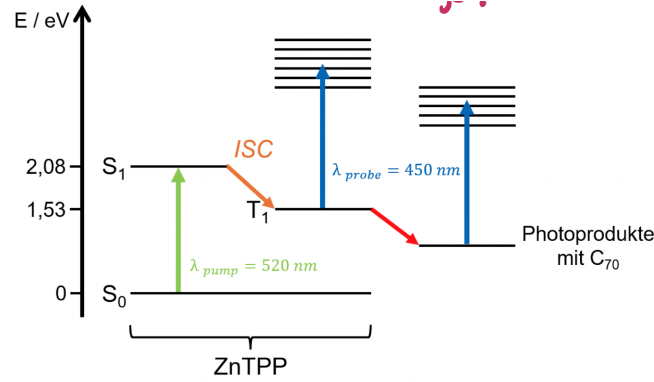


Figure 2.2: Jablonski scheme of the system of this experiment (ZnTPP and ZnTPP with fullerene C₇₀).³

To excite a system into from the ground state to the singlet state the system has to absorb a photon with the energy corresponding to the transition, which leads to an absorption pattern that reflects the structure of the energy levels of an atom. After absorption the electron relaxes back into the ground state (*Kasha's Rule*). The transition can be radiative or non-radiative, but it is also possible to perform a transfer to a triplet state if the energy gap is small enough and one spin is flipped, which results in a sufficiently large spin-orbit coupling. The transition between singlet to triplet states is called Inter System Crossing (ISC). The Jablonski scheme of this transition process for the relevant molecule of this experiment (ZnTPP and ZnTPP with fullerene C₇₀) is shown in Figure 2.2.

The radiative transition of an electron from the singlet state to the ground state is called **Fluorescence** and from a triplet state to the ground state **Phosphorescence**. Both mentioned transitions are examples for *radiative decays* with the emission of a photon. In case of ISC it is a *non-radiative decay*, since the energy of the excited singlet state gets dissipated due to ISC. The lifetime τ of the excited state will be given by the expression

$$\tau = \frac{1}{k_r + k_{nr}}, \quad (2.1)$$

with the k_r and k_{nr} as the decay rates of the radiative and non-radiative decay. The determination is achieved by a pump-probe experiment, which will be discussed in Chapter 4.2.³ Since the process of ISC is non-radiative one can not directly measure ISC, but if the energy level of the singlet state is known and the decay rate of the triplet state will be measured, it is possible to indirectly measure the energy loss of ISC.

2.2 Kinetics of Triplet State Decay

The kinetics of a triplet state decay can be described by the following differential equation

$$-\frac{d}{dt}C_T = k_1C_T(t) + k_2(C_T(t))^2 + k_3C_T(t)C_G(t) , \quad (2.2)$$

with C_T as concentration of the triplet state and C_G as concentration of the ground state. The relaxation in the ground state is described by the reaction rate k_1 and various bimolecular deactivation processes by the rates k_2 and k_3 . Assume that the concentration of the triplet state $C_T(t)$ is smaller than the concentration of the ground state $C_G(t)$, because of the pump laser which excites the electrons into the singlet state and the process of intersystem crossing. Additionally assume that $C_G(t) = C_G = \text{const}$, since the pump there is a finite number of singlet states. All these assumptions lead to the expression

$$\Rightarrow -\frac{d}{dt}C_T = (k_1 + k_3C_G)C_T(t) = k_0C_T(t) . \quad (2.3)$$

Solving the differential equation for a given initial condition for the concentration of the triplet state $C_T(0)$ results in

$$\Rightarrow \boxed{C_T = C_T(0)e^{-k_0t}} .^3 \quad (2.4)$$

2.3 Transient Absorption Spectroscopy

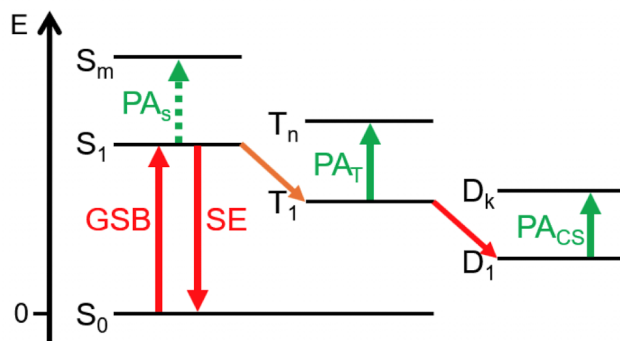


Figure 2.3: Ground state bleaching (GSB), stimulated emission (SE) and photoinduced absorption (PA) of different states.³

In the transient absorption spectroscopy gets the excited singlet state occupied by the stimulation by an excitation pulse (pump laser). With a fast ISC, the molecules in the triplet state can be further excited by a second excitation pulse (probe laser), which is weaker than the pulse of the pump laser. The absorption of this second pulse is proportional to the occupation of the triplet state. By varying the time interval between the two pulses (time delay), a time-resolved transient absorption spectrum can be obtained. This delayed pulse interacts with the matter in its excited state. The interaction of the delayed pulse with the material leads to three observable effects in the spectrum:

- **Ground State bleaching** (GSB),
- **transient absorption** (TA),
- **stimulated emission** (SE).

Ground state bleaching occurs because of the excitation process due to the lowered ground-state density, which can absorb less light. Transient absorption spectroscopy gives insight into energy transfer and charge transfer dynamics of the material systems. To make the mentioned effects visible, the intensity of the pump laser has to be sufficiently large.² In transient absorption spectroscopy occurs signals which are negative and positive. Negative signals are connected to the absorption of the ground state, whereas positive signals are correlated to the absorption of the excited state.¹

2.4 Influence of Polarization on Transient Absorption Spectroscopy

As laser light is often polarized, polarization effects can occur during the experiment. The effect happens because the absorption is sensitive to the position of the transition dipole moment to the electric field. This leads to a photon selection in the absorption. In the case of the experiment this effect is not important as probing happens on the scale of nanometers, when the vibration of the molecule is in the range of picoseconds.

3 Methods and Material

3.1 Experimental Setup

3.2 Effect of the used Lens in the Beam Path

3.3 Extend Shelf Life of the Solutions

3.4 Concentration of a Polymer

4 Evaluation

4.1 UV-VIS Spectroscopy

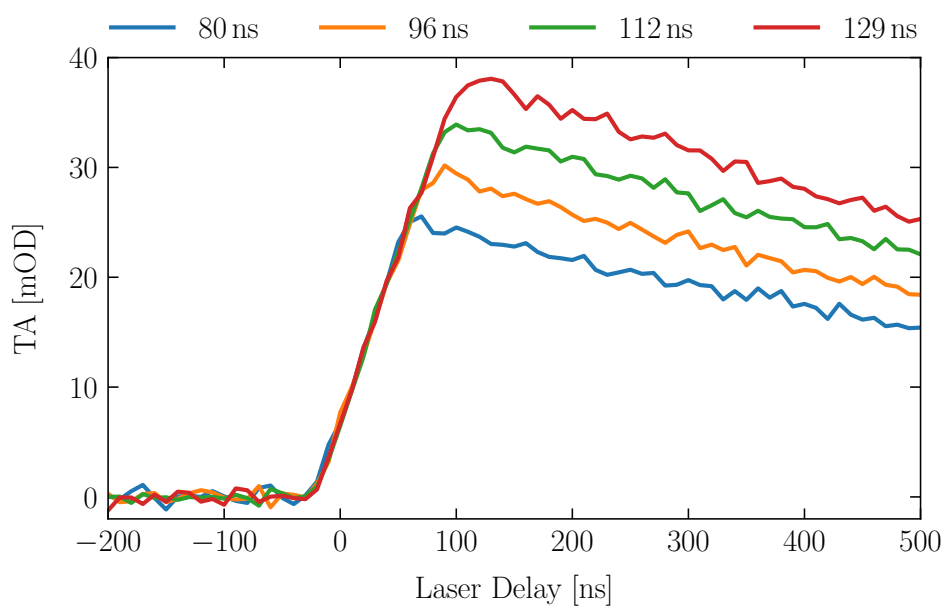


Figure 4.1: Transient absorption signal for different pump laser widths using ZnTPP in BN 0.8 mM.

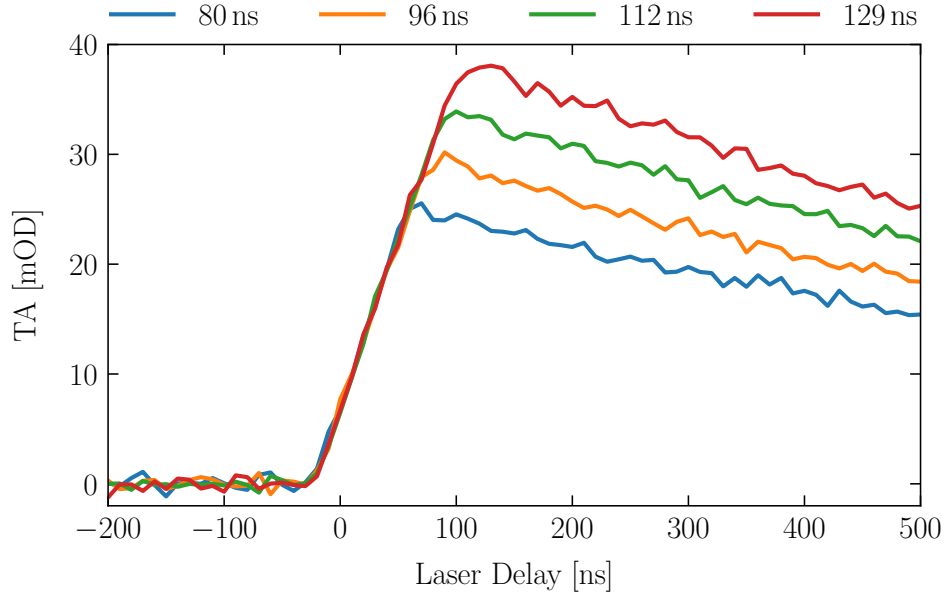


Figure 4.2: Transient absorption signal for different pump laser widths using ZnTPP in BN 0.8 mM.

4.2 Transient Absorption Spectroscopy

In this experiment different treatments were investigated in terms of lifetime τ of the solution itself. At the beginning we expect from theory that the decay of the concentration of the triplet state $C_T(t)$ is exponential and given by the relation

$$C_T(t) = C_T(0)e^{-k_0 t} + C_T^{\text{Off}} , \quad (4.1)$$

with the initial concentration C_T and the decay rate k_0 . Also, an offset concentration C_T^{Off} was added to encounter any offset caused by e.g. measuring methods. Since the transient absorption (TA) is proportional to $C_T(t)$, we can fit the same exponential decay for the transient absorption as well. The full set of fitted treatments and results of the exponential fit can be found in Tab. 4.1. The lifetime τ was calculated with the relation $\tau = 1/k$. The exponential fits itself are displayed in Fig. 4.5.

No	Treatment	k_0/ms^{-1}	τ/ns
1	ZnTPP in BN 0.8 mM	1089 ± 4	919 ± 3
2	ZnTPP in BN 0.6 mM	1077 ± 5	929 ± 4
3	ZnTPP in BN 0.4 mM	1069 ± 5	936 ± 4
4	ZnTPP in BN 0.2 mM	1057 ± 8	946 ± 7
8	ZnTPP in Tol 0.8 mM	1891 ± 3	529 ± 1
12	ZnOEP in BN 0.8 mM	2681 ± 5	373 ± 1

No	Treatment	$k_{\text{app}}/\text{ms}^{-1}$	τ/ns
5	ZnTPP:C70 in BN 1:0.1	1254 ± 5	798 ± 3
6	ZnTPP:C70 in BN 1:0.2	1385 ± 6	722 ± 3
7	ZnTPP:C70 in BN 1:0.3	1436 ± 6	697 ± 3

Table 4.1: Calculated decay rates k_0 and k_{app} and lifetimes τ ($\tau = 1/k$) for different types of treatments.

4.2.1 Influence of Concentration

First, we want to investigate the influence of concentration on the decay rate k_0 , i.e., the lifetime τ . For that we take a closer look at sample number 1 – 4 [Tab. 4.1]. In Fig. 4.5 (a) it is clear that higher maxima correspond with to higher concentration of ZnTPP, which aligns with our expectation that higher concentration leads to a greater amount of absorption. The lifetime τ on the other hand increases with the reduction of concentration, which follows the expectation from the theory. The kinetics of the decay of the triplet state are described by the equation

$$-\frac{d}{dt}C_T = k_1 C_T(t) + k_2 (C_T(t))^2 + k_3 C_T(t) C_G(t) , \quad (4.2)$$

where $C_G(t)$ is the concentration of the ground state and k_1, k_2, k_3 are decay rates. In further calculation the assumption $C_T(t) \ll C_G(t)$ will be made, which leads to the

discussed exponential decay [Eq. (4.1), Chapter 2.2]. But, this assumption gets less valid for an increasing population of triplet states, to the point at which one has to take the terms with $C_T(t)$ into account. This results in higher decay rates k_0 and shorter lifetimes τ of the triplet states. The same behaviour can be identified to the cases of higher concentration of ZnTPP in BN and explains the kinetics of the decay process.

4.2.2 Influence of Fullerene C_{70}

In the next paragraph the impact of the fullerene C_{70} on the lifetime τ will be addressed. We consider for this analysis sample 1 (base solution) and 5 – 7 [Tab. 4.1]. In Fig. 4.5 (b) one can see that the decreases the higher the concentration of the fullerene C_q gets, introducing a quenching process. This result was expected, because in theory the decay rate k_0 gets expanded as

$$k_0 \longrightarrow k_{app} = k_0 + k_q C_q , \quad (4.3)$$

with the new decay rate k_{app} and the reaction rate of quenching process k_q . The expansion of the decay rate k_0 leads to higher decay rates k_{app} ($k_q > 0$), which leads to shorter lifetimes τ . To determine the quenching reaction rate k_q , we take the calculated decay rates k_{app} and fit them against the concentration C_q [Eq. 4.3]. For the decay rate k_0 the decay rate of the base solution (sample 1) will be used. From the slope of the linear fit one can calculate the quenching reaction rate k_q . The linear fit can be seen in Fig. 4.3.

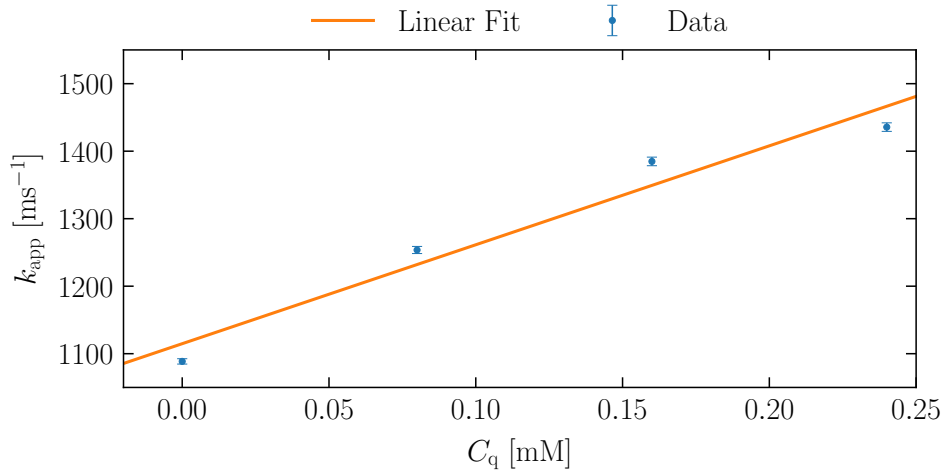


Figure 4.3: Linear fit of decay rate k_{app} for different fullerene concentration C_q .

The calculation yields

$$k_q = (1.5 \pm 0.2) \times 10^9 \text{ sM}^{-1} ,$$

which does not align with the result of Ito et al.⁴, who determined $k_q = 4.7 \times 10^9 \text{ sM}^{-1}$, but is in the right order of magnitude.

4.2.3 Influence of the Solvent

In this paragraph the influence of Solvent on the transient absorption (TA) signal and the lifetime τ will be discussed.

First, we look at the variation of ZnTPP with BN and Tol for the concentration 0.8 mM (sample 1 and 8 [Tab. 4.1]). In Fig. 4.5 (c) we can observe the nearly same maximum value for both solutions but different lifetimes τ , which are calculated in Tab. 4.1. This aligns with the UV-VIS spectroscopy from Chapter 4.1, because the polarity of BN makes it easier to induce more charges into the delocalized π -electron system. So, it is possible to observe a redshift and an increase of lifetime τ .

Next, we vary the zinc complexes of the solution from ZnTPP to ZnOEP, but we keep BN as second solvent of the solution with concentration 0.8 mM (sample 1 and 12 [Tab. 4.1]). The transient absorption signal can be found in Fig. 4.5 (d) with the corresponding decay rates k and lifetimes τ in Tab. 4.1. It is clearly visible that the maximum of the TA signal is for both zinc complexes the same but the lifetime τ for is much shorter for ZnOEP. The value of the TA maximum corresponds with the maximum concentration of the triplet state and is therefore correlated to the absorption of the pump laser light. Looking at the UV-VIS of ZnTPP and ZnOEP [Fig. 4.2] one can conclude that the absorbance for ZnTPP and ZnOEP does not differ from each other, which explains the same maximum value for the TA signal. The longer lifetime τ of ZnTPP can also be linked to the redshift compared to ZnOEP. Due to the four additional phenyl groups in ZnTPP, the conjugated electron system is bigger than in ZnOEP. So, a lower energy is needed to excite the electrons of ZnTPP.

Finally, we want to discuss the variation of the solution itself. For that, we take a look at sample 1 (ZnTPP in BN 0.8 mM) and 9 (P3HT in Tol 1.5 mM). In Fig. 4.4 it is visible that P3HT has a smaller maximum compared to ZnTPP. From the previous lifetime analysis one can assume trivial that the lifetime of P3HT is shorter compared to the lifetime of ZnTPP. Comparing the UV-VIS of P3HT from Ref. 5 to the evaluation from ZnTPP from Chapter 4.1 the observed redshift is also present for P3HT as well as the smaller absorbance compared to ZnTPP. The underlying process relates to the P3HT aggregates, which can consist of crystalline regions, amorphous domains or a combination of both. Amorphous chain sequences lead to structural defects, grain boundaries and coiled-like chain conformations that can reduce intra-chain order. Therefore, UV-VIS absorption signatures are broadened and blue shifted towards higher energies⁵, which results in the observed (TA) signal.

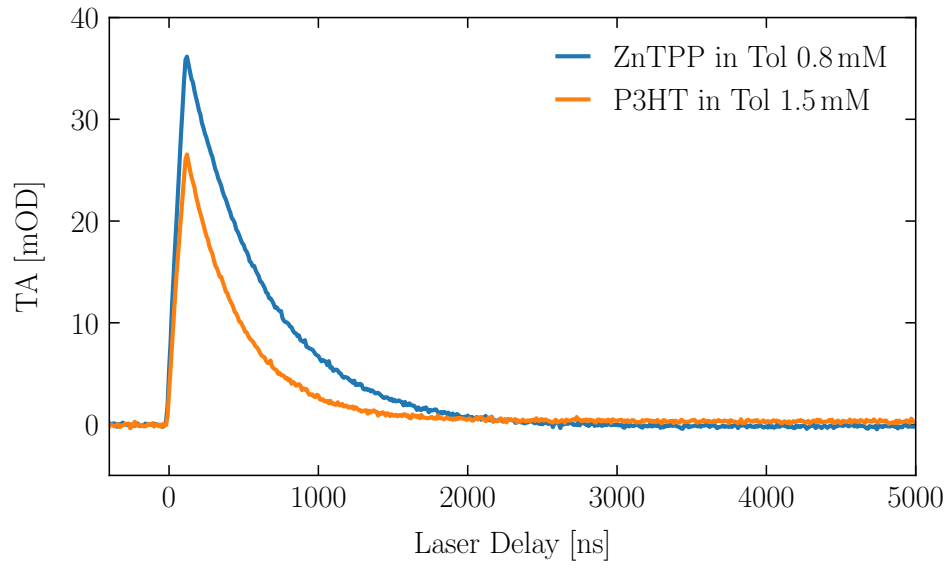


Figure 4.4: Transient absorption signal using different treatments with ZnTPP and P3HT

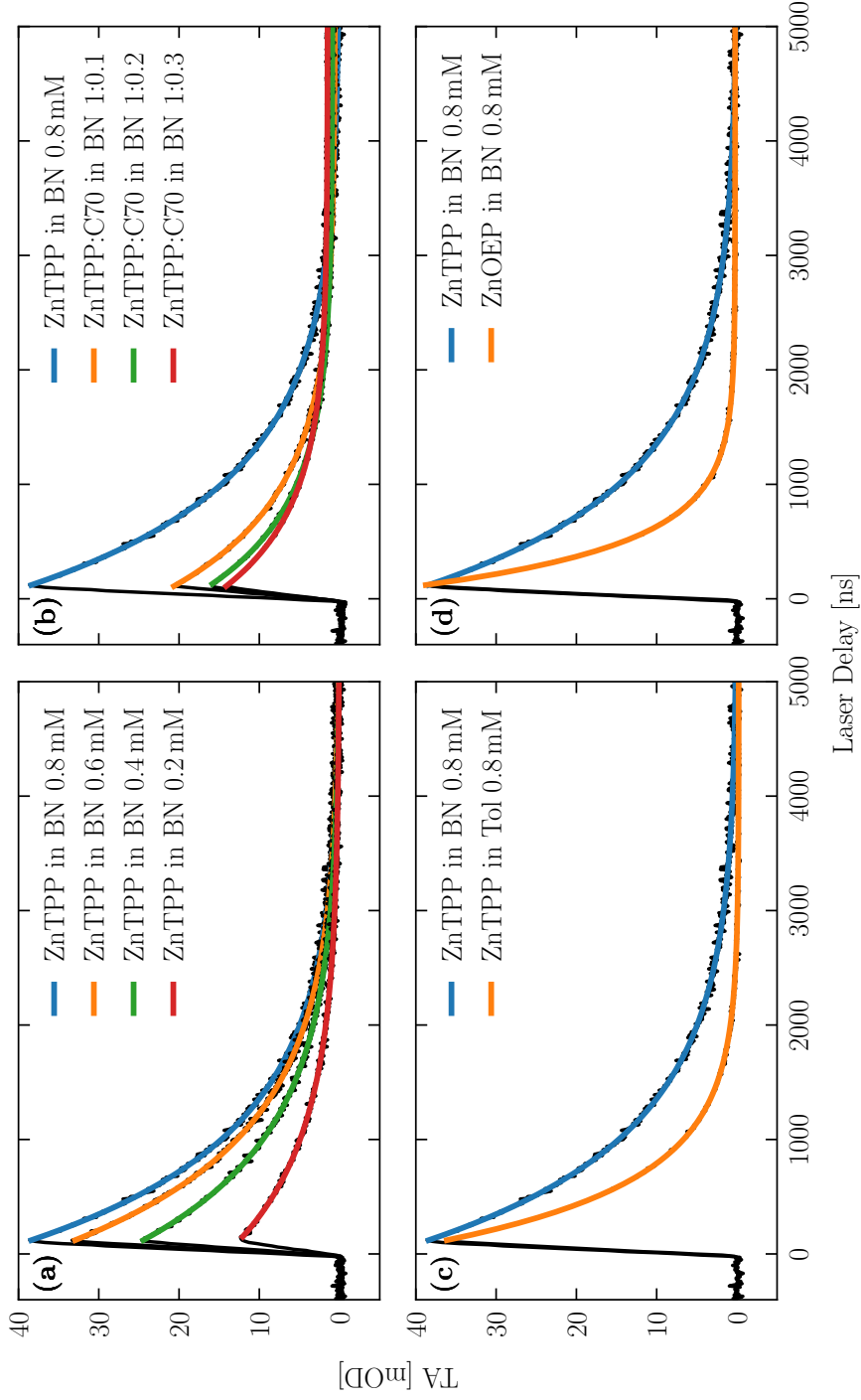


Figure 4.5: Comparison between data of the transient absorption of different treatments with the exponential fits colored for each treatment: (a) Different concentration of ZnTPP in BN, (b) Different dilutions of C₇₀ in ZnTPP in BN 0.8 mM, (c) Different Solvents (BN, Tol) with ZnTPP and a concentration of 0.8 mM and (d) Different Solvents (ZnTPP, ZnOEP) with BN and a concentration of 0.8 mM.

4.2.4 Influence of the Pump Laser Width

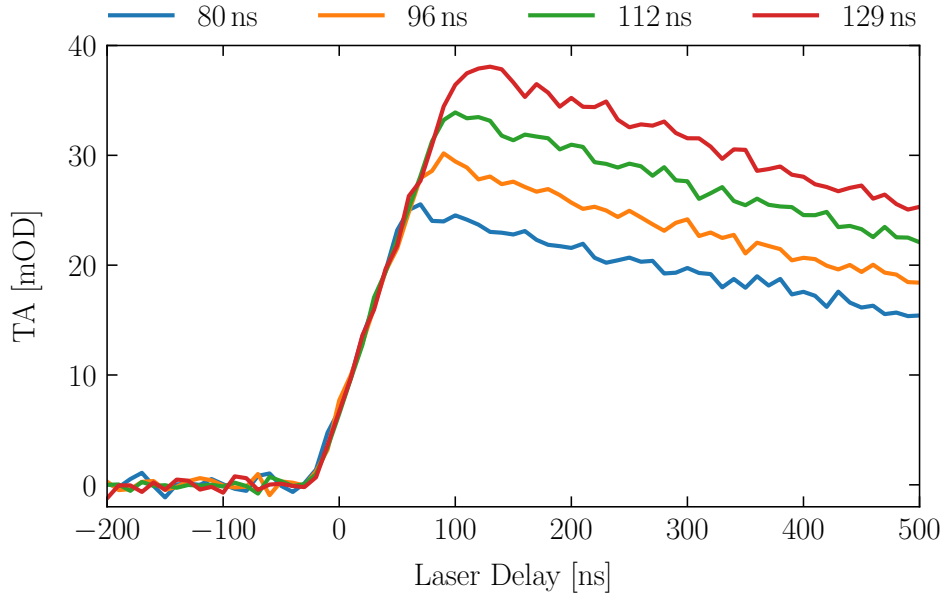


Figure 4.6: Transient absorption signal for different pump laser widths using ZnTPP in BN 0.8 mM.

To investigate the influence of the pump laser width on the transient absorption (TA) signal, we measured for sample 1 [Tab. 4.1] the TA using four different pump laser widths. The TA signal is displayed in Fig. 4.6. In Fig. 4.6 one can see that there is a shift in the TA maxima which correspond with the set pump laser width. This follows our expectations, since the longer pump laser should be able to excite more electrons to the triplet state. A closer look also shows that the pump laser width has no influence on the decay rate k_0 , i.e., the lifetime τ . But to be sure a longer time interval has to be measured to determine the long time behaviour of the decay process.

5 Closure

Bibliography

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