Transient Anisotropy in Degenerate Systems: Experimental Observation in a Cd-porphyrin

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Abstract. An unusual high transient anisotropy up to 0.65 in cadmium meso-tetraphenyl porphyrin in tetrahydrofuran was recorded which decays on a 100 ps timescale. Opposite to previous work, this behaviour was explained by an incoherent mixing of excited state absorption, ground state bleach and stimulated emission.

1 Introduction

Transient anisotropy is widely acknowledged as a powerful tool to study rotational reorientation and energy transfer. In addition, it is also thought to provide an important contribution to ultrafast molecular dynamics in degenerate systems such as electronic dephasing in the condensed phase [1]. For most systems, transient anisotropy can adopt values between 0.4 and -0.2. However, for molecular systems which show two degenerate or two nearly degenerate excited states, theory predicts that the limit of 0.4 can be exceeded and reach as high as 0.7 [2,3]. Some twenty years ago, the first direct experimental evidence for a transient anisotropy of 0.65 has been obtained by Hochstrasser and co-workers in magnesium tetraphenyl porphyrin (MgTPP) in tetrahydrofuran (THF) at room temperature [4]. This finding was explained by coherent excitation along the two transition dipole moments of the degenerate Q-band [1]. In contrast to MgTPP, the transient anisotropy of cadmium tetraphenyl porphyrin (CdTPP) showed a ground state bleach at very short delay times which was followed by excited state absorption for $t > 200$ fs. The discrepancy between both porphyrins was explained by the presence of “diffuse states” for CdTPP without a more detailed explanation [4]. In order to resolve the apparently unexpected behaviour, we performed an in depth study by scanning through different pump and probe wavelengths and recording anisotropy traces.

2 Experiments

Transient anisotropy measurements were performed using femtosecond pump-probe techniques with an entirely home-built femtosecond laser system. The laser produced pulses at 800 nm with an output energy of about 450 μ J and 75 fs pulse duration at a repetition rate of 1 kHz. It was used to generate pump and probe pulses by two independently tunable noncollinear optical parametric amplifiers (NOPAs) with a time resolution of 75 to 100 fs. Razor blades in the prism compressor of the NOPA's were used to spectrally narrow the shape of the pulses. For anisotropy measurements, the transients were recorded by the change of the optical density with probe pulse polarization either

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parallel ($\Delta OD_{\parallel}$) or perpendicular ($\Delta OD_{\perp}$) to the pump pulses by means of a tunable $\lambda/2$ plate (Alphas). The anisotropy $r(t)$ value was then determined by:

$$r(t) = (\Delta OD_{\parallel} - \Delta OD_{\perp}) / (\Delta OD_{\parallel} + 2 \times \Delta OD_{\perp}) \quad (1)$$

The measurements of CdTPP in THF (synthesis by the T. S. Balaban group, university of Marseille) were performed in a quartz flow-cell system (Hellma) to avoid degradation of the sample in the laser focus. In order to avoid aggregation effects, the concentration ($\sim 4.3 \times 10^{-4}$ mol/l) was adjusted such that the optical density of the sample equalled approx. 0.5 at 610 nm corresponding to the peak position of the Q(0,0)-band. As reference the dye Nile blue was chosen which showed anisotropy values between 0.35 and 0.4 in the corresponding probe wavelength region.

3 Results and Discussion

Outside the probe wavelength regime of $610 \text{ nm} < \lambda < 620 \text{ nm}$, a small change of the probe wavelength leads to a complex superposition of ESA, ground state bleach (GSB) and stimulated emission (SE) which is represented by an alternation of negative and positive ΔOD -values (see Fig. 1a). In essence, this superposition is caused by the presence of dark states (gerade-states in D_{4h} -symmetry) which are accessible via [1+1] excitation (see Ref. [5] for details). For most combinations of pump- and probe pulses, the initial anisotropy $r(0)$ is smaller than 0.4. This suggests that the high transient anisotropy value can only be observed when the spectral bandwidth of the probe laser is carefully adapted to the regime of stimulated emission.

The steady-state absorption spectrum of CdTPP is similar to that of MgTPP, and the optical $\pi^* \leftarrow \pi$ transitions are polarized in the plane of the molecule analogous to the transition from the two highest occupied orbitals (HOMO) with a_{1u} - and a_{2u} -symmetry and a set of e_g -orbitals (LUMO) [5]. Indeed, the Q-band absorption, which peaks around 610 nm, originates from the $e_g(\pi^*) \leftarrow a_{1u}(\pi)$ transition and is twofold degenerate in the molecular plane. The transient anisotropy in Fig. 1b decays from an initial value $r(0) \sim 0.65$ on the order of 100 ps (Fig. 1b). In contrast, the transient anisotropy of MgTPP decays biexponentially from about 0.7 within 2 ps to a long time value of approximately 0.1 [4]. It is noted that for coherent excitations, such as claimed for MgTPP, the anisotropy decay is usually on a few ps or faster. As mentioned above, the negative ΔOD -value might contain an incoherent superposition of ESA/GSB responses. It was demonstrated that these superpositions can influence transient anisotropy such that unusual high values can be observed [6]. In this case, one can simulate the experimental results in which the observed ΔOD -values are given by the ΔOD -value of ESA-component plus the ΔOD -value of GSB/SE-component:

$$\Delta OD_{\parallel/\perp}(\text{Experiment}) = \Delta OD_{\parallel/\perp}(\text{ESA}) + \Delta OD_{\parallel/\perp}(\text{GSB/SE}) \quad (2)$$

Here we assume that there is only one dark state that was taken into account in the simulation although it is likely that more low lying dark states are available in CdTPP [5b]. The simulation results are shown in Figure 1b and suggest that this is possible for those cases where ΔOD dark (about -0.2) is almost non-polarization dependent whereas the bleach (SE) contributions contain an “ordinary” anisotropy roughly 0.4 (Figure b, middle). The two anisotropy components of ESA and GSB/SE lead to the unusual high transient anisotropy which is observed in the experiment. The high symmetry favours these findings through a defined structure of gerade and ungerade states in porphyrins. The time dependence of the anisotropy on the fs-timescale is governed by rearrangements in the excited state which can have drastic variations given how small geometry changes can interchange between GSB, SE and ESA as observed in the wavelength dependence of the zero time anisotropies. Moreover, the long-time constant about 65 ps show that about 30% excited molecules can undergo direct intersystem crossing to triplet manifold in CdTPP and suggest an additional relaxation pathway competing with ground state bleach [5,7].

Fig. 1. a) Probe wavelength dependence of transients and corresponding transient anisotropy of CdTPP in THF after 610 nm excitation of the Q(0,0)-band. The pump-probe transients with the probe polarization parallel (black) and perpendicular (red) to the pump polarization. b) Simulation of transient anisotropy after excitation at 610 nm and probing at 615 nm. The inset shows the corresponding transient responses.

Another possible or additional reason for the slow decay of the transient anisotropy could be attributed to the specific structure of CdTPP which is more rigid. Theoretical calculations (see [5]) show that the Cd-atom is pushed slightly outside the porphyrin ring and the whole molecule is bent due to the relative large radius of Cd-atom, but still preserving a quasi-degenerate system allowing for a high anisotropy. The restricted flexibility (no fluctuation of the Cd-atom in and out of the porphyrin plane) may also be the reason for the much longer anisotropy (dephasing) decay. On the other hand, this structural stiffness may favour instability of the molecule upon irradiation leading to consecutive reactions on a much longer timescale.

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