Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science
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Kasha or State Selective Behavior in the Photochemistry of *ortho*-Nitrobenzaldehyde? Supplementary Information

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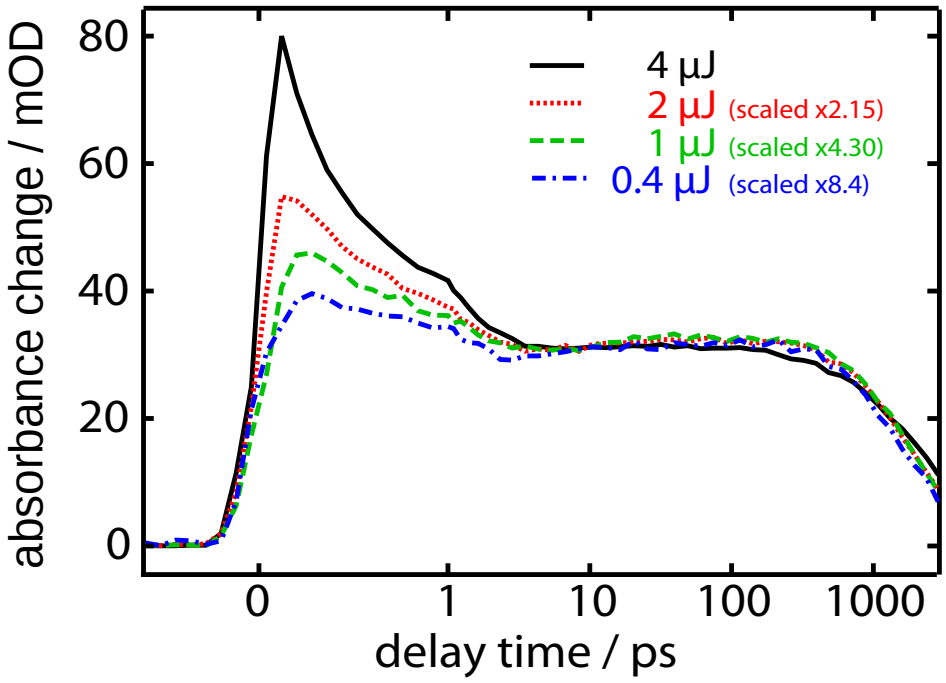

Figure 1S: Dependence of the UV/Vis transient absorption on the irradiance. The excitation wavelength was equal to 388 nm. Since pulse duration and beam diameter were constant the pulse energies given in the graph are proportional to the irradiance. The lowest pump energy corresponds to an irradiance of 40 GW $\cdot$ cm^{-2}. For the time traces depicted the probe wavelength was 450 nm. All time traces were normalized to the same value for a delay time of 10 ps (scaling factors are given in the graph). The data set shows that for pump energies larger $\sim$ 1 µJ an additional fast component shows up — presumably due to two-photon absorption.

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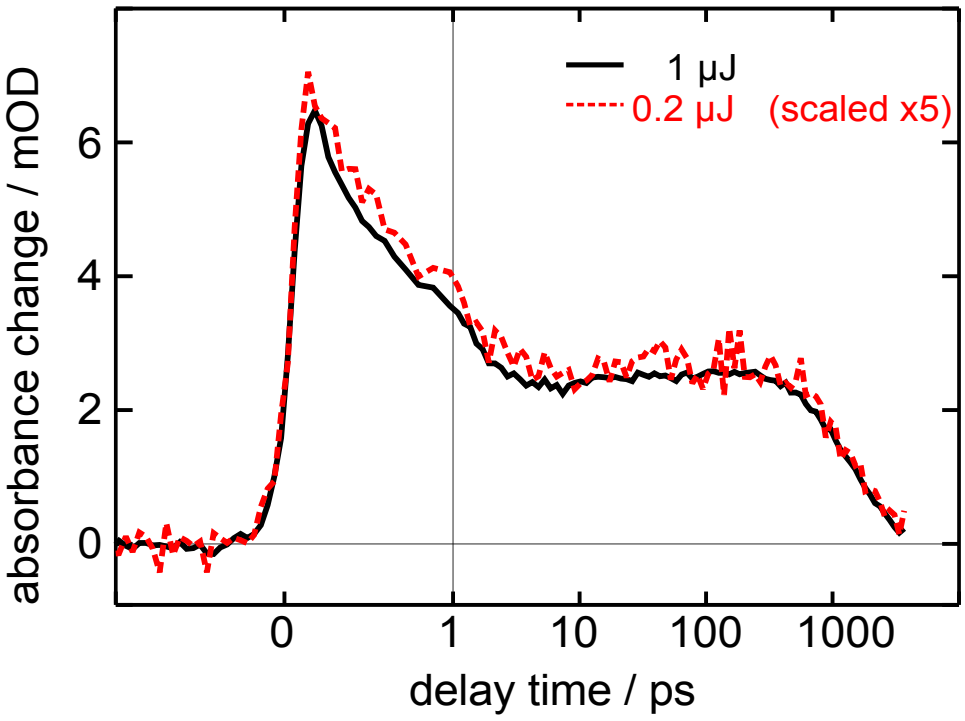

Figure 2S: Dependence of the UV/Vis transient absorption on the irradiance. The excitation wavelength was equal to 266 nm and the concentration amounted to 49 mM. Since pulse duration and beam diameter were constant the pulse energies given in the graph are proportional to the irradiance. The lowest pump energy corresponds to an irradiance of 3,9 $GWcm^{-2}$. For the time traces depicted the probe wavelength was 450 nm. The two time traces were normalized to the same value for a delay time of 100 ps (scaling factors are given in the graph).

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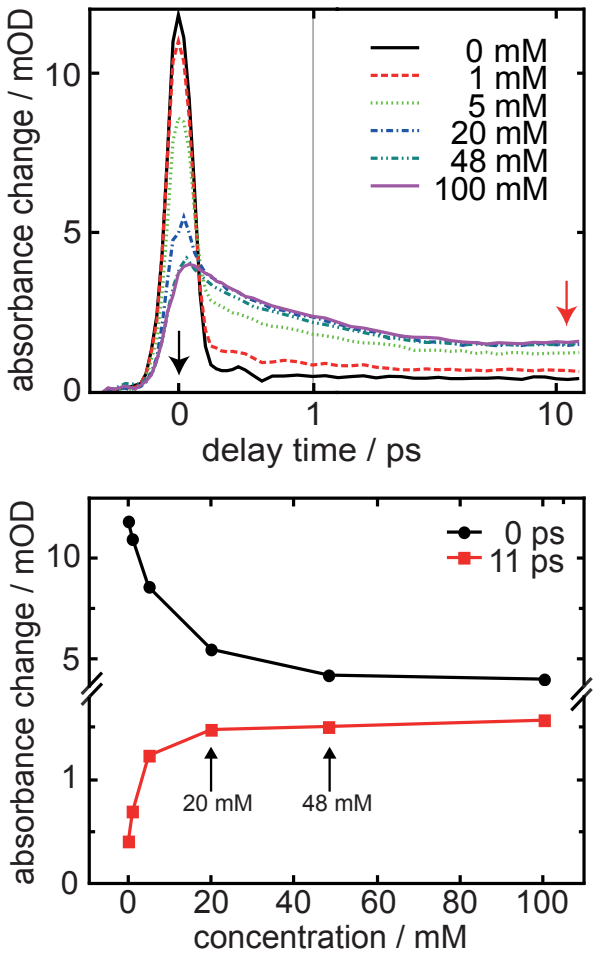

Figure 3S: Dependence of the UV/Vis transient absorption on the concentration of NBA. The excitation wavelength was equal to 266 nm. The concentration was varied in the range 0 (neat THF) to 0.1 M. Time traces for a probe wavelength of 440 nm are depicted as recorded — they are not normalized (upper viewgraph). The dependence of the difference absorption on the concentration at time zero (black bullets) and for a delay time of 11 ps (red squares) is plotted in the lower viewgraph. With increasing concentration the signal approaches the "solute only value". At a delay time of 11 ps this approach is steeper than at time zero. The solvent contribution at time zero is presumably due to the simultaneous absorption of a probe and a pump photon. The solvent signal at latter delay times is caused by a two-photon absorption of the pump light. The latter effect is expected to be more sensitive towards inner filter effects of the solute, as observed here.

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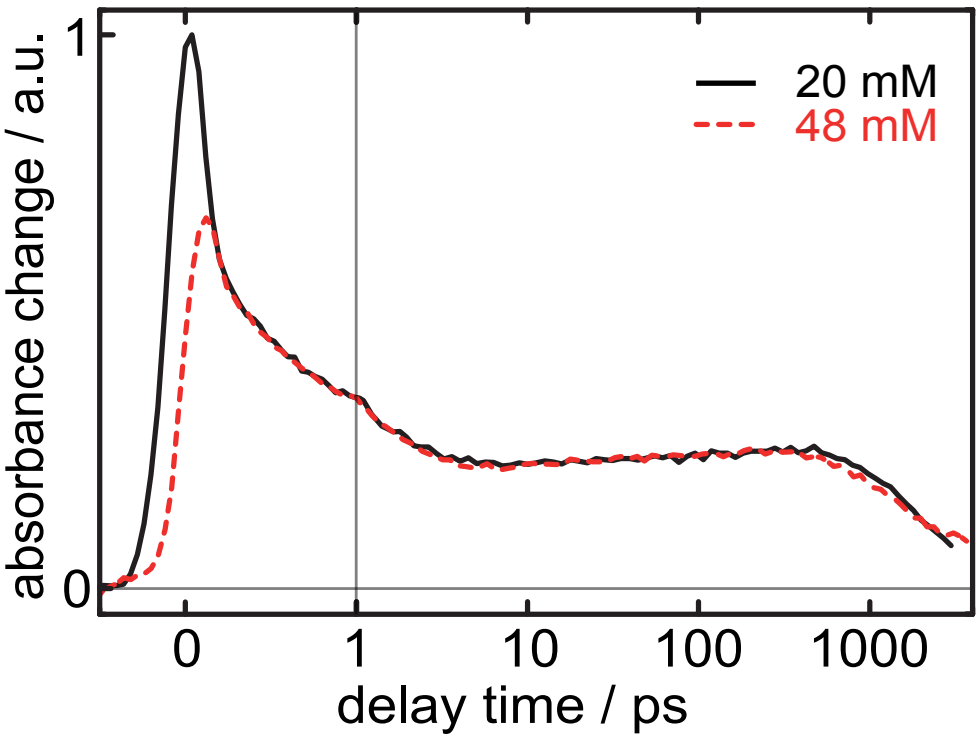

Figure 4S: Comparison of UV/Vis time traces for 20 and 48 mM NBA in THF. The excitation wavelength was around 260 nm. Normalized time traces for a probe wavelength of 440 nm are plotted. Note that the two traces merge at around 1 ps.