

Contents

Summary	i
Zusammenfassung.....	v
List of abbreviations.....	x
1 Introduction.....	1
2 Fundamentals	5
2.1 Femtosecond time-resolved spectroscopy	5
2.1.1 Femtosecond pulse properties	5
2.1.2 Nonlinear optical effects	7
2.1.3 Application, generation and modification of femtosecond laser pulses.....	13
2.1.4 Frequency conversion in the visible and near infrared region	16
2.1.5 Generation of white light continua.....	17
2.2 Theoretical methods	18
2.2.1 (Time-dependent)-Density functional theory.....	19
2.2.2 Complete active space self-consistent field method	21
3 Experimental conditions.....	23
3.1 Steady state spectroscopy	23
3.2 Transient absorption spectroscopy using selected probe wavelengths.....	23
3.2.1 Frequency conversion in the ultraviolet.....	23
3.2.2 Experimental setup.....	25
3.3 Transient absorption spectroscopy using white light continuum	27
3.4 Analysis of transient absorption data.....	30
3.5 Samples.....	32
3.5.1 Nitrophenols and corresponding phenolates	33
3.5.2 Photoinitiators	35
3.6 Theoretical methods	36

4	Ultrafast dynamics of nitrophenols and corresponding nitrophenolates	37
4.1	Introduction	37
4.2	Dynamics of <i>ortho</i> -nitrophenol (<i>o</i> -NP) after intramolecular charge transfer excitation	40
4.2.1	Steady state spectroscopy and calculated vertical transitions	40
4.2.2	Transient absorption spectroscopy	42
4.2.3	Quantum chemical calculations	47
4.2.4	Relaxation pathways of <i>ortho</i> -nitrophenol (<i>o</i> -NP).....	50
4.2.5	Conclusion.....	55
4.3	Dynamics of <i>meta</i> - and <i>para</i> -nitrophenol (<i>m</i> - and <i>p</i> -NP) after intramolecular charge transfer excitation	57
4.3.1	Steady state spectroscopy and calculated vertical transitions	57
4.3.2	Transient absorption spectroscopy in solution	60
4.3.3	Occurrence of stimulated emission in water	71
4.3.4	Dynamics in chloroform and 2-propanol	73
4.3.5	Dynamics in water.....	82
4.4	Dynamics of nitrophenolates after intramolecular charge transfer excitation.....	85
4.4.1	Steady state spectroscopy and calculated vertical transitions	85
4.4.2	Transient absorption spectroscopy in solution	92
4.4.3	Quantum chemical calculations	95
4.4.4	Relaxation pathways of nitrophenolates	100
4.5	Influence of isomerism, solvent environment and deprotonation	103
5	Ultrafast dynamics of selected type-I photoinitiators.....	107
5.1	Introduction	107
5.2	Steady state spectra and calculated vertical transitions	111
5.3	Transient absorption spectroscopy	116
5.4	Relaxation pathways of the photoinitiators after intramolecular charge transfer excitation	119
5.4.1	Benzoin (Bz) and 4-methyl-benzoin (4MB)	119
5.4.2	2-methyl-4'-(methylthio)-2-morpholinopropiophenone (MMMP).....	124
5.5	Conclusion	127

A. Appendix for Chapter 3.....	131
B. Appendix for Chapter 4.....	132
C. Appendix for Chapter 5.....	152
References	163
List of Publications.....	175
Curriculum Vitae.....	177
Danksagung.....	179