

Surface Electron Transfer Dynamics in the Presence of Organic Chromophores

von

Lars Gundlach

im Fachbereich Physik
der Freien Universität Berlin
eingereichte Dissertation

Berlin, 2005

Tag der Disputation: 12.07.2005

Erstgutachter: Prof. Dr. Frank Willig
Zweitgutachter: Prof. Dr. Martin Wolf
Drittgutachter: Prof. Dr. Ulrich Höfer
Prof. Dr. Thomas Fauster
Befürwortender Professor: Prof. Dr. Nikolaus Schwentner

Lars Gundlach

Surface Electron Transfer Dynamics in the Presence of Organic Chromophores

Kurzzusammenfassung

Die Dynamik des heterogenen Elektrontransfers (ET) zwischen optisch angeregten, organischen Molekülen und Einkristalloberflächen wurde mit Hilfe der zeitaufgelösten Zwei-Photonen-Photoelektronen-Spektroskopie (TR-2PPE) untersucht. Den Schwerpunkt dieser Arbeit bilden verschiedene, chemisch modifizierte Perylen Farbstoffe, die auf der (110) Oberfläche von Rutil TiO_2 adsorbiert wurden. Es wurden jedoch auch andere Kombinationen aus organischen Adsorbaten und Halbleiter- sowie Metalleinkristallen untersucht. Die für die Untersuchung des heterogenen ET nötige Zeitauflösung wurde mit Hilfe zweier, parallel betriebener nicht-kollinear optisch parametrischer Verstärker (NOPA) erreicht. Beide NOPA wurden bei 150 kHz betrieben und lieferten eine Kreuzkorrelation von 35 fs FWHM. Die Präparation der Adsorbatschicht erfolgte durch Chemisorption aus einer Lösung in einer speziellen Präparationskammer, in der es möglich war zwischen UHV und Inertgas Atmosphäre zu wechseln. Die sauberen, sowie die adsorbatbedeckten Oberflächen wurden mit Hilfe üblicher Methoden der Oberflächenphysik, wie UPS, XPS und LEED, untersucht. Zusätzlich wurden transiente Absorptionmessungen an einigen Proben durchgeführt zum Vergleich mit den TR-2PPE Messungen. Die geordneten, organischen Adsorbatschichten, mit einer Bedeckung unter einer Monolage, die sich auf den TiO_2 Oberflächen bildeten, ermöglichten es, die Bindungsgeometrie in Abhängigkeit der beiden verwendeten Ankergruppen (Carboxyl- und Phosphonsäure) zu untersuchen. Die Bindungsgeometrie wurde mit Hilfe der winkel- und polarisationsabhängigen 2PPE und unter Verwendung der Fresnel Gleichungen ermittelt. Zeitabhängige 2PPE Messungen an Perylen Chromophoren, die mit langen, steifen Abstandsgruppen ausgestattet waren, zeigten die zu erwartenden, langen Injektionszeiten, im Gegensatz zu früheren Messungen an den gleichen Molekülen, die in schwammartigen Kolloidschichten adsorbiert waren und mittels transientser Absorptionsspektroskopie untersucht wurden. Die Messungen an den Kolloidschichten zeigten nicht zu erwartende, kurze Injektionszeiten, die durch die engen Poren in den Kolloidschichten bedingt waren. TR-2PPE Messungen an Perylen Chromophoren, die mit kurzen Abstandsgruppen ausgestattet waren, ermöglichten es, den Elektronentransport der injizierten Elektronen in dem oberflächennahen Bereich des TiO_2 Substrats zu untersuchen. Um diese Transportdynamik näher zu untersuchen, wurden Messungen an Cate-

chol bedeckten TiO_2 Einkristallen und an Perylen bedeckten Silbereinkristallen vorgenommen. Die Auswertung dieser Messungen mit Hilfe von optischen Bloch Gleichungen und Ratenmodellen ermöglichte es, die Injektionszeiten für verschiedene Perylenderivate aus den TR-2PPE Messungen zu erhalten. Die Injektionszeiten werden mit denen aus früheren transienten Absorptionsmessungen unserer Gruppe verglichen. Des weiteren wurde bei den TR-2PPE Messungen an dem Perylen bedeckten Silbereinkristall ein Zustand beobachtet, der einem adsorbatinduziertem Bildladungszustand zugeordnet werden kann. Auf der saubere TiO_2 Oberfläche konnte die Lebenszeit eines Oberflächenzustands gemessen werden. Die mittels 2PPE gemessenen Energieverteilungen der injizierten Elektronen gibt das vollständige Elektrontransferspektrum wieder. Es entspricht einer kompletten Marcus Kurve die bei heterogenem Elektrontransfer im so genannten "wide band limit" realisiert wird. Die gemessenen Elektrontransferzeiten sind daher nur durch die elektronische Kopplungsstärke und die elektronische Zustandsdichte im Festkörper bestimmt.

Lars Gundlach

Surface Electron Transfer Dynamics in the Presence of Organic Chromophores

Abstract

The dynamics of heterogeneous electron transfer between photoexcited organic adsorbate molecules and single crystal surfaces are investigated by means of time-resolved two-photon photoemission spectroscopy (TR-2PPE). Whereas, the focus of this work is set on different chemically modified perylene chromophores attached to the (110) surface of TiO_2 rutile crystals, other combinations of organic molecules on semiconductor and metal surfaces are investigated. The necessary time resolution for TR-2PPE measurements is achieved via a novel setup consisting of two non-collinear optical parametric amplifiers operated simultaneously at a repetition rate of 150 kHz delivering a crosscorrelation function with 35 fs FWHM. The preparation of the adlayers is performed by chemisorption from solution in a special preparation chamber allowing for switching between ultra-high vacuum and inert gas conditions. The adsorbate covered as well as the bare single crystal surfaces are characterized by means of standard surface science techniques like UPS, XPS and LEED. Transient absorption spectroscopy is carried out on some of the samples for comparison with the TR-2PPE experiments. The well ordered organic adsorbate layers with sub-monolayer coverages formed on the surface of TiO_2 enable the determination of the binding geometry of the molecules for two different anchor groups, i.e. carboxylic and phosphonic acid. The adsorption geometry is deduced from angular and polarization dependent 2PPE measurements by applying Fresnel equations. Time dependent 2PPE measurements of perylene chromophores equipped with long rigid spacer groups yield the expected slow injection times in contrast to earlier measurements of the same molecules attached to colloidal TiO_2 films via transient absorption spectroscopy. The latter gave unreasonable short injection times as a result of the narrow pores in the colloidal film. TR-2PPE measurements of perylene chromophores equipped with short anchor groups enable the investigation of electron transport in the surface region of TiO_2 after injection of the electron. To further elucidate these transport processes, reference measurements were carried out on a catechol covered TiO_2 surface and on a perylene covered $\text{Ag}(110)$ surface. The fit to the TR-2PPE measurements of these samples by means of optical Bloch equations and rate equations enabled the extraction of the injection times for perylene attached to the TiO_2 surface via short anchor/spacer groups. The resulting time constants are compared with those of earlier measurements carried out in our

group. TR-2PPE measurements on the perylene chromophore attached to a silver surface give rise to an adsorbate induced image potential state not present on the bare surface. Furthermore, the lifetime of a surface state on the bare surface of $\text{TiO}_2(110)$ is resolved via TR-2PPE. Complete electron transfer spectra were measured for the first time as energy distributions of the 2PPE signals. These spectra represent the whole Marcus curve that is realized for heterogenous electron transfer in the wide band limit. The measured electron transfer times are thus controlled only by the strength of electronic coupling and the density of electronic acceptor states in the solid.

Contents

| | |
|--|-----------|
| Contents | i |
| Publications | iii |
| List of Figures | viii |
| List of Tables | viii |
| Acronyms | ix |
| Abbreviations | xi |
| 1 Introduction | 1 |
| 2 Background | 5 |
| 2.1 Electron transfer | 6 |
| 2.2 Hot electron dynamics | 10 |
| 2.3 Energy level alignment | 14 |
| 2.4 TR-2PPE | 16 |
| 2.4.1 Rate equations and optical Bloch equations | 18 |
| 2.5 Ultrafast spectroscopy | 20 |
| 2.5.1 Generation and characterization of ultrashort laser pulses | 21 |
| 2.6 Experimental systems | 25 |
| 2.6.1 The molecules | 25 |
| 2.6.1.1 Perylene | 25 |
| 2.6.2 The substrates | 31 |
| 2.6.2.1 Titanium dioxide | 31 |
| 2.6.2.2 Copper and silver | 37 |
| 3 Experimental setup | 39 |
| 3.1 The laser system | 39 |
| 3.2 Ultra-high vacuum chambers | 44 |
| 3.2.1 Measurement chamber | 45 |
| 3.2.2 Preparation and transient-absorption chamber | 46 |
| 3.2.3 ESCA chamber | 46 |
| 3.3 Time of flight spectrometer | 47 |
| 3.4 Sample preparation | 49 |

| | | |
|----------|--|------------|
| 3.4.1 | Colloidal TiO ₂ films | 49 |
| 3.4.2 | Rutile TiO ₂ (110) single crystals | 49 |
| 3.4.2.1 | Coating the surface with molecules | 50 |
| 3.4.3 | Copper and silver single crystals | 51 |
| 4 | Results and discussion | 53 |
| 4.1 | Sample characterization | 53 |
| 4.1.1 | Rutile Crystals | 53 |
| 4.1.2 | Metal single Crystals | 55 |
| 4.1.3 | Perylene derivatives on TiO ₂ (110) | 57 |
| 4.1.3.1 | Level alignment at the interface | 57 |
| 4.1.3.2 | Binding geometry | 61 |
| 4.2 | Time-dependent 2PPE signals of the bare surfaces | 72 |
| 4.2.1 | TR-2PPE on bare Ag and Cu single crystal surfaces | 72 |
| 4.2.1.1 | Cu(111) | 72 |
| 4.2.1.2 | Ag(111) | 74 |
| 4.2.1.3 | Ag(110) | 76 |
| 4.2.2 | TR-2PPE on the bare TiO ₂ (110) surface | 77 |
| 4.3 | TR-2PPE on adsorbed chromophores | 87 |
| 4.3.1 | Pe'-tripod and Pe'-rod on TiO ₂ | 87 |
| 4.3.2 | Pe-thiol on Ag(110) | 91 |
| 4.3.3 | Catechol on TiO ₂ | 100 |
| 4.3.4 | Pe' with short anchor groups on TiO ₂ | 110 |
| 5 | Summary | 117 |
| A | Experimental parameters | 121 |
| | Bibliography | 122 |
| | Acknowledgement | 139 |
| | Curriculum vitae | 141 |

Publications

1. L. Gundlach, R. Ernstorfer, E. Riedle, R. Eichberger, and F. Willig, *Femtosecond two-photon photoemission at 150 kHz utilizing two noncollinear optical parametric amplifiers for measuring ultrafast electron dynamics*, Appl. Phys. B **80** (2005) 727
2. L. Gundlach, R. Ernstorfer, C. Zimmermann, R. Eichberger, S. Felber, L. Töben, E. Galoppini, Q. Wei, and F. Willig, *Heterogeneous electron transfer probed with femtosecond two-photon photoemission spectroscopy*, in: M. M. Martin, J. T. Heynes (Eds.), *Femtochemistry and Femtobiology, Ultrafast Events in Molecular Science*, Elsevier, 529-532, 2004.
3. L. Gundlach, S. Felber, W. Storck, E. Galoppini, Q. Wei, and F. Willig, *Femtosecond two-photon photoemission probing electron injection from the excited singlet state of perylene attached to a long rigid tripod anchor-cum-spacer on rutile TiO₂(110)*, Res. Chem. Intermed. **31**, 39-46, 2005.
4. L. Gundlach, R. Ernstorfer, and F. Willig, *Escape dynamics of photo-generated electrons at the surface of TiO₂*, Phys. Rev. B., submitted, 2005.
5. L. Töben, L. Gundlach, R. Ernstorfer, R. Eichberger, T. Hannappel, and F. Willig, *Dynamics of electron scattering between bulk states and the C₁ surface state of InP(100)*, Phys. Rev. Lett. **94** (2005) 067601
6. L. Töben, L. Gundlach, T. Hannappel, R. Ernstorfer, R. Eichberger, and F. Willig, *Dynamics of electron scattering between bulk states and the C₁ surface state of InP(100)*, Appl. Phys. A **78** (2004) 239
7. L. Töben, T. Hannappel, R. Eichberger, K. Möller, L. Gundlach, R. Ernstorfer, and F. Willig, *Two-photon photoemission as a probe of unoccupied and occupied surface states of InP(100)*, J. Cryst. Growth. **248C** (2003) 206.
8. R. Ernstorfer, L. Töben, L. Gundlach, S. Felber, E. Galoppini, Q. Wei, R. Eichberger, W. Storck, C. Zimmermann and F. Willig, *Femtosecond electron injection from optically populated donor states into the conduction band of semiconductors*, Proc. SPIE Int. Soc. Opt. Eng. **5223**, 110, 2003.

9. R. Ernstorfer, L. Gundlach, S. Felber, R. Eichberger, C. Zimmermann, W. Storck and F. Willig, *Ultrafast molecule to semiconductor electron transfer via different anchor groups in ultrahigh vacuum*, in: T. Kobayashi, T. Okada, T. Kobayashi, K. A. Nelson, S. De Silvestri (Eds.), *Ultrafast Phenomena XIV*, Springer, 2005.
10. R. Ernstorfer, L. Gundlach, S. Felber, W. Storck, R. Eichberger, C. Zimmermann and F. Willig, *Ultrafast electron transfer via a bridge extended donor orbital*, in: T. Kobayashi, T. Okada, T. Kobayashi, K. A. Nelson, S. De Silvestri (Eds.), *Ultrafast Phenomena XIV*, Springer, 2005.
11. R. Ernstorfer, L. Gundlach, S. Felber, C. Zimmermann, R. Eichberger, Q. Wei, E. Galoppini, and F. Willig, *Influence of molecular spacers on ultrafast heterogeneous electron transfer*, in: M. M. Martin, J. T. Heynes (Eds.), *Femtochemistry and Femtobiology, Ultrafast Events in Molecular Science*, Elsevier, 521, 2004.
12. R. Ernstorfer, L. Gundlach, C. Zimmermann, F. Willig, R. Eichberger, and E. Riedle, *Generation of sub-20 fs tunable visible pulses from a 100 kHz NOPA for measuring ultrafast heterogeneous electron transfer*, *Ultrafast Optics IV*, 389, 2004.
13. M. Neges, K. Schwarzburg, L. Gundlach, L. Toeben and F. Willig, *Measuring and modeling hot electron dynamics for third generation solar cells*, in: Technical Digest. 14th International Photovoltaic Science and Engineering Conference 26-30 January 2004. Bangkok, Thailand. PVSEC-14., 761-762, 2004.
14. J. Piel, E. Riedle, L. Gundlach, R. Ernstorfer, and R. Eichberger, *Tunable sub-20 fs visible pulses at 100 kHz repetition rate*, as manuscript.

List of Figures

| | | |
|------|--|----|
| 2.1 | Diabatic energy surfaces for the reactant DA and product $D^+ A^-$ state along the reaction coordinate RC. | 6 |
| 2.2 | Harmonic oscillator nuclear wavefunctions for three different reaction-free energies. | 8 |
| 2.3 | The time scales for various different processes in metals. Taken from Ref. [1]. | 12 |
| 2.4 | Generation of secondary electrons. | 13 |
| 2.5 | Escape of electrons from the detection range given by λ_{esc} | 14 |
| 2.6 | Level alignment between a semiconductor and a molecule. | 15 |
| 2.7 | Left: Possible 2PPE processes (the final state was added to the picture). Right: Conservation of the parallel momentum in the photoemission process. | 17 |
| 2.8 | Noncollinear phase matching. | 22 |
| 2.9 | The SPIDER apparatus. | 23 |
| 2.10 | Structural formula of perylene and the different spacer and anchor groups. | 26 |
| 2.11 | Absorption and emission spectra of perylene. | 27 |
| 2.12 | Absorption and emission spectra of the perylene derivatives solution. | 28 |
| 2.13 | Structural formula of Pe-CH-2-S. | 30 |
| 2.14 | Rutile bulk structure from Ref. [2] | 32 |
| 2.15 | Rutile bulk band structure from Ref. [3] | 32 |
| 2.16 | The rutile (110) surface structure. | 33 |
| 2.17 | Binding conformations of formate on $\text{TiO}_2(110)$ | 36 |
| 3.1 | Output energy and spectra of the first NOPA. | 40 |
| 3.2 | Spectra and intensity autocorrelation traces of the first NOPA. | 41 |
| 3.3 | Fundamental and SHG spectra of the first NOPA. | 42 |
| 3.4 | Setup for two 150 kHz NOPAs pumped with one 400 nm SHG pulse. | 43 |
| 3.5 | Fundamental and SHG spectra of the second NOPA. | 43 |

| | | |
|------|---|----|
| 3.6 | Preparation chamber | 45 |
| 3.7 | The new time of flight spectrometer | 47 |
| 3.8 | GUI of one of the data processing tools. | 48 |
| 4.1 | UPS spectra of rutile single crystals. | 54 |
| 4.2 | XPS C1s spectra of rutile single crystals. | 55 |
| 4.3 | XPS Ti 2p spectra of rutile single crystals. | 56 |
| 4.4 | LEED pattern of a vacuum annealed TiO ₂ (110) surface (127 eV). | 56 |
| 4.5 | UPS spectra of Pe'-tripod and of pure perylene in gas phase. | 57 |
| 4.6 | 2PPE spectrum of Pe'-CH ₂ -PO(OH) ₂ on TiO ₂ | 59 |
| 4.7 | Level alignment of Pe'-tripod on TiO ₂ | 61 |
| 4.8 | 2PPE kinetic energy spectra of Pe'-tripod p- and s-polarized. | 62 |
| 4.9 | Adsorption geometry: Pe'-derivatives on rutile | 64 |
| 4.10 | Diagram of the experimental setup for angular resolved 2PPE measurements. | 65 |
| 4.11 | Schematic representation of a plane, linear polarized wave incident at an angle Θ | 66 |
| 4.12 | Peak height of the 2PPE difference signal between p- and s-polarized pump pulse (Pe'-CH=CH-COOH). | 67 |
| 4.13 | Coordinate systems used for Eq. 4.1.10. $[x, y, z]$ is fixed with respect to the \vec{E} -field and $[\tilde{x}, \tilde{y}, \tilde{z}]$ is fixed with respect to the long molecular axis. | 68 |
| 4.14 | Peak height of the 2PPE difference signal between p- and s-polarized pump pulse (Pe'-rod). | 69 |
| 4.15 | Plot of equation 4.1.10 for three different tilt angles. | 71 |
| 4.16 | Balls and sticks model of the adsorption geometries of Pe'- rod on TiO ₂ | 71 |
| 4.17 | Surface projected bulk band structure and dispersion of image potential state for Cu(111). | 73 |
| 4.18 | Transients for the n=0 surface state and n=1 image po- tential state at Cu(111). | 74 |
| 4.19 | Surface projected bulk band structure and dispersion of image potential state for Ag(111). | 75 |
| 4.20 | Transients for the n=1 and n=2 image potential state at Ag(111). | 76 |
| 4.21 | 2PPE map of Ag(110) measured with 280 nm + 440 nm pulses. | 77 |
| 4.22 | TR-2PPE map of the vacuum and O ₂ annealed surfaces of TiO ₂ (110). | 78 |
| 4.23 | 2PPE map of TiO ₂ (110) with 440 nm s-polarized. | 79 |

| | | |
|------|--|-----|
| 4.24 | Difference spectrum of the p- and s-polarized measurement | 80 |
| 4.25 | Background subtracted 2PPE map of TiO ₂ (110) with 320 nm, p-polarized. | 81 |
| 4.26 | Temporal width (FWHM) of a Gaussian fit to time traces extracted at the respective kinetic energies given at the abscissa. . . | 81 |
| 4.27 | Background subtracted 2PPE map of TiO ₂ (110) with 280 nm and 440 nm p-polarized. Heavily sputtered surface. | 82 |
| 4.28 | Assignment of the different 2PPE peaks to intermediate state energies. | 84 |
| 4.29 | Comparison between a TR-2PPE measurement on a sam- ple coated with a chromophore and an uncoated sample. | 86 |
| 4.30 | Pe'-tripod Transient absorption | 87 |
| 4.31 | Pe'-tripod TR-2PPE | 88 |
| 4.32 | Pe'-rod: Comparison of transient absorption and TR-2PPE | 89 |
| 4.33 | Pe'-COOH: Comparison of transient absorption and (ex- pected) TR-2PPE | 91 |
| 4.34 | (a) XPS S2p doublet emission. (b) HOMO and HOMO-1 of perylene on Ag(110) measured via UPS. | 92 |
| 4.35 | TR-2PPE map of Pe-CH ₂ -SH adsorbed on Ag(110)- 440 nm p-polarized. | 93 |
| 4.36 | 2PPE map of Pe-CH ₂ -SH adsorbed on Ag(110) - 440 nm s-polarized. | 94 |
| 4.37 | 2PPE at t_0 with the 2.8 eV pulse p- and s-polarized. | 95 |
| 4.38 | The time trace at 2 eV from the thiol coated sample | 96 |
| 4.39 | Dispersion of peak A and B (Ag:thiol). | 97 |
| 4.40 | Peak assignment for Ag:thiol. | 98 |
| 4.41 | UPS spectrum of catechol on /tio. | 102 |
| 4.42 | Calculated JDOS and measured absorption spectrum of catechol on rutile colloids. | 103 |
| 4.43 | Transient bleach of catechol ground state. | 104 |
| 4.44 | Excited state energy spectra for the catechol coated rutile TiO ₂ surface at different time delays. | 105 |
| 4.45 | Time trace at 2 eV intermediate state energy measured on the catechol coated sample. | 106 |
| 4.46 | Time trace at 600 meV intermediate state energy (circles) and fitted curve using the model shown in the inset (line). | 107 |

| | | |
|------|--|-----|
| 4.47 | The rate model for the catechol system (a) and the rate model for the perylene derivatives with short anchor groups (b). | 109 |
| 4.48 | 2PPE spectra at different delay times for the perylene derivatives and catechol. | 111 |
| 4.49 | Time dependent 2PPE signal measured at the excited state energy for the different perylene derivatives. | 115 |

List of Tables

| | | |
|-----|---|-----|
| 2.1 | Perylene S_0 - S_1 transition energies | 29 |
| 4.1 | Perylene HOMO and excited state energy position. | 60 |
| 4.2 | Fit Parameter for the perylene derivatives with short anchor groups. | 113 |
| 4.3 | Comparison between electron injection times measured via TR-2PPE and transient cation absorption spectroscopy | 113 |
| A.1 | Experimental parameter | 121 |

Acronyms

| | |
|---------|---|
| 2PPE | two-photon photoemission at coincidence of pump and probe pulse |
| AC | autocorrelation |
| BBO | β -barium borate |
| CB | conduction band |
| CC | cross-correlation |
| CT | charge transfer |
| DFT | density functional theory |
| DOS | density of states |
| DTB | di-tertiary-butyl |
| EA | electron affinity |
| ET | electron transfer |
| FWHM | full width half maximum |
| GVD | group velocity dispersion |
| GVM | group velocity mismatch |
| HOMO | highest occupied molecular orbital |
| IP | ionization potential |
| IR | infrared |
| JDOS | joint density of states |
| LUMO | lowest unoccupied molecular orbital |
| NIR | near infrared |
| NOPA | non-collinear optical parametric amplification/amplifier |
| OPA | (collinear) optical parametric amplification/amplifier |
| Pe | perylene |
| Pe' | di-tertiary-butyl-perylene |
| SAM | self-assembly of monolayer |
| SHG | second harmonic generation |
| TDDFT | time-dependent density functional theory |
| TR-2PPE | Time-resolved two-photon photoemission |
| TTB | tetra-tertiary-butyl |
| UHV | ultrahigh vacuum |
| UPS | ultraviolet photoelectron spectroscopy |
| UV | ultraviolet |
| VB | valence band |

VL vacuum level

XPS X-ray photoelectron spectroscopy

Abbreviations

| | |
|--------------------|--|
| E_* | effective barrier height |
| E_{Fermi} | Fermi energy |
| E_n | eigenvalue of state n |
| $E_{probe}(t)$ | probe field |
| $E_{pump}(t)$ | pump field |
| E_{Vac}, E_V | vacuum energy |
| e | electron charge |
| FC | Franck-Condon-weighted density of states |
| ΔG^+ | activation energy |
| ΔG^0 | standard Gibbs free energy |
| h | Planck's constant |
| \hbar | $h/2\pi$ |
| k_B | Boltzmann constant |
| k_{ET} | rate of electron transfer |
| λ | reorganization energy |
| m_e | free electron mass |
| $\boldsymbol{\mu}$ | transition dipole |
| t_0 | time zero, coincidence of pump and probe pulse |
| T_1 | energy/population relaxation time |
| T_2 | dephasing time |
| T_2^* | "pure" dephasing time |
| t_d | delay time |
| V_R | electronic coupling matrix element |