Femtosecond Time-resolved Exciton Dynamics and Non-linear Imaging with Sub-wavelength Resolution in Organic Semiconductors

by

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Femtosecond Time-resolved Exciton Dynamics and Non-linear Imaging with Sub-wavelength Resolution in Organic Semiconductors
Dedicated to my family
Abstract

In the last 25 years, nano science has developed rapidly because of increased scientific demand and technological interest not only in material science, but also in e.g. life sciences and other related fields. The properties of bulk and nano-structured materials differ considerably; therefore the interest to investigate the fundamental properties of materials on a nanometer scale continues to grow.

In our research, we focus on the investigation of elementary processes, including energy transfer, charge transport, and exciton diffusion in nano-systems, which also involve the vibrational properties of these systems and their environments. These processes occur on ultrashort time scales, and therefore require femtosecond temporal resolution as well as high spatial resolution for their investigation.

However, the standard far-field diffraction-limited microscopic techniques cannot access the detailed local properties of nanostructure-based organic electronic devices made of thin films, whereas certain local details can severely hamper the performance of organic semiconductors. In order to obtain relevant information, the best if not the only solution is to apply a technique able to access high spatially localized and temporal information, and to this end, the combination of scanning near-field microscopy (SNOM) with time-resolved spectroscopy offers a superior tool, which can be used.

In this thesis, we demonstrate that the combination of nanometer spatial resolution and femtosecond time resolution is feasible for model samples of novel organic semiconductors. We introduce different nonlinear spectroscopic techniques such as pump-probe transient absorption measurements as well as coherent anti-Stokes Raman
scattering (CARS), combined with scanning near field optical microscopy and apply them to different organic semiconductor systems, focusing mainly on 3, 4, 9, 10-perylene tetra carboxylic dianhydride (PTCDA) and poly 3-hexylthiophene (P3HT).
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Chapter 1

Introduction

The history of spectroscopy began when Newton (1666-1672) showed that white light from the sun is dispersed into a regular arrangement of colors (rainbow) in the increasing or decreasing order of wavelength or frequency after passing through a glass prism. He for the first time introduced the word “SPECTRUM” describing this phenomena, which is one of the most fundamental and fruitful example of the beginning of optical spectroscopy. When light interacts with matter (a system of particles including atoms, molecules, etc.), then light energy could be absorbed, reflected, scattered as well as emitted by the system. In order to study different chemical and physical properties of a material system, optical spectroscopy is the most popular and powerful technique for the understanding of structure of the molecules and dynamics of the molecules within the system.\(^1\)

The invention of the laser in 1960, which can provide intense and coherent light, opened up several fields of optical spectroscopy research, and the laser is used today in various applications as a tool-kit. After their discovery, lasers were used to generate short laser pulses in nanosecond time scale (using Q-switching techniques) and ultrashort laser pulses (using mode-locking techniques) with high peak powers. The interaction of ultrashort laser pulses with matter can generate nonlinear effects, what led to the introduction of a new field of spectroscopy called nonlinear spectroscopy.\(^2\)^{3}
Introduction

1.1 Why ultrashort laser pulses

Many dynamical processes like vibration of nuclei in any biological or chemical reaction take place in an ultrashort time scale. Hence in order to monitor such fast processes, nonlinear spectroscopic technique with ultrashort laser pulses can be used.

Ahmed Zewail and his coworkers in 1985, for the first time investigated the disintegration of cyanogen iodide (ICN) into iodide (I) and cyanide (CN) in ultrashort time. They used a femtosecond pump-probe technique and were able to photograph the formation of an I-CN transition state, where the I-C bond breaks within femtosecond time scale. Ahmed Zewail then employed femtosecond pump-probe spectroscopy to different systems and measured in real time complex reaction dynamics directly and was awarded a noble prize for his pioneer work in femto-chemistry.\(^4\),\(^5\)

The availability of commercial femtosecond laser systems has led to fast development of nonlinear spectroscopy and has made this field even more attractive.\(^4\),\(^5\) Since femtosecond time-resolved spectroscopic techniques can be used in order to access molecular dynamics in different complex systems. Among the different nonlinear spectroscopic techniques, the third-order nonlinear spectroscopic techniques, including pump-probe (PP) and coherent anti-Stokes Raman scattering (CARS), which\(^6\),\(^7\) is a special type of four wave mixing (FWM), are and is frequently used by different research groups for the investigation of electronic and molecular dynamics in various systems. Lauberau, Zinth, and Kaiser reported time-resolved coherent Raman scattering on ultrashort time scale for the first time.\(^6\),\(^7\) The observation of the wave packets dynamics occurring in the ground and excited states of iodine vapors using femtosecond time resolved CARS spectroscopy was reported by A. Materny and co-workers.\(^8\),\(^9\)
Introduction

The use of ultrafast laser pulses is not limited to the investigation of dynamical processes different systems but it is has also led to the development of nonlinear optical microscopy, with various applications in different fields of science, especially in Biology for high chemical contrast imaging.

1.2 Why nonlinear microscopy

Different microscopic techniques like fluorescence microscopy and confocal fluorescence microscopy provide three dimensional images of specific targets. However, cells or molecules that are not fluorescent need to be labeled with fluorescent tags, which can be toxic and could alter the physiological environment.\textsuperscript{10,11} As opposed to fluorescence microscopy, the Raman imaging technique is based on vibrational contrast and is useful for imaging without labeling. The conventional Raman microscopy can achieve noninvasive and high chemical selectivity but cannot provide high sensitivity. Its drawback is the weak Raman signal (one signal photon out of 10 million photons), which can be further overshadowed by a strong background due to fluorescence in many biological samples and in colored samples in general.\textsuperscript{12}

On the other hand, nonlinear microscopy techniques based on nonlinear optics are powerful tools, which can be used for imaging and non-invasive examination of the investigated samples. A few common nonlinear techniques are two-photon excitation fluorescence microscopy techniques (TPEFM), second harmonic generation (SHG) microscopy technique, Pump-probe microscopy, CARS microscopy, stimulated Raman scattering (SRS) microscopy, etc.
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Two-photon excitation fluorescence microscopy uses two photons in the infrared region for excitation in order not only to reduce the scattering efficiency in the sample but also to penetrate deeply into the sample. The background signal in this case is minimized due to multiphoton absorption. In addition, sample damage is avoided the use of longer wavelength light. Denk and coworkers in 1990 studied multiphoton microscopy for three dimensional in vivo imaging of cells and tissues.\(^{13}\) The main drawback of using infrared light is its relatively low spatial resolution as well as high water absorbance.

Second harmonic generation (SHG) microscopy is another type of nonlinear technique, which provides imaging contrast. Xiyi Chen et al. used SHG microscopy for imaging fibrillar collagen in tissues.\(^{14}\) However, being a second order coherent process based on $\chi^2$, this technique is limited only to non-centro symmetric media.

Pump-probe microscopy is the simplest and most useful time-resolved microscopic technique extensively used by different research groups in various fields. In pump-probe microscopy, a pump pulse energizes the sample of interest and a probe pulse is then used to look at the changes produced in the sample due to the pump pulse. Pump-probe microscopic techniques include excited state absorption (ESA) microscopy, stimulated emission (SE) microscopy and ground state depletion (GSD) microscopy.\(^{15-17}\) Pump-probe microscopy can achieve high selectivity and specificity, since in this technique the light wavelength has always to be in resonance with electronic/molecular transition.

Using pump-probe transient absorption (TA) in a typical case, where the pump and probe beams are focused on a sample surface using a normal objective lens or mirror to form a focus spot size in the micro to millimeter range, only very little information about the internal structure and local dynamics of molecules in the sample of interest can be
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obtained. When the sample has micro or even nano domain structures that are much smaller than the focused light spot size, the TA measures the average over many different domains with micro/nano-structured features, what leads to a rather speculative result. In order to investigate the fine local structures within e.g. a thin material film, it is important to reduce the size of the sample area for each individual observation. Different research groups have used ultrashort pump-probe microscopy techniques to investigate different dynamical processes in various semiconductor materials in far-field\textsuperscript{18-23}, where the inhomogeneity in the sample cannot be detected due to diffraction limit.

Some of the nonlinear spectroscopic techniques, for example stimulated Raman scattering (SRS) microscopy\textsuperscript{24} and coherent anti-Stokes Raman scattering (CARS) microscopy, etc. are more informative for nonlinear imaging. CARS microscopy is a third-order nonlinear microscopy technique, which has attracted a lot of attention. It is frequently used for the vibrational imaging of chemical and biological samples, especially for lipids\textsuperscript{25-27}. In order to generate the CARS signal, unlike pump-probe absorption, any two wavelengths can be chosen in such a way that a vibrational resonance is achieved. Therefore, in principle no electronic resonances are required as long as only ground state vibrational dynamics have to be accessed. The main drawback of this technique is the nonresonant background contribution in the signal yield.

As already mentioned, all of the above mentioned nonlinear microscopic techniques can provide high resolution images, however the signals measured in the far-field that is diffraction limited, neither provide the accurate local dynamics nor sufficient spatial resolution in the nanometer scale. Therefore, it is important to investigate the local dynamics with high temporal and spatial resolution at the same time, which is only
Introduction

possible using the near-field microscopy technique in combination with time-resolved spectroscopy.

1.3 Why ultrafast scanning near-field spectroscopy/microscopy

High spatial resolution techniques like AFM, STM, etc. provide only topographical information with no chemical specificity. The scanning near field optical microscopy technique provides resolution below the diffraction limit. Eric Betzig, Stefan W. Hell, and William E. Moerner were awarded the 2014 Nobel prize for developing a super-resolution microscopy techniques exploiting the fluorescence of given molecules.$^{28,29}$

The combination of both space and time resolved measurements is of interest for many researchers in experimental physics. The optical near-field microscopy in combination with ultrafast spectroscopy (ultrafast SNOM) provides an experimental technique, which helps not only to capture images with high chemical specificity and very high spatial resolution, but also to record the dynamics localized within nanometer scale with high temporal resolution. This combination is very challenging because of its high technical complexity and thus very few scientific research data have been published. For example, such a technique is extremely promising when applied to study the charge carrier dynamics in organic semiconductors and metal nanostructure systems.

1.4 Why SNOM on organic semiconductors

The application of ultrafast SNOM to organic semiconductors is very important for many reasons. On the one hand, organic semiconductors are of considerable interest for the design of electronic devices due to their light weight and the need to find a solution to increasing energy demands. In addition they have attracted considerable attention since
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cheap and simple designs of electronic devices such as field effect transistors, light emitting diodes or solar cells might become a big market in the near future. However, a number of problems still have to be solved. The efficiency and life time of the devices needs to be improved for practical applications. The efficiency of organic photovoltaic (OPVs) is still low. On the other hand, in order to improve the performance of organic electronic devices, it is important to know the fate of the photo-generated excitons. Many dynamical processes in organic semiconductors, including the photo generated exciton formation, the conversion of formed excitons to self-trapped excitons, exciton-exciton annihilation, exciton transfer to the donor/acceptor interfaces, charge separation and transfer of charges to their respective electrodes are very fast and take place on a femtosecond and picosecond time scale. All these processes, which depend on local structural or morphological details, can be highly localized and play an essential role in the device performance and hence need to be investigated. In order to access the local dynamical information about nano structures, the near-field transient absorption microscopy technique is favored over far-field diffraction limited techniques, especially in such cases where the true picture of local details are to be visualized. In our research work, we combine nonlinear spectroscopy techniques (e.g. femtosecond pump-probe and CARS) with scanning near field microscopy (SNOM) in order to generate images with high chemical contrast and at the same time record the localized exciton dynamics in organic semiconductors.
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1.5 Thesis organization

This thesis includes seven chapters, which are shortly summarized in the following:

Chapter 1 presents a brief introduction to ultrashort laser pulses, nonlinear optical techniques and their combination with near-field microscopy.

Chapter 2 gives a theoretical background of nonlinear optical spectroscopy and the third-order nonlinear polarization. This chapter includes the mathematical expression describing the generation of ultrashort laser pulses, time-resolved spectroscopy, and perturbation theory. It also introduces the two nonlinear techniques, the so called pump-probe transient absorption and coherent anti-Stokes Raman scattering (CARS), and the necessary theoretical conditions for their implementation. This chapter also discusses the microscopy approach for pump-probe transient absorption and CARS.

Chapter 3 describes scanning near-field optical microscopy in detail, with an emphasis on its importance and different variations.

Chapter 4 presents the experimental setup and methods for the experiments discussed in this thesis.

Chapters 5 and 6 present the results obtained in the framework of this Ph.D thesis, which are based on the two important nonlinear techniques introduced earlier, namely pump-probe transient absorption and coherent anti-Stokes Raman scattering, each in combination with scanning near field optical microscopy. In the first part of the thesis, the combination of pump-probe transient absorption with SNOM is used for studying the exciton dynamics in organic semiconductors. The main system of interest in the thesis is P3HT (i.e. poly(3-hexylthiophene)) used as a model system of organic electronic devices in both the femtosecond pump-probe and CARS experiments performed using the SNOM
technique. In addition, PTCDA, which is another interesting model system for organic electronics, is used for the pump-probe transient absorption experiments performed in this thesis using the near-field approach.

Chapter 5 includes two sections. Section (5.1) presents results on thin films of the organic semiconductor PTCDA (i.e. 3, 4, 9, 10 perylene tetracarboxylic dianhydride) by using femtosecond time-resolved non-degenerate pump-probe experiments in the near-field called PP SNOM. The applied technique provides quantitative information about the exciton dynamics and their dependence on exciton density. We demonstrate that highly time-resolved and spatially resolved exciton dynamics can be obtained in the near-field. Unlike AFM images, high chemical contrast can be obtained in the SNOM images, which clearly indicates an advantage of PP SNOM over conventional SNOM. Section (5.2) presents the pump-probe technique in the near-field to observe changes in the ultrafast exciton dynamics at the interface between the regio-regular P3HT polymer and gold contact. Interfaces between the metal electrode and the semiconductor active medium are essential for charge separation which determines the performance of electronic devices. We demonstrate in this section that the relevant local information can be achieved by applying a PP-SNOM technique using a metalized coating tip, where far-field technique fails to provide such local details.

Chapter 6 also contains two sections. Section (6.1) introduces coherent anti-Stokes Raman scattering (CARS) imaging of polystyrene beads as a test sample. Polystyrene beads are available in different sizes and have highly Raman-active vibrations in the range of 800-3000 cm$^{-1}$. For the experiments discussed here, we have used 3 µm beads and preliminary results are obtained from polystyrene beads by using micro-CARS (far-field)
experiments. In section (6.2) the CARS technique was then employed to an organic semiconductor (P3HT) in the near-field. This combination provides highly spatially resolved images of P3HT nano-structures with vibrational contrast. Chapter 7 belongs to summary and the outlook.
Chapter 2

Theory

2.1 From linear to nonlinear optical spectroscopy

The first nonlinear effect was reported by J. Kerr in 1875. He observed a change in the refractive index of an isotropic transparent medium, which was placed in a high electric field produced by a high voltage source, and the observation is known as Kerr electro-optic effect or DC Kerr effect. In 1960 after the laser invention, the electrical voltage was replaced by a high enough electric field strength obtained from a laser source, which also induced a Kerr effect and the letter is known as the optical Kerr effect or AC Kerr effect. The foundation stone of nonlinear optics was laid down in 1960 by P. A. Franken and coworkers, when for the first time they observed the second harmonic generation by focusing a pulsed ruby laser into a quartz crystal. They observed that light with frequency $\omega$, when incident on quartz crystal, generates second harmonic $2\omega$ at the output. After this observation, the field of nonlinear spectroscopy developed very rapidly.

The linear spectroscopy (based on the application of weak electric fields of a few V/m) and nonlinear spectroscopy (based on the application of strong and intense electric fields of more than $10^8$ V/m) could be explained by the interaction of the electric field component of electromagnetic radiation with a system of electric charges such as atoms and molecules of a material.

The electromagnetic field thus induces an electric dipole movement in the bound electron in a dielectric due to its slight displacement from its equilibrium position and is given by

$$\mu(t) = -e\mathbf{r}(t) \quad (2.1)$$
Theory

Where $\mathbf{\mu}(t)$ is the dipole moment induced due to light matter interaction, $e$ is the electron charge, and $\mathbf{r}(t)$ is the displacement vector directed from negative charge (electron) to the positive charge (nuclei). The magnitude of dipole depends on the displacement, which indicates how the electron is bound to the nuclei. The electron binding potential energy close to the positive nuclei can be considered as a harmonic potential. For a system of $N$ oscillators (electrons) the macroscopic polarization can be written as

$$ \mathbf{P}(t) = N\mathbf{\mu}(t) $$

The polarization is defined as the dipole moments per unit volume and is linearly proportional to the applied “weak electric field” $\mathbf{E}(t)$:

$$ \mathbf{P}(t) = \epsilon_0 \chi \mathbf{E}(t) \quad (2.2) $$

Here $\epsilon_0$ is the permittivity of the medium and $\chi$ is the linear susceptibility. Equation (2.2) indicates that for small electric field strength the relation between polarization and applied field is linear. However, higher electric field strength can produce nonlinear polarization. The total electric polarization induced in a material by an interacting electromagnetic radiation can be expressed in a power series of the electric field component as follows:

$$ \mathbf{P}(r, t) = \epsilon_0 \left[ \chi^{(1)}(r, t) \mathbf{E}(r, t) + \chi^{(2)}(r, t) \mathbf{E}^2(r, t) + \chi^{(3)}(r, t) \mathbf{E}^3(r, t) + \ldots \right] \quad (2.3) $$

The quantities $\chi^{(2)}, \chi^{(3)}$ are known as the second and third-order nonlinear optical susceptibilities. When the order of susceptibility increases, its magnitude decreases, i.e. for condensed matter $\chi^{(1)}$ is of the order of unity, $\chi^{(2)} = 10^{-12}$ m/V, $\chi^{(3)} = 10^{-23}$ m$^2$/V$^2$ and so on. Therefore, the corresponding non-linear material responses are only significant for highly intense fields.
The interaction of electromagnetic field with matter can be understood by using the well-known Maxwell’s equations. The differential form of Maxwell’s equations can be written as,

\[ \nabla \cdot \mathbf{E} = \rho / \varepsilon_0 \]  
\[ \nabla \cdot \mathbf{B} = 0 \]  
\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  
\[ \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \]

Here, \( \mathbf{D} \) is called the displacement vector and is related to the electric field by relation,

\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \]

The correlation between nonlinear polarization and the applied field is given by Maxwell’s equations

\[ \nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \mathbf{P}^T}{\partial t^2} \]

Where \( \mathbf{P}^T \) is the total polarization including linear and non-linear terms and is given by \( \mathbf{P}^T = \mathbf{P}^L + \mathbf{P}^{NL} \) as depicted in figure 2.1. The speed of light linked to electric permittivity \( \varepsilon_0 \) and magnetic permeability \( \mu_0 \) is given by \( c = 1/\sqrt{\varepsilon_0 \mu_0} \)

Figure 2.1 The linear (a) and nonlinear (b) response of the medium
Theory

Equation (2.9) is a second order differential equation. A general solution is given by,

\[ E(r,t) = E_0 \exp^{-i(\omega t - kr)} + c.c \]  

(2.10)

Where c.c. denotes the complex conjugate. The term \( E_0 \) is the amplitude of the signal wave and \( (K \cdot r - \omega t) \) is its phase; \( K \) is the propagation wave vector, which points towards the direction of propagation of the light wave having a magnitude equal to,

\[ |K| = K = \frac{2\pi}{\lambda} = \frac{\omega}{c} \]

The induced polarization in the wave equation acts as a source term providing the corresponding signal and is described by a solution of the same form as (2.10)

\[ P(r,t) = P \exp^{-i(\omega t - k \cdot r)} + c.c \]

(2.11)

The generated nonlinear signal can be specified by the linear combination of frequencies and wave vectors of the incident fields. The different interacting laser fields having wave vectors \( K_1, K_2, K_3 \ldots \) and frequencies \( \omega_1, \omega_2, \omega_3, \ldots \) coherently generate an induced signal with wave vector \( K_S \) and frequency \( \omega_S \), which satisfy the conservation of energy and momentum as follows:

\[ \omega_S = \sum_j \pm \omega_j \]  

(2.12)

Equation (2.12) can be read as energy conservation and

\[ K_S = \sum_j \pm K_j \]  

(2.13)

Equation (2.13) is called the momentum conservation, where \( \Delta K = K_S - (\sum_j \pm K_j) \). The momentum conservation gives the phase matching condition for nonlinear processes. For \( \Delta K = 0 \) the phase matching condition is fully satisfied and an efficient signal can be
Theory

generated. The phase mismatch between the signal wave vector and the wave vectors of the incoming fields occurs when $\Delta K \neq 0$.

When intense light is employed to non-linear material, a variety of nonlinear effects can be produced including second-harmonic generation (SHG) at $2\omega$, sum frequency generation (SFG), and difference frequency generation (DFG). These nonlinear effects correspond to the second order nonlinear susceptibility $\chi^{(2)}$. Similarly, third-harmonic generation (THG), four-wave mixing (FWM), optical Kerr effect, stimulated Raman scattering (SRS), self-focusing, self-phase modulation, pump-probe transient absorption and coherent anti-Stokes scattering (CARS) correspond to $\chi^{(3)}$. In this thesis, two nonlinear process will be discussed in more detail, the pump-probe and CARS spectroscopy.

2.2 Pump-probe spectroscopy / microscopy

The most important and simplest time-resolved technique is the pump-probe technique, which is a third-order nonlinear process. The pump-probe technique needs two ultrashort laser pulses for its operation. The first one, the so called ‘pump’ pulse with frequency $\omega_{pu}$ perturbs the sample at time $t = 0$ and the second one acts as a ‘probe’ pulse and is used to monitor the changes produced in the sample initiated by the pump pulse. Different geometries are used for the different pump-probe experiments including non-collinear and collinear geometry. In non-collinear geometry, the pump and probe beams after traversing different optical paths are focused on the sample surface using a lens as shown in figure 2.2. In this setup $\Delta T$ is the delay time between pump and probe and L stands for the focusing lens. In non-collinear geometry no special filters are used and the probe can easily be separated from the pump after interaction with the sample. The transmitted probe
Theory

can then be detected by the detector, which provides information about different dynamics taking place within the sample.

![Diagram showing pump-probe setup](image)

*Figure 2.2 Schematic diagram for pump-probe in non-collinear geometry experiment*

In collinear geometry however, the pump and probe beams after traversing different optical path lengths are made collinear using a beam splitter before they pass through the sample. The collinear pump and probe pulses are then focused on the sample surface using a lens. After interaction with the sample the pump can be filtered out and the probe can be detected by the detector. The collinear geometry is not suited for degenerate pump-probe (same pump and probe wavelengths) experiments, where the pump and probe beams cannot be separated easily by using filter. In the near-field experiments, the collinear geometry is used with non-degenerate pump and probe wavelengths, which is described in chapter 4 (experimental setup in detail). The scheme for collinear geometry is depicted in figure 2.3 where BS is the beam splitter, M is the mirror and ΔT is the delay time between pump and probe for monitoring the dynamics in the sample of interest.
Theory

In a transient absorption pump-probe experiment (in the following we will only concentrate on this type of pump-probe spectroscopy), the pump pulse initially excites the sample to an excited electronic state, inducing a change in the transmitted intensity ($\Delta I$) of the probe, which is resonant with the absorption starting from this excited state. The changes in the transmitted probe intensity allow for an investigation of different relaxation processes depleting the state initially populated by the pump laser pulse.

The scheme of the transient absorption pump-probe experiment for a system of three electronic energy levels $U_a$, $U_b$, and $U_c$ is shown in figure 2.4, where the pump and probe, with frequencies $\omega_{pu} = \omega_b - \omega_a$ and $\omega_{pr} = \omega_c - \omega_b$, are resonant with the transitions between $a, b$ and $b, c$ states, respectively, and their timing is controlled by varying the path length of the probe pulse with respect to the pump.
As described, the pump pulses excite the system from an electronic ground state “a” to a higher electronic state “b”. Close to time zero (time coincidence between pump and probe laser pulses), the wave packet generated in state “b” can be resonantly transferred into state “c” by the probe laser interaction. The intensity of the transmitted probe as a function of delay time between pump and probe is recorded. The probe pulse thus monitors the wave packet formed at the potential surface $U_b$ at different delay times. These measurements provide information about the lifetime of the excited state, which depends on different relaxation processes.

The intensity of the probe laser before and after the interaction of the pump pulse can be described for different delay times using the Beer-Lambert law

$$I_{pr} (\omega, t) = I_{pr} (\omega, 0) e^{-\alpha L N(\Delta t)}$$  \hspace{1cm} (2.14)
Theory

Where \(\alpha\) is the absorption coefficient at frequency \(\omega\), \(N(\Delta t)\) is the population of the absorbing species and \(L\) is the thickness of the sample. From equation (2.14), the optical density or absorbance is derived as

\[
OD = \ln\left(\frac{I_{pr}}{I_{pr}(\omega, \Delta t)}\right) = \alpha L N(\Delta t) \tag{2.15}
\]

For exponentially decaying population (N), the decay time \(\tau\) can be obtained by varying \(\Delta t\) so that\(^3\)

\[
\ln OD (\Delta t) = \ln N(0) \alpha L - \Delta t/\tau \tag{2.16}
\]

The Beer-Lambert law for linear absorption, \(\Delta A\) can also be written as\(^{31,38}\)

\[
\Delta A = A_{\text{with pump}} - A_{\text{without pump}} = \log \left[\frac{I_n}{I_T}\right]_{\text{with pump}} - \log \left[\frac{I_n}{I_T}\right]_{\text{without pump}} \tag{2.17}
\]

Where \(I_n\) is the incident intensity and \(I_T\) is the transmitted intensity.\(^{39}\)

Different research groups investigated ultrafast dynamics in various fields of science using this pump-probe technique and have achieved a wealth of information about the systems. For example, Ombinda et al.\(^{37}\) used the pump-probe spectroscopic technique for studying ultrafast energy transfer in photosynthetic systems of plants and photodynamic therapy drugs. They investigated biological and chemical processes happening on a femtosecond time scale which enabled them to obtain information about energy transfer and molecular dynamics. Besides for biological samples, the pump-probe technique has also been used to investigate the ultrafast processes in organic semiconductors. For example the formation of excitons, the conversion of excitons to self-trapped excitons, exciton-exciton annihilation and other relevant processes, which are very fast, could be studied using ultrashort laser pump-probe techniques.\(^{40-43}\)
The pump-probe technique is not only important for obtaining spectroscopic information but can also be used for high contrast imaging. The application of the pump-probe technique as a tool for microscopy based on excited state absorption was first demonstrated by Warren and co-workers. Xie and his group also used pump-probe microscopy for chemical imaging, including excited state absorption microscopy, stimulated emission microscopy and ground state depletion microscopy. The combination of the time-resolved laser interaction with microscopy provides an imaging capability with high chemical contrast and high chemical specificity. Grancini et al. reported pump-probe transient absorption images in polymer blend and in hybrid polymer nanoparticle blends. The morphological investigation using ultrafast confocal pump-probe microscopy reveals a strong influence of the complex local structure on the photo generated carrier dynamics. However it is important to note here that all the above mentioned pump-probe microscopic techniques are used in the far-field and are diffraction limited.

2.3 From spontaneous to coherent Raman spectroscopy/microscopy

In 1928 C.V. Raman discovered for the first time the phenomenon of inelastic scattering of light called Raman scattering that explains the shift in frequency of incident light when scattered by molecules of the medium.

When monochromatic light of frequency $\omega_{pu}$ is incident on a medium, it generates both elastic and inelastic light scattering. The elastic scattering of photons on interaction with the system produces no change in its frequency or energy. Conversely, in inelastic scattering, a shift in frequency (change in energy) of the scattered photon takes place on its interaction with the molecules of the system. Thus three kinds of phenomena can occur
Theory

during light matter (molecular) interaction, which is depicted in figure 2.5 by an energy level diagram.30,47,48

1. The interaction of light with molecules of a medium in such a fashion that the light doesn’t lose or gain energy (E = E₀), so that the scattered light has the same frequency as that of incident light frequency (ω = ω₀). This type of scattering is called Rayleigh scattering. Here E₀ and ω₀ are the energy and frequency of the incident photon, while E and ω are the energy and frequency of the scattered photon, respectively.

2. A light-matter interaction were the photon loses some energy, i.e., the frequency of the scattered photon is less than that of the incident photon (E = E₀− E_vib, assuming that the shift is due to the excitation of a molecular vibration with energy E_vib). This inelastic process is called Stokes Raman scattering.

3. A light-matter interaction where the photon gains e.g. vibrational energy from the molecule, i.e., the scattered photon frequency is higher than that of the incident photon (E = E₀ + E_vib). This process is called anti-Stokes Raman scattering.

The frequency shifts observed in Raman spectroscopy in most cases correspond to some specific molecular motions (vibration, rotation, etc.), which are unique for each type of molecule, and the spectra can therefore be used to identify the molecules (molecular fingerprints). Thus Raman spectroscopy can be used for the chemically specific detection of molecules. At room temperature the strength of the Stokes signal is higher than the anti-Stokes signal because there is less population in the excited (vibrational or rotational) state as compared to the ground state to generate anti-Stokes signal (Boltzmann statistics). Therefore, the Raman spectra are mainly recorded at the Stokes side.
Spontaneous Raman scattering has become an extensively used technique for molecular analysis, however it is a weak process having very low cross section since only 1 out of $10^6$ photons is Raman scattered and thus results in a very low quantum yield.\cite{47}

Maker and Terhune in 1965 for the first time demonstrated the phenomenon of coherent anti-Stokes Raman scattering.\cite{49} At that time they simply called this process a wave mixing mechanism and later on, in 1974 Bely proposed the name, coherent anti-Stokes Raman scattering (CARS).

The CARS process involves three laser beams, the pump beam having frequency $\omega_{pu}$, the Stokes beam having frequency $\omega_S$ and the probe beam having frequency $\omega_{pr}$. CARS spectroscopy can be used for time-resolved spectroscopy when short laser pulses are employed for excitation and probing of coherent vibrational motions in molecules. In the experiments discussed here, pump and Stokes pulses are always temporally and spatially overlapped in the medium. The simultaneous interaction of the two fields with the sample, results in a coherent excitation (preparation of wave packets) of the vibrational mode $\omega_R$. During the coherence time of the excited vibrational mode $\omega_{pu} - \omega_S = \omega_R$ a probe pulse
Theory

(ωpr) is inelastically scattered from the coherently excited vibrations to generate a coherent pulse at the anti-Stokes frequency ωas.

CARS is a parametric generation process, where both energy and momentum (phase matching) are conserved within the photons. This is expressed by the following two equations:

\[ ω_{as} = ω_{pu} + ω_{pr} - ω_s \quad (2.18) \]
\[ k_{as} = k_{pu} + k_{pr} - k_s \quad (2.19) \]

Equation (2.18) is the energy conservation, while equation (2.19) describes momentum conservation (phase matching). When pump and probe frequencies are equal, i.e. ωpu = ωpr, equation (2.18) can be written as,

\[ ω_{as} = 2ω_{pu} - ω_s \quad (2.20) \]

When the frequency difference ωR between pump ωpu and Stokes ωs frequencies matches the energy gap of a particular vibrational transition, then the oscillators are driven coherently in phase (wave packets) within the focus. The resulting vibrational coherence further interacts with the probe beam to generate a coherent radiation at the anti-Stokes frequency at ωas = 2ωpu − ωs. The variation in time delay between pump-Stokes pair and the probe pulse can be used to study the dynamics of the ground vibrational states as well as in the excited vibrational states.

If ΔT is the temporal separation between probe and pump-Stokes pulses, the CARS signal develops as a function of the delay time ΔT. The time T = 0 means that all the three pulses are reaching the sample at the same time. For ΔT < 0, i.e. negative time delay the probe pulse comes before the time coincident pump-Stokes pulse pair, creates a wave packet in the excited electronic state shown by energy level diagram in figure 2.6.
The evolution of this wave packet is probed by the interaction of the time coincident pump-Stokes pulse pair, after a delay time $\Delta T$ to give the CARS signal.

The signal then oscillates at resonance frequency corresponding to the vibrational energy spacing in the excited electronic state. Similarly for $\Delta T > 0$, the pump and Stokes pulses interact coherently and create a wave packet in the electronic ground state, which is then probed with variable time delay by the probe pulse to get the CARS signal. A sharp peak is observed at $\Delta T = 0$, which is called coherent artifact having a very short life time and occurring due to the non-resonant contributions to the CARS polarization.

### 2.3.1 Non-resonant contribution

The CARS signal intensity for partial degeneracy ($\omega_{pu} = \omega_{pr}$) in terms of third-order nonlinear polarization is given by

$$ I_{CARS} \propto \left| P^{(3)}_{as}(\omega_{as}) \right|^2 = \left| \chi^{(3)}_{asS} \right|^2 I_{pu} I_S $$

(2.21)
Theory

\[ |\chi^{(3)}|^2 = |\chi^{(3)}_{r}(\omega_{as})|^2 + |\chi^{(3)}_{nr}|^2 + 2\chi^{(3)}_{r}(\omega_{as}) \chi^{(3)}_{nr} ] \tag{2.22} \]

\[ I_{\text{CARS}} \propto |\chi^{(3)}_{r}(\omega_{as})|^2 + |\chi^{(3)}_{nr}|^2 + 2\chi^{(3)}_{r}(\omega_{as}) \chi^{(3)}_{nr} |I_{pu}I_{S}^2 \tag{2.23} \]

The first term \( \chi^{(3)}_{r}(\omega_{as}) \) on the right hand side of equation (2.23) is the frequency dependent resonant contribution, which is a source of coherent radiation at the CARS frequency (\( \omega_{as} \)). The second term \( \chi^{(3)}_{nr} \) is the non-resonant contribution, while the third mixing term \( \chi^{(3)}_{r}(\omega_{as}) \chi^{(3)}_{nr} \) (including resonant and non-resonant contributions) is superposed on the resonant signal generated in a nontrivial way, which gives rise to a dispersive line shape of the vibrational resonances in the CARS spectrum. Possible processes are shown in the energy level diagram depicted in figure 2.7.

![Energy level diagram](image)

Figure 2.7 Energy level diagram. Panel (a) shows the resonant contribution to the CARS signal (dotted lines shows virtual states), panel (b) shows a non-resonant contribution, which might become strong due to electronic resonance of two-photon processes, and panel (c) displays the non-resonant contribution in case the pump and Stokes frequency difference is not tuned to vibrational resonance.
The magnitude of the non-resonant background signal shown in panel (b) depends on the excitation lasers and their two-photon resonances with the molecular system and is independent of the Raman shift. In order to minimize this non-resonant electronic contribution to $\chi^{(3)}$ near-IR excitation pulses can be used. By using near-IR excitation, also photochemical damages to the sample can be reduced. The long excitation wavelength also minimizes the Rayleigh scattering in heterogeneous samples and consequently enables large penetration depths for thick samples. Recently, various methods have been developed to reduce the non-resonant back ground signal in CARS including, Polarization-CARS and epi-CARS, etc. Unfortunately, the use of NIR or IR laser pulses does not allow for an access to excited electronic states and therefore this approach is not suited for the experiments described in this thesis.

### 2.3.2 Phase matching in CARS

The intensity of the CARS signal is given by the mathematical expression $^{47}$,

$$ I_{\text{AS}} \propto N^2 \left| \chi^{(3)}_{\text{CARS}} \right|^2 I_p^2 I_s^2 \frac{\sin^2 \left( \frac{\Delta K}{2} \right)}{\left( \frac{\Delta K}{2} \right)^2} \quad (2.25) $$

It is clear from the equation that the CARS signal depends on the following parameters:

- The square of the third-order nonlinear susceptibility
- The square of the the pump intensity
- The square of the number of oscillators
- The Stokes intensity
Theory

- The phase matching function, which presents a sinc function (the signal intensity is high when \( \Delta K \) tends to zero, which is the condition for phase matching; compare figure 2.8).

\[ \Delta k \neq 0 (\Delta k = 2K_{pu} - K_S - K_{as}) \] is called momentum or phase mismatch. The phase mismatch is directly related to the dispersion of the medium. A large mismatch considerably reduces the intensity of the CARS signal. In order to maximize the CARS signal intensity, an adapted wave vector geometry for the interacting beams is required. The BOX-CARS geometry is one of the commonly used arrangements for achieving the phase matching, in which the signal is filtered out from the involved three beams and the generated signal is emitted in the phase matching direction. The BOX-CARS geometry is difficult to be realized in a microscope arrangement. The use of normal lenses with low numerical aperture (NA) can reduce the three dimensional sectioning capability of the microscope. The advantage of filtering the signal spatially could only be used in the far-field and the spatial resolution will be of the order of 100 micrometer. A collinear arrangement is not phase matched and thus reduces the signal intensity. However, using
collinear geometry in combination with a high NA objective can relax the phase matching condition. Both collinear and BOX-CARS geometry are depicted in figure 2.9.

![Diagram of collinear and BOX-CARS geometry](image)

*Figure 2.9 Panel (a) collinear geometry and panel (b) BOX-CARS geometry*

### 2.3.3 CARS microscopy

Like pump-probe spectroscopy, CARS is also used for producing high contrast images in microscopy. The vibrational selectivity in the CARS process makes it useful for images, which provide chemical contrast and high chemical specificity.

CARS microscopy was first reported by Duncan et al. in 1982. They used the non-collinear geometry of pump and Stokes beams from visible pulsed lasers and detected the anti-Stokes signal in the phase matching direction. Andreas Zumbusch et al. in 1999 used a microscope objective with high numerical aperture to focus the beam tightly in a collinear arrangement. In this type of setup the phase matching condition is relaxed due to the short interaction length and large cone of the wave vectors. The nonlinear intensity
Theory

dependence thus produces excitation in a very small region of the laser focus, which also is efficient for the rejection of background signal. In collinear geometry, the excitation fields (pump-Stokes pair) and the CARS signal are in the same direction. Therefore, the separation of the CARS signal from the excitation fields is more difficult and can only be done by spectral filtering.

Tuning the difference frequency, i.e. \( \omega_{pu} - \omega_S = \omega_R \), the unique vibrational spectrum of a molecule can be recorded, which yields the specific vibrational resonances of molecules of the sample and can be used for vibrational imaging. The major difference between CARS and spontaneous Raman microscopy is that CARS is a nonlinear coherent process, where the molecular vibrations in the excitation volume oscillate in phase leading to constructive interference, while the spontaneous Raman process is a non-coherent process. Thus, the CARS signal varies as \( N^2 \) while spontaneous Raman scattering has linear concentration dependence linearly on \( N \), where \( N \) is the number of molecules per unit volume.

Coherent anti-Stokes Raman scattering (CARS) microscopy is an attractive technique to vibrational imaging of biological sample having the following advantages.

1. The intensity of the CARS signal can exceed \( 10^4-10^5 \) times the intensity of the signal obtained from spontaneous Raman scattering.

2. The anti-Stokes signal frequency \( \omega_{as} = 2\omega_p - \omega_S \) is higher than the frequency of the pump and Stokes fields. Therefore, the CARS signal is not affected by a fluorescence background.

3. CARS is more sensitive than spontaneous Raman microscopy, so it requires only moderate average power of excitation.
Theory

4. CARS can easily be used to produce three-dimensional images due to the nonlinearity of the effect.

5. As a nonlinear wave mixing process, CARS also allows for time-resolved experiments when short laser pulses are used for excitation and probing.

CARS microscopy has been proven to be useful for chemical and biological sample imaging, like for example the investigation of lipids in cells. The high density of CH\textsubscript{2} oscillations in lipids results in high CARS signal strengths. Xie et al. used CARS microscopy for vibrational contrast images of lipids in biological systems.\textsuperscript{34,50,54} Since the CARS signal is only generated in the vicinity of the focal volume where the excitation density is high it is an efficient technique for fast three-dimensional noninvasive imaging of tissues. Different important CARS microscopic techniques are Forward-CARS, Epi-CARS, and Polarization-CARS.\textsuperscript{26,51} In forward CARS the signal is detected close to the phase matching direction; it can be so strong that it can even be seen with naked eye. However, as mentioned before, the forward CARS signal also includes a non-resonant contribution from the surrounding material. Since the non-resonant signal does not yield any contribution to the vibrational contrast and due to the nonlinear mixing with the resonant signal part also complicates the resonant CARS spectrum, it usually is an unwanted contribution. In order to avoid the non-resonant contribution, the CARS signal can be detected in the backward direction minimizing the interaction of the lasers with the medium; this geometry is called Epi-CARS. Due to the phase mismatch, Epi-CARS requires strongly scattering samples. Another approach is the use of polarization sensitive detection. Polarization CARS (P-CARS) enhances the image quality by reducing the non-resonant background based on its polarization properties.
Chapter 3

Near Field Microscopy

3.1 Introduction

Optical microscopy is a part of science and is an important method for imaging of small structures for over more than 400 years; it has played an important role especially in cell biology. In the 16th century Hans and Zacharias Janssen invented the first microscope. Robert Hooke and Antony van Leeuwenhoek (1632-1723) had started to work with normal lenses microscope. They later on invented a microscope with magnification of around 300 times. This microscope with high magnification capability was better suited for investigating the microbiology of single cells and bacteria. They observed certain features of plant tissue “cells” in biology. Hooke for the first time used the word “cell” to identify the microscopic structures in microbiology55 and was titled as the father of microscopy. The field of microscopy was modified rapidly with passage of time and has been used as a standard tool for all disciplines of science by providing fruitful information and allowing investigation of samples at ambient conditions.

In conventional optical microscopy, the sample under investigation is illuminated by polychromatic plane waves. After interaction with the sample, light is transmitted or reflected and is collected by an objective lens placed several wavelengths far away from the object surface, which is then imaged onto a detector (in the simplest case, the eye of the observer). At the end of nineteenth century Abbe (1873) demonstrated that the diffraction of light prevents one from resolving two objects that are closer than half the
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wavelength of the illuminating light, which in turn was able to produce only a blurry image. Thus the diffraction limit, present in standard light microscopes, doesn’t allow researchers to resolve features shorter than half a wavelength of the field of illumination.

The low spatial frequencies, contained in the propagating light, can be collected by lens and are diffraction limited due to the Abbe criterion. According to Abbe, the resolution of every optical system is limited by diffraction limit, which is given by the mathematical expression,

$$\Delta d = \frac{0.61\lambda}{NA}$$  \hspace{1cm} (3.1)

Equation (3.1) is the limit of resolution in its simplest mathematical form, in which $\Delta d$ is the resolvable feature size and $\lambda$ is the wavelength of the incident light. Abbe for the first time introduced the term numerical aperture given by $NA = n \sin \theta$, where $n$ is the index of refraction, and $\theta$ is the half angle, over which the objective can accept or collect light from the specimen. From the mathematical expression in equation (3.1) it becomes obvious that the resolution depends not only on the excitation wavelength but also on the numerical aperture. A higher value of numerical aperture enables more light to pass through an objective and resolve fine details of sample features at a fixed object distance. For a numerical aperture of 1, the resolution is limited approximately to half the wavelength of the illuminated light. Theoretically, in order to get a better resolution in conventional microscopy, a light source of very short wavelength e.g ultra violet (UV) and an objective with $NA \approx 1$ could be used to get a resolution of approximately 200 nm. Any object below a size of 200 nm would not be resolved by standard far-field microscopy.
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Using confocal microscopy can improve the resolution in vertical direction (depth resolution). However, the diffraction barrier still plays a role and limits the resolution. This diffraction barrier is a fundamental parameter and arises from the assumption that the detector is placed several wavelengths away from the sample and hence interference effects influence the image resolution. In order to beat the diffraction limit and improve the resolution one can e.g. reduce the detector size (probe) and approach in the near-field zone of the sample of interest, i.e. to distances shorter than the light wavelength. Until now, many research groups have used different approaches to get super resolution and thus a variety of super resolution microscopic techniques have been developed, which overtake the diffraction limit. Stimulated emission depletion (STED) microscopy is one of several types of super resolution microscopy techniques, developed by Hell and Wichmann in 1994.\textsuperscript{58} STED provides very high lateral resolution down to the level of 30 nm and an axial resolution approx. to 50 nm.\textsuperscript{(Reference)} At the end of last year (2014) Erik Betzig, Stefan. Hell and W. E. Moerner have been awarded the 2014 Nobel prize in chemistry for the development of super-resolved fluorescence microscopy.\textsuperscript{59} Another super resolution microscopic technique is photo activated localization microscopy (PALM) technique. This super resolution microscopic technique can achieve a lateral resolution of approx. 30 nm and an axial resolution of 60 nm (Huang et. Al 2008). -Both of the techniques (STED and PALM) are applicable to fluorescent species. The most important ultra-high resolution technique, which is called scanning near-field optical microscopy abbreviated as SNOM or NSOM, provides not only very high lateral resolution of the order of 20 nm (reference) but also can achieve high axial resolution. The use of SNOM with ultrashort laser pulses as a nonlinear microscopic technique can
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provide super resolution beyond the diffraction limit with an advantage that unlike the above two mentioned technique (STED and PALM) the samples under investigation don’t need to be fluorescent.

3.2 SNOM History

In 1928 the Irish scientist Edward H. Synge had published articles which give idea about the ultra-high resolution optical microscope. The concept behind this idea was to use an intense light source to illuminate the sample through a thin, opaque metal film with a 100 nm tiny aperture, placed in optical near-field distance to the sample and observe the transmitted light. The image could be obtained by scanning the tip (aperture) over the sample surface where the resolution in this case depends on the aperture size. The idea proposed by Synge was fruitful, however the basic experimental instruments, for example piezo electric materials, laser and sub-wavelength aperture probe etc. were not invented during his time. In 1972, almost half a century later, Ash and Nicholls for the first time used the same technique (demonstrated by Synge) for microscopy and reported a resolution of $\lambda/60$. They used radiation in the micro-wave region (3 cm) and achieved images with 500 μm resolution of metallic gratings. However, with visible light (400-700 nm) it was still not possible to achieve high resolution because the aperture and sample surface couldn’t be in the lowest possible contact (a few nm) position in the near-field zone.

Scanning probe microscopy (SPM), which allowed for keeping distances between probe and surface in the nanometer range, was invented in 1980, which explored the nano world. It has produced a great revolution in nanotechnology, where sample features in
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nanometer scale were resolved. SPM provides much higher spatial resolution than conventional microscopy system due to the exploitation of near-field, which surpasses the diffraction limit. In SPM local probes are employed that interact in close proximity (few nanometers) to the sample surface.\textsuperscript{61,62} A tremendous development in nanotechnology and its applications in different research fields only became possible due to the influence of SPM, especially in optoelectronic devices such as photonic crystals, quantum dots and carbon nanotubes, etc. In parallel, the SPM as a nanoscopy technique was also developed for the use in other research areas, for example in medical and biological sciences.\textsuperscript{63-66} SNOM became one of the different SPM techniques. It works on the bases of atomic force microscopy (AFM), which is one of two dozen types of the SPM. In the beginning, very few research groups designed and demonstrated SNOM by using small aperture tip or apertureless tip (described in section 3.3) due to its high technical complexity.

In 1984, Pohl et al. demonstrated the first near-field microscopy experimental setup, where high resolution could be achieved, using the sub-wavelength aperture at the apex of a transparent tip. The tip was coated with a metallic film for high collection efficiency.\textsuperscript{67} The sub-wavelength aperture was illuminated with a laser and the transmitted light intensity through the target sample was recorded. The sample in this case is scanned in close proximity (few nanometers) relative to the fixed probe, where the vertical distance is controlled by a feedback mechanism. These authors claimed a resolution of $\lambda/20$ using an excitation wavelength of 488 nm. Lewis et al., in the same year (1984) independently built and demonstrated the first near-field optical microscope by using an aperture type tip, and achieved a resolution down to $\lambda/10$ at 488 nm.\textsuperscript{68}
Near Field Microscopy

In 1991, Betzig et al. employed a single mode optical fiber which is the widely used popular probe today.\textsuperscript{69} One year later, Betzig and Trutman used the aperture SNOM for investigation of fluorescence imaging of biological samples beyond diffraction limit.\textsuperscript{70} SNOM that provides us with eyes for the nano world is a combination of light microscope and SPM which exploits the evanescent field at the material surface. The evanescent waves are non-propagating waves and can be detected in the near-field zone before diffraction occurs. Thus, in near-field microscopy the resolution does not depend on the illuminated light wavelength but strongly depends on the size of the local probe, which collects (or excites) the evanescent field, and hence allows sharp and much better image resolution than obtained by conventional microscope.\textsuperscript{61,71-77}

3.3 Types of SNOM

The two important types that localize the optical field in a controlled manner are the so-called (a) aperture SNOM and (b) aperture-less SNOM

3.3.1 Aperture SNOM

In this type of SNOM, small apertures of diameters in the range of typically 50-250 nm, i.e. smaller than the half wavelength of visible light, are used. SNOM can achieve not only very high lateral resolution, but also high axial resolution that can be achieved through the collection of light in near-field. In a SNOM setup, one can implement a technique in the near-field where the scattered light from the sample is collected with a tip with a nano sized aperture in close proximity to the sample (5-10 nm) or use the small aperture to illuminate the sample. At very close proximity to the interface of the sample, there are not only the propagating plane waves (which can be observed in the far-field)
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but also exponentially decaying evanescent waves are present in the near-field zone. The evanescent field can provide high resolution only if it is “collected” within its decay length (several nanometers). The near-field and far-field regions are clearly illustrated in figure 3.1

![Near Field Microscopy Diagram](image)

*Figure 3.1 Scheme for the basic principle of sub-wavelength resolution in near-field (SNOM)*

The most important part of the near-field scanning optical microscope is the sub-wavelength aperture (collector). The light collector collects light from an excited small area and then guides the transmitted light to a detector. The other possibility is that light passes through a small aperture and then illuminates a sample placed within its near field zone. In our experiments we employed collection mode geometry to avoid the broadening of the femtosecond laser pulses due to dispersion in the glass fiber used for transmission. The SNOM light collector in most cases consists of an optical glass fiber coated with a metal, having a tapered part with an aperture at its end. A typical tapered tip with an aperture is shown in figure 3.2
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Figure 3.2 Schematic diagram of collection mode of aperture SNOM

In the taper region the diameter of the fiber becomes smaller so that, the modes of a given wavelength cannot freely propagate and become evanescent (the cut off frequency). This results in an exponential decrease of the light intensity. In order to achieve high throughput a short apex and a large taper angle is essential.

The aperture size is a key feature of the SNOM tip and is responsible for high resolution; therefore, elaborate techniques are involved to produce the tip as small as possible. A typical method implemented is the so called “heat pulling” where the fiber glass is heated with a CO$_2$ laser and its edge is uniformly pulled in a controlled way to form a conical structure. The SNOM tips fabricated by using this technique are very sharp and have elongated apex and small taper angle, which leads to low light throughput. The optical fiber acts as a waveguide for the evanescent field that takes information to the detector in the far-field. The optical fiber consists of a core and cladding, where the cladding medium has a smaller index of refraction, allowing for a total internal reflection inside the fiber and “guiding” the light. For minimizing the transport losses along the fiber, an opaque metal film aluminum (Al) or gold (Au) can be used. Further coating with
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chromium of can be applied to protect these metal coatings. Characteristic for the material (Al or Au) is the small penetration depth of electromagnetic fields. Nevertheless, the coating thickness also imposes limitations on the aperture size. In order to prevent penetration of waves through the walls of the tip, the metal film has to have a well-defined thickness on the order of \( \text{in the range from } 100 \text{ to } 200 \text{ nm, } (\text{nanonics provided us tips with metal coating of approx. } 200 \text{ nm}) \) which widens the effective tip size.

The other technique to make the probes is chemical etching, in which the fiber is dipped into HF solution covered with an over layer of an organic solvent and the end tip of the fiber is formed at the interface of HF and organic solvent at the meniscus. The characteristic of taper angle can be controlled and can be optimized by changing the etching solution and in this way it overcomes the major problem caused by the pulled tips process.

3.3.2 Aperture-less SNOM

The aperture-less type of SNOM uses a sharp metallic probe with a dimension much smaller than the wavelength \( (d < \lambda) \) of light without using the optical fiber implemented in the aperture type of SNOM. The probe consists of a normal AFM tip having a metallic ball at its apex. The metallic nano-particles are found to generate strong electromagnetic fields in the optical near-field range. This localized field enhancement effect is induced due to the surface plasmon excitation at resonance wavelength. In addition the lightning rod effect can also enhance the field close to the strongly curved nano feature. The geometry and type of metal nano particles play a crucial role for the collective response of free electrons and can greatly enhance the field strength of the incoming
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radiation at the tip apex (where the metal nanoparticle is attached). The signal generation at the metal tip thus provides a strong localized field, which can be used to produce high resolution images. The most important and well known metals are gold (Au) and silver (Ag) that are nonlinear materials and cause higher harmonic generation, when energized with laser pulses of high peak powers. In order to implement such a resonant field enhancement effect, a metallic nano-particle could be attached to the end of an AFM tip which scans the sample surface to generate images with resolutions better than those achieved using aperture based SNOM. However, image interpretation can become problematic.

Figure 3.3 Schematic diagram of an apertureless SNOM where a small nanoparticle of Au or Ag is attached to the tip apex

3.4 SNOM implementation

As already emphasized, not only the tip size but also the tip-to-sample distance is important for near-field microscopy. For maintaining a constant distance of the tip over the sample during the scan, a normal force feedback mechanism can be implemented. Normally in tapping mode, the tip is driven to oscillate with a certain resonance frequency above the sample surface. In order to maintain a constant distance between the tip and sample during the scan, a normal force feedback mechanism can be
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The principle is based on the van der Waals forces occurring between tip and sample at very short distances.\textsuperscript{82,83}

Initially, the tip (attached to tuning fork) is oscillating perpendicularly to the sample surface, with a resonant frequency typically in the range from 30 to 40 KHz. As long as the tip is far away from the sample surface, the amplitude, frequency and phase of the oscillation are constant. When the tip approaches the sample surface, a change in the resonance frequency leads to a change in phase and amplitude. The motion of the tip on the sample surface can be controlled by using feedback mechanism (phase feedback or amplitude feedback). In our case, the SNOM tip is attached to an oscillating tuning fork.

Information about the distance of the tip to the sample is given by a piezoelectric crystal, which is capable of generating a voltage proportional to a corresponding applied stress. Initially, the tip (attached to tuning fork) is oscillating perpendicularly to the sample surface, with a resonant frequency typically in the range from 30 to 40 KHz. As long as the tip is far away from the sample surface, the parameters like amplitude, frequency and phase of the oscillation are not perturbed. When the tip approaches the sample surface, a change in the resonance frequency of the tuning fork is observed. The change in resonance frequency leads to the change in phase and amplitude. The motion of the tip on the sample surface can be controlled by using the feedback mechanism (phase feedback or amplitude feedback).

The phenomenon can be described by classical mechanics, modeling the system as viscously damped oscillator. The simplest expression for Hooke's law is

\[ F(Z) = m \frac{d^2Z(t)}{dt^2} = -kZ \quad (3.10) \]
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In a perturbed system, there are two additional forces besides the tension in the tuning fork, which affect the motion of tuning fork and hence the tip, they are the damping and driving forces.

Damping is a friction force and is given by

$$F_{\text{damping}} = -b \frac{dZ(t)}{dt} \quad (3.11)$$

and the driving force given by piezoelectric crystal on the cantilever is given by the expression

$$F_{\text{driv}} = F_0 \cos(\omega_d t) \quad (3.12)$$

Summing up the forces, one can approximate the system as a driven damped harmonic oscillator

$$\Sigma F = F_{\text{tfork}} + F_{\text{damp}} + F_{\text{driv}} \quad \text{so,}$$

$$m \frac{d^2Z(t)}{dt^2} + b \frac{dZ(t)}{dt} + kZ(t) = F_0 \cos(\omega t) \quad (3.13)$$

The above equation is a second order differential equation and the corresponding solution for the amplitude is:

$$Z(t) = \frac{k\omega}{(\omega^2 + \omega_0^2 \pm \sqrt{(\omega^2 + \omega_0^2)^2 - 4k\omega})} \cos(\omega t) \quad (3.14)$$

$$Z(t) = \frac{(F/m)\exp^{-i\omega t}}{(\omega_0^2 - \omega^2 - i\omega b \omega)} \quad (3.14)$$

Where "b" is the viscous damping factor, k is the spring constant, $\omega_0$ is the resonant frequency and $\omega$ is the angular driving frequency. The amplitude of oscillation mainly depends on tip-to-sample surface distance, and can be used effectively as a feedback signal.
Near Field Microscopy

When the tip is in contact to the sample surface, a shift in the resonance frequency can be detected due to the force gradients of the interactions between the tip and sample surface. The shift in resonance frequency can produce change in the amplitude and phase of the vibration, which is used as a feedback signal and can be controlled by feedback loop mechanism. In our NWS software (provided by Nanonics), we have an option of amplitude and phase feedback. Normally we are using phase feedback mechanism, because it is more sensitive and the corresponding signal provide better image contrast.

The force gradient between tip and sample surface change the effective spring constant and is given by $K_e = K - F$, where the force gradient $F$ in the $Z$ direction is expressed as,

$$ F = \frac{dF_z}{dz} $$

The force gradient changes the spring constant $K$ and thus induces a shift in the resonance frequency of the tip (reference). The resonance frequency of the tuning fork (to which the tip is attached) in the presence of force gradient can be written as,

$$ \omega = \sqrt{\frac{K_e}{m}} = \sqrt{\frac{(K-F)}{m}} \quad (3.15) $$

For small force $F$ compared to $K$, equation (3.15) can be expressed as

$$ \omega = \sqrt{\frac{K}{m}} (1 - \frac{F}{K}) \approx \omega_0 \left(1 - \frac{F}{2K}\right) \quad (3.16) $$

When the force of attraction between tip and sample surface increases, $F$ is positive and the resonance frequency decreases.

Typically, one can impose a limit for the ratio between initial amplitude and amplitude during damping. This would correspond to the height of interest and once this limit is reached, the approach of the tip will cease and constant height is kept.
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3.4.1 Operation modes

Despite of many technical problems (including heating, defects due to manufacturing process, sensitivity, etc.) aperture SNOM has become a very popular method and can achieve high resolution images. The aperture type SNOM operates in different operational modes depicted in figure 3.4.

![Figure 3.4 Schematic illustration of different modes [(a)-(e)] of aperture SNOM](image)

In figure 3.4, panel (a) shows the transmission mode aperture SNOM. In this case, the light is transmitted through the sample after illumination and is detected e.g. by an avalanche photo diode (APD) or photo multiplier tube (PMT). Panel (b) shows the transmission illumination/collection mode in which the tip is used to illuminate the sample and the light signal through the sample and is collected by the probe and is sent to the detector. Panel (c) shows the illumination collection mode imaging scheme. Panel (d) shows the reflection mode imaging, in which light sent through the tip is reflected and then collected externally. Panel (e) shows the reverse case. The sample is illuminated from the top and the scattered signal is collected by the SNOM tip.
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3.5 SNOM techniques applied to organic semiconductors

After the invention of SPM, the field of nanotechnology has further advanced. The word “nanostructure” is defined as a structure at the atomic or molecular level in a size range of 100 nm or less, which cannot be resolved even with high numerical aperture conventional optical microscopes. Properties of nano-structures are partially different from those of bulk material and a detailed investigation is therefore very important e.g. for improving device performance. An optical access is possible in the near-field, since as was already pointed out earlier conventional far-field optical microscopy is diffraction limited and is not able to resolve the nano structures. The use of SNOM can be especially useful for studying inhomogeneous materials or surfaces, like nano particles and polymer blends. Semiconductor devices have already been studied by SNOM. As an example, Nechay et al. have performed a combined femtosecond pump-probe and SNOM experiment to investigate carrier dynamics in inorganic semiconductor GaAs/AlGaAs single quantum well samples and demonstrated that the high spatial resolution provided by SNOM allowed to observe the effect of lateral carrier diffusion on the exciton dynamics. In our studies, we have employed the SNOM technique to study exciton dynamics in different organic semiconductor systems, and achieved interesting results, which are discussed in chapters 5 and 6.

3.6 Our SPM system

Our scanning probe microscope (SPM set-up) offers the possibility to use and combine different microscopy techniques. It consists of an integrated system, in which a SPM is integrated into a twin-microscope, i.e. a combination if upright and inverted optical microscope. The SPM is placed between the two objectives of these microscopes.
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and the scanning probe is designed such that it can be accessed optically from top and bottom. For transmission mode, the bottom objective is used to focus the light on the sample surface, while the top long working distance (LWD) objective is used to collect the far-field light and send it to the detector. For reflection mode the top objective is used both for focusing and collection of the signal. Both the objectives used in the experiments are having magnification of 10x and numerical aperture of 0.25 (other objectives are possible, but have not been used).

The inverted microscope (parts from Olympus Corporation, Tokyo, Japan) is combined with a scanning probe microscope (SPM) system (Multiview 2000, Nanonics imaging Ltd), which can be used for both AFM and SNOM imaging. The sample of interest can be placed on an XYZ translator stage controlled by a piezo controller. The main parts of this set-up are described in the following subsections.\(^{32}\)

### 3.6.1 Multiview 2000 tower

The tower, as shown in figure 3.7, consist of an upper scanner (the tip is mounted to this scanner that can scans the sample surface), Z stepper motor, XY stepper motors, pre-amplifier and electrical connectors for these scanners. The tip approaches toward or away from the sample surface by the Z stepper motor in a controlled way. The motion of the stepper motor can be viewed in the glass window on top of the tower as can be seen in figure 3.7. There is a lower scanner below the upper scanner on which the sample of interest can be placed. The lower scanner can move the sample in the XY plane; it is controlled by two stepper motors. In this setup the tower and the lower scanner stage are placed on an interface plate. The interface plate is placed on the XY stage of the inverted optical microscope. The tower can be rotated manually to mount the tip using the
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fastening screw part, which requires a large preparation effort and is depicted in the bottom panel of figure 3.5

![Figure 3.5 Top panel: Tower with upper scanner. The upper scanner includes the tip, which is displayed in the bottom panel.](image)

3.6.2 SPM controller

The SPM controller is the heart of the system. The rear panel of SPM controller has a controller card, which is used for controlling the feedback of scanner and a lock-in amplifier card for signal processing.

The front panel of the SPM controller has a mode selector (contact mode or intermittent contact mode) and feedback-gain control knobs. A proportional-integral-differential (PID) control circuit is used to control the z-piezo (attached to the tip) to hold the tip at a set point by generating an error signal (error signal = set point – current value of the signal). The error signal is processed by the SPM controller through a lock-in amplifier.
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and the PID feedback gains. The output of the controller unit is used to control the Z position of the probe. For driving the piezo scanner a HV amplifier stage is used. The block diagram for the control circuit is given in figure 3.6

![Block diagram SPM control unit](image)

**Figure 3.6 Block diagram SPM control unit**

### 3.6.3 High Voltage Piezo Driver (HVPD)

The high voltage piezo drivers control the displacement of the stage, and that of the probes in three dimensions through the NWS software provided by Nanonics. The HVPD supplies a high voltage signals from the SPM controller to move the piezo crystals in the scanners. On the front side of the HVPD, the voltages given to the X, Y and Z axes are displayed (left panel of figure 3.7). During the scan, these values are monitored and can
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be adjusted by the respective potentiometer knobs (if necessary) that adjust the channels internal voltages. The Piezo Driver can operate in different modes, including positioning mode, scan and offset mode, and scan and slope compensation mode.

3.6.4 Low Voltage Adaptor
The low voltage adaptor is used to allow for the selection of either tip or sample scanning and z-feedback components.

3.6.5 DT Interface
The data translational (DT) interface houses the electronic connections providing an interface between the data translational card in the computer and the SPM controller and scanner. The HVPD is also attached to the DT interface.

3.6.6 System Power Supply
The SPM Controller, DT Interface, and HVPD are connected to the power supply. The front panel of power supply has a power LED indicator only while the rear panel includes three outputs. Output 1 is used for HVPD, output 2 for the SPM controller, and output 3 for the DT Interface.

3.6.7 Probes
Nanonics provides us with probes of different sizes. The SNOM probes are attached to a tuning fork and an optical fiber having a length of 300 cm. The complete probe ensemble is stored in transparent boxes as depicted in figure 3.8. The probe parameters (tip size, resonance frequency, Q-factor) are labeled on the boxes. The other end of the fiber has a
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connector, with which the fiber output is coupled to a collimator. The signal guided through the fiber is then finally directed to the detector.

The whole system including SPM controller, HVPD for upper and lower scanner, etc. is depicted in figure 3.7

![Figures showing system setup](image)

Figure 3.7 Complete Multiview 2000 system setup

![SNOM tip image](image)

Figure 3.8 SNOM tip having an aperture of 200 nm, with tuning fork and fiber (3m).
Chapter 4

Experiment

The first section of this chapter describes the generation of femtosecond laser pulses and their amplification based on chirped pulse amplification (CPA). The pulse characterization, the tuning wavelength units, and the related experimental setup for pump-probe and CARS microscopy are discussed subsequently.

4.1 Generation and amplification of femtosecond laser pulses

Many dynamical processes in different systems, like exciton relaxation in organic semiconductors, or charge transfer processes in molecular nanostructures, can occur on a picosecond (ps) and femtosecond (fs) time scale.\textsuperscript{23,37,85-87} In order to investigate such ultrafast processes, ultrashort laser pulses (typically, femtosecond laser pulses) are required.

Generally, the femtosecond laser pulses are generated by the mode locking technique, which is based on the interference of distinct longitudinal modes (q, q+1...and so on), which are fixed in phase (“mode locking”), inside a laser cavity.

For example, assuming a laser cavity of optical length ‘L’, the two modes q and q+1 would have the wavelengths $\lambda_q$ and $\lambda_{q+1}$ given by\textsuperscript{3,30,36}

$$\lambda_q = \frac{2L}{q} \quad \text{and} \quad \lambda_{q+1} = \frac{2L}{q+1}$$

The resonant frequencies of these two resonant modes in terms of speed of light $c$ and cavity length are

$$\nu_q = \frac{c}{\lambda_q} = \frac{qc}{2L} \quad \text{and} \quad \nu_{q+1} = \frac{c}{\lambda_{q+1}} = \frac{c(q+1)c}{2L}$$

The difference in these two frequencies is
Experiment

\[ \Delta \nu = \frac{c}{2L} \quad (2.14) \]

The laser output provides “wave packets” obtained from the constructive interference (when modes are in phase) of longitudinal modes inside the laser cavity and a series of pulses occurs with a period of

\[ T = \frac{2L}{c} \]

where \( T \) is equal to the time of the round trip in the optical cavity. The longitudinal modes are equally spaced along the frequency coordinate. Starting from the fundamental mode there are an infinite number of overtones allowed in the cavity. However, only a certain number “\( N \)” of modes are generated in the cavity of length \( L \) due to the amplification profile of the laser active medium, resulting in a pulse is produced due to constructive interference. The gain curve and the excited modes are depicted in the bottom panel of figure 4.1

Figure 4.1 The upper panel shows the equally spaced theoretically allowed longitudinal modes of the laser resonator of length \( L \). The bottom panel shows the situation due to the gain profile of the laser active medium. The output spectrum is restricted and determines the pulse length in case of mode locking.

The single pulse temporal duration is then given by
Experiment

\[ t_p = \frac{T}{N} = \frac{2L}{cN} \quad (2.15) \]

The pulse temporal width thus depends on the number of active longitudinal modes and
the length of the cavity (spacing of modes). For a large number of longitudinal modes
“N”, shorter pulses are generated. The shortest pulse duration is possible only when all
the longitudinal modes are in phase and produce constructive interference. The pulse
temporal width and the spectral bandwidth of short pulses are linked by the Fourier
transform relation between time and frequency domain and is given by

\[ f(t) = \int_{-\infty}^{+\infty} g(\omega) e^{-i\omega t} d\omega \quad (2.16) \]

\[ g(\omega) = \int_{-\infty}^{+\infty} f(t) e^{i\omega t} dt \quad (2.17) \]

The functions \( f(t) \) and \( g(\omega) \) are the Fourier transformed functions of one another.\( f(t) \) is a function with duration of \( \Delta t \) and \( g(\omega) \) is a function with spectral width \( \Delta \omega \).

The Fourier transform relation between the spectral width \( \Delta \omega \) and the pulse width \( \Delta t \)
depends on the pulse shape. The product of pulse length and bandwidth is given by the
Fourier transform limit relation,

\[ \Delta \omega \Delta t \geq K \quad (2.18) \]

Equation (2.18) gives the lower limit of the product of pulse duration \( \Delta t \) and spectral
bandwidth \( \Delta \omega \).\(^{30} \) For different pulse shapes different values of \( K \) result. For example, its
values are 0.140, 0.142, 0.515, and 0.441, for an exponential, Lorentzian, sech\(^2\), and
Gaussian shape, respectively.\(^{30} \)

The energy of the femtosecond laser pulses produced in standard femtosecond laser
systems (“oscillator stage”) is very small and often in the range of nano Joules only; in
amplified laser systems, it can however be amplified to e.g. milli Joules, which is
required especially for many nonlinear optical effects.
Experiment

Our femtosecond laser system work on the bases of above principle, where the pulses from the oscillator (ring fiber laser oscillating at 40 MHz) at 100 fs have energies of less than one nJ and are then amplified to mJ. This amplification can be done by a compact laser system (Clark-MXR CPA 2010) where the chirped pulse amplification (CPA) technique is used to amplify the femtosecond pulses generated by the oscillator. As mentioned above, the energy of the laser pulses generated by the femtosecond laser oscillator lies in the range of nJ, which is not enough for many spectroscopic applications and needs to be amplified. However, the peak power of the short amplified femtosecond laser pulses easily can damage the gain medium and other optics inside the laser, which prevents a straight-forward amplification of such pulses e.g. to the mJ range. This problem can be solved by stretching the pulses by introducing linear chirp before amplification (in our case by a factor of approx. $10^4$), which ultimately reduces the peak power.

The four major parts of our laser system are the SErF (Erbium-doped fiber) fiber oscillator, the pulse stretcher (for chirped amplification; both situation in the bottom level of the laser housing), Ti-Sapphire regenerative amplifier pumped by a Nd:YAG (neodymium-doped yttrium aluminum garnet) laser, and pulse compressor (top level of laser housing) as depicted in figure 4.2. The SErF fiber laser (ring laser) is pumped by a continuous wave laser diode at 980 nm. After pumping, the fiber laser emits pulses at 1550 nm. After frequency doubling to 775 nm, the pulses are stretched to approx. 200 ps to avoid the damage to the amplifying gain medium and other optics in the cavity. The stretched pulse acts as a seed and is guided to the top level of the laser system, where it is amplified in the regenerative amplifier. The regenerative amplifier consists of a
Experiment

Titanium-Sapphire (Ti:Sapphire) crystal as gain medium and a Q-switched Nd:YAG laser with 10 ns pulses with 7.6 Watt power at 1 kHz repetition rate for pumping the gain medium in the laser cavity. The Nd:YAG laser itself is pumped by a flash lamp (approx. 25 A current) and has its emission at 1064 nm. This output of the YAG rod is frequency doubled to 532 nm by using a KTP crystal (Potassium titanyl phosphate). The green output at 532 nm is then used to resonantly pump the Ti:Sapphire crystal. The seed pulse at 775 nm is injected into the amplifier, using a time gated polarization device (Pockels cell) triggered by the 1 kHz repetition rate of the ND:YAG laser. I.e., from the many pulses the oscillator produces (repetition rate in the MHz range) only few pulses are amplified. The pulses remain inside the amplifier cavity for several round trips where they are amplified with each pass through the Ti:Sapphire crystal to attain maximum amplification by reaching saturation (this also reduces the intensity noise of the output). The pulses after saturation are coupled out again using the Pockels cell. The amplified beam at the last stage is then recompressed by means of a setup using a transmission grating to approx. 150 fs pulse length.
Experiment

After amplification and compression each pulse has energy of 1 mJ at a repetition rate of 1 KHz. The specifications and the block diagram of our femtosecond laser system are shown in table 4.1 and figure 4.3, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central wavelength</td>
<td>775 nm</td>
</tr>
<tr>
<td>Pulse width</td>
<td>150 fs</td>
</tr>
<tr>
<td>Power output</td>
<td>1 Watt</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>1 KHz</td>
</tr>
</tbody>
</table>

*Table 4.1 Output characteristics of the Clark-MXR, CPA 2010 femtosecond laser*
The peak powers of such pulses are very high in the range of $10^{12}$ W. The intensity for a pulse with 1mJ energy from our CPA laser system with pulse width of 150 fs when focused to a spot with diameter of 0.1 mm is about 84.96 TWcm$^{-2}$ (TW = Terra Watt = $10^{12}$ Watt). The high peak powers and high intensities of such ultrashort laser pulses are ideally suited for generating non-linear optical processes and can be used to monitor the ultrafast interaction in atoms, molecules, and other ultrafast chemical reactions taking place in different systems.
4.2 Optical Parametric Amplifiers (TOPAS)

Two multi-pass travelling optical parametric amplifiers (Light conversion TOPAS) are used in order to generate the required wavelengths for different experiments. The CPA output is divided into two beams using a 50:50 beam splitter, which pumps two optical parametric amplifiers (OPAs). The OPA-system generates wavelengths in the UV-Visible-IR region by a combination of different nonlinear optical effects (computer controlled).

The basic effect uses is the optical parametric generation (OPG), which converts the incoming CPA pulse in a non-linear crystal inside the OPA into a signal and idler pulse according to the conservation of energy, i.e. \( \omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}} \) or for the wavelengths \( \frac{1}{\lambda_{\text{pump}}} = \frac{1}{\lambda_{\text{signal}}} + \frac{1}{\lambda_{\text{idler}}} \). By tuning the phase matching angle, a large spectrum of infrared wavelengths can be generated. The CPA output also pumps amplification stages yielding sufficient output powers. For conversion to wavelengths in the visible range, additional non-linear crystals are used to produce second harmonic generation (SHG) or sum frequency generation (SFG) involving signal, idler and pump pulses. Thus the tuning range of the wavelength is extended to 270 – 2,700 nm. The output pulses from the two TOPAS are compressed through prism compressor units down to 80-90 fs.

4.3 Pulse characterization

The pulses have to be characterized. For the measurement of the spectrum, a standard monochromator setup is used. Since the pulses are compressed to pulse lengths close to the Fourier transform limit a characterization of the chirp of the pulses was in most cases not required. A four-wave mixing frequency-resolved optical gating (FROG) system was
Experiment

used for this purpose, but is not described here. As no electronic detector is able to temporally resolve the intensity of the ultrashort laser pulses, in order to find the pulse duration an autocorrelator was used. The autocorrelator (Mini, APE) measures the temporal length of the pulses by overlapping them with their own replica. The autocorrelator is based on the principle of a Michelson interferometer. Here, the output of the Michelson interferometer is frequency doubled the second harmonic is measured by a detector as shown in figure 4.4.

![Interferometric Autocorrelator Diagram](image)

*Figure 4.4 Setup of interferometric autocorrelator. The incident laser beam is split into two using a beam splitter and directed towards the arms of a Michelson interferometer. The beam is focused onto a BBO crystal that generates a sum-frequency signal detected after filtering by a photodiode.*

Initially, the incoming beam splits into two parts in the interferometer. At one of the lever arms of the interferometer along which the beams are propagating, a movable mirror is placed, which produces a time delay between the two outgoing beams. The two beams are then passed through a non-linear crystal, where the beams temporally overlap and
generate the sum frequency of the two. The intensity of the sum frequency signal is monitored at the detector as a function of the time delay between the pulsed beams. The autocorrelation function is fitted with an envelope function (e.g. Gaussian or sech^2), from which the pulse width is deduced.

After measuring the pulse width before and after compression using the autocorrelator, the pulses can be passed through Berek compensators (BC), where the polarizations of these pulses can be adjusted.

The so generated beams (e.g. pump, Stokes, and probe for a CARS experiment) then hit retro-reflecting mirrors, which are mounted on computer-controlled translation stages. In a Michelson-like arrangement this allows for the temporal delay of the pulses via the change of their optical path lengths. For the microscope experiments, the laser beams are made collinear by using a beam splitters. The collinear pulses are then pair-wise focused into a cuvette filled with CS₂ to find time zero by measuring the optical Kerr effect (OKE) produced when both pulses interact with the molecules at the same time.

After finding the time coincidence (time zero) with the desired wavelengths the pulses are used for the pump-probe or coherent anti-Stokes Raman scattering (CARS) experiments.

4.4 Far-field experimental setup

After finding time zero the collinear beams are coupled into the inverted microscope (see description above). The beam is focused onto the sample surface by using a 10x objective having a numerical aperture of 0.25 from the bottom having a focal spot size of ≈ 5 μm. The transmitted probe signal in case of a transient absorption pump-probe experiment or CARS signal in the case of a CARS experiment is collected and collimated by the
Experiment

objective (10x, NA 0.25) of the upright microscope as depicted in figure 4.5. Edge filters are used to filter the transient absorption/CARS signal from the other pulses before detection by an avalanche photo diode (APD; STM1DAPD 10, Amplification technologies, USA). A boxcar amplifier was used to reduce the noise and background signals.

4.5 Near-field experimental setup

In the near-field setup the collinear beams are again coupled into the inverted microscope fitted with the SPM system (Nanonics Multiview 2000; description see above). The sample is placed on the XYZ translator stage of the SPM, controlled by piezo actuators. The inverse microscope focusses the laser pulses into the sample (the focal point can be moved along the sample axis e.g. close to the sample surface) with the objective lens (Olympus PLAN N 10x, NA=0.25) positioned below the sample.
Experiment

The SNOM tip is positioned above the sample in axis with the focal point. Nanonics provided the cantilevered optical fiber SNOM tips with different aperture sizes ranging from 50 to 300 nm. The tip is coated with a thin film of Au of 0.2 μm thickness, which increases the collection efficiency of the tip and also contributes a surface enhancement effect as will be discussed later. The attached multimode optical fiber extension guides the collected near-field signal towards the filter and detector as described above for the far-field experiment. The fiber tip could additionally be used to record the AFM topography of the investigated sample with a spatial resolution limited by the SNOM tip diameter.

Figure 4.6 The near-field pump-probe and CARS experimental setup
4.6 Systems under investigation

Different organic semiconductors have been investigated. In the following they are shortly described.

4.6.1 Perylene tetra carboxylic dianhydride (PTCDA)

Time-resolved spectroscopy using SNOM techniques have been done earlier on inorganic systems based e.g. on Gallium arsenide (GaAs). Here, we have implemented, for the first time, the pump-probe SNOM technique to investigate the dynamics and chemical imaging in an organic system. We have chosen PTCDA as one of the model systems because of the following properties:

1. Being a perylene derivative, PTCDA it is highly stable molecule. Other organic or biological molecules that are of immense interest, like polystyrene, chlorophylls or carotenoids are rather unstable to work with using high intensities.

2. PTCDA has a very high absorption cross section. In addition its energy levels and bulk reaction dynamics are well known.

3. PTCDA molecules form well-ordered layers in various substrates and therefore are interesting model systems in the field of organic electronics.

4. Being an organic semiconductor, PTCDA has been used for field effect transistors and photo voltaic devices.

Figure 4.7 The left panel shows well-ordered layers of PTCDA on a substrate and the right panel displays the molecular structure and molecular formula

\[C_{24}H_{8}O_6\]
4.6.2 Poly 3-hexylthiophene (P3HT)

Another model sample, which is frequently used in our experiments, is Poly 3-hexylthiophene (P3HT; C_{10}H_{14}S). It is an organic semiconductor and can be applied particularly for solar cells. Besides for solar cells it is also used in transistors and other electronic devices. P3HT is a very promising organic semiconductor having the following properties:

1. The energy levels of P3HT are well studied, therefore allowing for the exact tuning of the frequencies of the laser pulses used for pump or probe interaction.

2. P3HT is a promising candidate for organic solar cells especially when it is blended with phenyl C_{61} butyric acid methyl ester (PCBM. In this case, P3HT acts as donor while PCBM acts as acceptor in the semiconductor device. Besides for solar cells, it is also used in transistors when in contact with metals.

3. It possesses high third-order nonlinearity.

4. It has a high optical damage threshold.

5. It has a strong Raman-active mode at 1450 cm\(^{-1}\).

Figure 4.8 Structure of Poly (3-hexylthiophen-2,5-diyl) (C_{10}H_{14}S)\(_n\) polymer
Chapter 5

**Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field**

Femtosecond time-resolved spectroscopy has been combined with scanning near-field microscopy to study the exciton dynamics in perylene tetracarboxylic dianhydride (PTCDA) and at the gold-Poly 3-hexylthiophene diyl (Au-P3HT) contact. We demonstrate that the SNOM technique is a powerful tool that provides information about nanostructures, which cannot be obtained from far-field microscopy.

5.1 Exciton dynamics in perylene tetracarboxylic dianhydride (PTCDA)

5.1.1 Introduction

Organic semiconductors play an important role in opto-electronic devices such as light emitting diodes (LEDs), solar cells, and field-effect transistors (FETs), etc. due to their low cost, light weight, and small sizes. In solar cells, light excitation creates electron-hole pairs (electron in LUMO and hole in HOMO) forming excitonic states. The generated excitons in the active medium separate due to the energy offset between the lowest unoccupied molecular orbital (LUMO) or conduction bands of the donor and highest occupied molecular orbital (HOMO) of the acceptor materials. After dissociation, the electron migrates to the acceptor, while the hole remains on the donor, and is then collected at the respective electrodes. If some defects, like traps, etc. are present in the active medium or at the contacting interface, unwanted charge recombination would make the transport of charge carriers inefficient and the cell performance decreases (low current). Besides other processes, the exciton-exciton annihilation could also reduce the
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field device performance especially in optical light emitting diodes (OLED)\(^{90}\) where the singlet-singlet annihilation is a responsible mechanism for this loss. Therefore it is important to understand the annihilation process in detail and to look for the parameters, which cause annihilation that consequently affects the device performance. In order to study the exciton dynamics and especially the exciton-exciton annihilation mechanism, the organic semiconductor 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) as a model system has been considered. Among different organic semiconductors, PTCDA was extensively studied using different techniques. Dai-suke et al. reported the ultrafast excited state dynamics in PTCDA thin films.\(^{91,92}\) Engel et al. used femtosecond pump-probe spectroscopy to study ultrafast relaxation and exciton-exciton annihilation in thin films of PTCDA using high pump excitations.\(^{39}\) Yago et al. investigated self-trapping exciton diffusion in β-perylene crystals using ultrafast transient absorption microscopy.\(^{23}\) On the bases of known properties of PTCDA described in section 4.6.1 of this thesis and in reference 23, the exciton dynamics in PTCDA thin film have been further investigated in the near-field. It is important to note at this point that Yago et al. has used far-field spectroscopic technique where only the average information could be obtained. So the far-field technique could not provide the local details of hidden nanostructures that have significant importance in electronic device performance.

As was mentioned above, SNOM is a powerful microscopic technique that beats the diffraction limit providing very high spatial resolution images.\(^{67,84,93,94}\) Different research groups combined the time resolved pump-probe technique with SNOM for investigation of ultrafast dynamics in different systems like quantum wires, quantum dots of inorganic semiconductors especially in GaAs.\(^{95-98}\) The organic semiconductor PTCDA is an
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field attractive model system also for optical electronic devices. Since nanostructures and interfaces play an important role in these devices, it is essential to study the optical properties of PTCDA also using near-field techniques.

We have combined femtosecond time-resolved pump-probe spectroscopy with SNOM in order to investigate exciton dynamics in PTCDA, which take place in picosecond and femtosecond time scale.99

Thin films of PTCDA having a thickness of 160 nm, composed of nano-crystals, are prepared on glass by molecular beam evaporation method in ultra-high vacuum. The absorption spectrum of the PTCDA thin film is very broad. The central wavelength lies at 490 nm, which is obtained due to the excitation to the first singlet (S₁) excitonic state as shown in figure 5.1.1

![Absorption spectrum of a 170 nm thin film of PTCDA on glass](image)

**Figure 5.1.1 Absorption spectrum of a 170 nm thin film of PTCDA on glass**

Our interest in this experiment is to use pump-probe scanning near-field optical microscopy (PP-SNOM) for the investigation of ultrafast local exciton dynamics with sub-wavelength resolution resulting in chemical imaging of PTCDA.
5.1.2 Experimental

The experimental set up was already described in detail above and has been shown in figure 4.6 (section 4.5). We employed a pump wavelength of 520 nm for excitation and the probe wavelength was chosen to be 650 nm for transient absorption measurements. The collinear pump and probe beams were focused on the PTCDA thin film with an objective lens (Olympus PLAN N 10x, NA=0.25) positioned below the sample and transmitted through the sample. The experimental arrangement is such that excitons are formed in the PTCDA thin film by the light transmitted through the sample. The transmitted signal is collected from above the sample, in the near-field, by a SNOM tip (an aperture of 100 nm) placed above sample surface at a distance of ≈ 10 nm. A tuning fork (cantilever) attached to the tip helps to maintain near-field contact through a feedback mechanism. A multimode optical fiber extension guides the collected near-field signal towards the detector. After filtering out the pump-pulse frequency using a long-pass edge filter (Semrock, 532), the probe pulse (650 nm) was detected using an avalanche photo diode (STM1DAPD 10, Amplification technologies, Inc). The height of the tip above the sample was controlled with a phase feedback mechanism and therefore, the fiber tip could additionally be used to obtain the AFM topography of the investigated sample with a spatial resolution limited by the SNOM tip diameter.

5.1.3 Results for self-trapping process in PTCDA

The pump pulse having a central wavelength of 520 nm is incident on the sample surface to generate free excitons (F) in the $S_1$ state, which are then monitored by the probe pulse. The transient absorptions as a function of delay time of the probe at different pump
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field intensities (20 pJ/pulse, 120 pJ/pulse and 350 pJ/pulse) were investigated by using a SNOM tip of 100 nm and the results are shown in figure 5.1.2.

The F-excitons produced in the S₁ state are relaxed through the phonon-exciton coupling resulting in self-trapped (ST) excitons. The relaxation of the self-trapped excitons happens via radiative and non-radiative decay to the ground state S₀, and intersystem crossing to the lowest triplet state (T₁). The self-trapped excitons are also quenched by the impurities in the PTCDA crystal. The dynamics of the population of free excitons (F) and self-trapped excitons (ST) are different for different pump intensities as can be seen from figure (5.1.2).

5.1.4 Annihilation process in PTCDA and reaction scheme
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field

For the lowest pump intensity of 20 pJ/pulse, the decay in the absorbance is mono-exponential. At higher intensities, i.e., at 120 pJ/pulse and at 350 pJ/pulse, we observe a multi-exponential decay.

The average exciton densities at these three pump energies (energy/pulse) are 8.12x10^{18}, 3.828x10^{19} and 9.86x10^{19} cm^{-3}, respectively. From the decay profile we can conclude that the exciton-exciton annihilation becomes efficient only for exciton densities higher than 10^{19} cm^{-3}.

From the above observations we conclude that more absorbance takes place at higher excitation densities and the intensity-dependent decay profiles can be modeled by considering the mechanism discussed in the following. Yago et al, used a similar model to describe exciton dynamics in β-perylene crystals.\textsuperscript{23} The generation and decay of the singlet excitons consists of the following three processes, exciton-exciton annihilation, relaxation of the free excitons (F) to the self-trapped excitons (ST) and relaxation of the self-trapped excitons (ST) to the ground state S\textsubscript{0} through radiative and non-radiative channels\textsuperscript{23}.

\[
\begin{align*}
(h\nu) + S_0 & \longrightarrow S_{1F} \quad \text{(pump-excitation)} \\
S_{1F} + K_F & \longrightarrow S_{1ST} \quad \text{(self-trapping)} \\
S_{1F} + S_{1F} & \longrightarrow S_n + S_0 \quad \text{(annihilation)} \\
S_n + S_0 & \longrightarrow S_{1F} + S_0 \quad \text{(internal-conversion)} \\
S_{1ST} & \longrightarrow S_0 T_1 \quad \text{(impurities or defects; relaxations)}
\end{align*}
\]

In this scheme, S\textsubscript{0} shows the molecules in the ground state. When the pump beam having energy (h\nu) is focused on the sample surface, the lowest excited singlet states are populated thus forming the free-excitons (S\textsubscript{1F}). The free excitons (S\textsubscript{1F}) in the excited
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field state are relaxed to self-trapped \((ST)\) excitons with a relaxation constant, \(K_{FS}\). The rate equation also describes the relaxation of self-trapped excitons \((ST)\) via radiative and non-radiative decay to the ground state \(S_0\), and intersystem crossing to the lowest triplet state \((T_1)\). The annihilation of free excitons \((F)\) results in a population of both \(S_0\) ground state and \(S_n\) higher excited singlet states. The \(S_n\) state rapidly relaxes to the \(S_1\) state through internal conversion and thus the annihilation of two excitons in the \(S_1\) state effectively reduces the number of excitons in this state to half.

The whole relaxation process can be obtained from the following rate equations.

\[
\begin{align*}
\frac{dn_F(t)}{dt} &= -K_{FS}n_F(t) - \frac{\gamma}{2} n_F(t)^2 \\ \frac{dn_{ST}(t)}{dt} &= -K_{FS}n_F(t) - K_{SG}n_{ST}(t)
\end{align*}
\]

Here, \(n_F\) is the population of the free-excitons, \(n_{ST}\) is the population of the self-trapped excitons \((ST)\), \(K_{FS}\) is the relaxation constant of the free-excitons \((F)\) to self-trapped excitons \((ST)\), and \(K_{SG}\) is the relaxation constant of the self-trapped exciton \((ST)\) to the ground-state \((G)\) and \(\gamma\) is the rate constant of annihilation. The value of \(K_{SG}\) is taken from reference \(^{39}\).

The transient absorbance \((OD)\) of the probe signal is due to the sum of the contributions from the free and self-trapped excitons. The transient absorption \(A(t)\) is given by

\[
A(t) = [\varepsilon_Fn_F(t) + \varepsilon_{ST}n_{ST}(t)]Z
\]

Here, \(\varepsilon_F\) and \(\varepsilon_{ST}\) are the absorption coefficient of free and self-trapped excitons, respectively. The term \(\alpha = \frac{\varepsilon_{ST}}{\varepsilon_F}\) is the ratio of the absorption coefficient of self-trapped excitons \((ST)\) and the absorption coefficient of free excitons \((F)\) and \(Z\) is the thickness of the sample. Putting the value of \(\varepsilon_{ST}\) in equation \((5.1.3)\), after simplification we get,
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field

\[ A(t) = [n_p(t) + \alpha n_{SF}(t)] \epsilon P Z \] (5.1.4)

By using the solutions of equation (5.1.1), (5.1.2) and (5.1.3) to fit the time profiles of transient absorbance, the different constants can be obtained.

Since the intensity profile of the cross-section of the femtosecond laser pulses is described by a Gaussian distribution, the intensity is not uniform within the focal point area. Therefore, the absorbance recorded using the SNOM tip at different locations within the focus area is different. Different colors labeled by P.1, P.2, P.3, P.4, P.5, P.6 show dynamics recorded at different locations on the focal spot size starting from center of the focal spot (where the intensity is maximum) to the end of focal spot (where the intensity is minimum). The intensity profile of the pump laser focus along the cross-section line is shown in the inset of figure 5.1.3. The figure displays the exciton dynamics measured at different points on this line. The different relaxation dynamics can be clearly seen from the transient absorption plots.

![Figure 5.1.3 Time profile of transient absorption of the probe at 650 nm at different pump (520 nm) intensities present at different points within the focal area of the pump](image)

*Figure 5.1.3 Time profile of transient absorption of the probe at 650 nm at different pump (520 nm) intensities present at different points within the focal area of the pump*
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field laser on the PTCDA film. The inset shows the variation in intensity along the cross-section line of the pump laser focus.

5.1.5 PP-SNOM images

The near-field technique cannot only be used to study the ultrafast dynamics but also can be used for sub-wavelength resolved imaging of the PTCDA thin films with chemical specificity. Panels (a) and (b) of figure 5.1.4 show the SNOM and AFM images of the edge of a thin PTCDA film on a glass substrate, respectively. The color code shows the variation in the transmitted probe pulse intensity, with red for lowest and blue for highest intensity.

![Figure 5.1.4 Panel (a) shows the PP-SNOM image of the edge of a thin PTCDA film, based on the transient absorption of the 650 nm probe pulse, with an initial 520 nm pump excitation (at a probe pulse delay time of 200 fs relative to the initial pump pulse) and panel (b) shows the AFM topography.]

The AFM image gives only topographic information while the PP-SNOM image gives chemical information relevant to the thin film (here, the exciton density at a given time).

The probe pulse is delayed by 200 fs with respect to the pump pulse in order to record the image of the free-excitons (F) in the thin film. From the PP-SNOM image in panel (a) of figure 5.1.4, we see the contrast in the image. The reason for this contrast is explained as follows,
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field

1. The intensity of the probe beam is high at the glass surface (less probe intensity is absorbed by the glass) on the left hand side in panel (a) of figure (5.1.4)

2. The intensity of the probe beam is low in the thin film (more absorption in thin film) on right hand side in panel (a) of figure (5.1.4). The reason for this low intensity is the absorption of the probe by the free-excitons in the thin film.

We can also see that the PP-SNOM image is slightly different from the AFM image. This also has to do with the fact that the resolution of the SNOM image is higher than that of the AFM image. The tip size active in AFM is bigger than the aperture size relevant for SNOM, which is 100 nm in the present case.

Figure (5.1.5) shows the PP-SNOM image with pump and without pump for a measurement, which was observing a single laser pulse per point of the image. The glass on the left and the PTCDA film on the right side of the image are clearly visible in the PP-SNOM. The image shows inhomogeneity.

When the pump is on, we see a contrast in the image based on the absorption of the probe laser pulse, which is high there were high exciton densities are produced in the PTCDA film. In the absence of the pump pulse, the probe laser is very weakly absorbed, as expected. It has to be pointed out that the color code is based on a normalized intensity scale for each image, i.e. the colors in the two images do not correspond to the same absolute intensities. The variation of the probe laser pulse intensity in panel (b) is very small and results mainly from scattering processes.
In summary, we have used femtosecond time-resolved pump-probe spectroscopy for the investigation of ultrafast exciton dynamics in PTCDA semiconductors. The combination with scanning near-field optical microscopy (SNOM) allowed for spatial resolution below the diffraction limit. Thus, femtosecond time resolved spectroscopy could be used to locally probe exciton dynamics and also obtain images based on this dynamic information. We could demonstrate that the exciton annihilation is strongly dependent on exciton density, which again depends on the excitation energy. At low excitation energy where the exciton density is below $10^{18}\text{cm}^{-3}$ the exciton relaxation was found to be mono-exponential, i.e., annihilation processes did not yet play a major role, while for exciton densities above $10^{19}\text{cm}^{-3}$ the decay was multi-exponential due to the additional contribution of exciton-exciton annihilation. The rate observed for the exciton relaxation is different in the far- and near-field measurement. We observed a time constant of 1.6 ps in the far-field and 1.3 ps in the near-field measurements when the SNOM was positioned in the center of the pump focal area. This is due to the fact that the far-field experiment observes the whole focal area and thus averages over different pump laser intensities, resulting in different exciton densities and exciton-exciton annihilation contribution.
5.2 Exciton dynamics at gold-poly 3-hexylthiophene diyl (Au-P3HT) contact

5.2.1 Introduction

As described above in section 5.1.1, organic semiconductors are of considerable interest for the design of electronic devices such as light emitting diodes and solar cells due to their low costs and the simplicity for application. Interfaces between metal electrodes and the semiconductor active medium are essential for charge transfer. However, while a lot of work has been done to investigate the exciton dynamics at the interfaces formed between the active polymer domains in organic semiconductors, the photo physics (exciton dynamics) at the interface between the polymer layer and the metal contact has not been studied in detail.

Many investigations show that charge transfer processes at the metal contact depend strongly on the magnitude of the energy barrier arising from the mismatch between the Fermi level of the metal electrode and the polaronic states of semiconducting organic materials. Insights into the magnitudes of these barriers can be obtained by studying the energy level alignment at metal-organic interfaces using X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) etc. The Au-P3HT contact has been the most widely explored among model systems for conjugated polymer-based electronic devices; this is because P3HT is a very promising candidate for organic electronics applications and gold is known to provide a very good Ohmic contact with P3HT, since the work function of gold is very close to the HOMO level of P3HT. Using an (organic field effect transistor) OFET-like device with differently modified P3HT-SiO₂ interfaces, Pittner et al. employed electroreflectance (ER) spectroscopy as a spatially resolved technique for charge modulation analysis to
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study the charge transport, which takes place in the accumulation layer buried at the organic semiconductor-insulator interface. The optically investigated charge transport helped these authors to gain insights into the energetic disorder, which exists inside the P3HT-SiO$_2$ accumulation layer and influences the local charge transport. The significant change in the dielectric function ER spectral fingerprints due to charge injection at the metal-polymer contact was observed to depend on the distance from the injection contact as well as on the treatment method applied to the SiO$_2$ substrate, and this observation was attributed to differences in the energetic relaxation during charge transport. In addition Wagner and co-workers$^{113}$ demonstrated the applicability of megahertz operation of organic thin film transistors based on P3HT for high speed switching, and showed that the metal-semiconductor contact effects, which can be described by the contact resistance, present a limiting factor for the maximum operational frequency in organic transistors with submicron channel lengths.

Although the many reported works show the importance of studying different processes at the metal organic interfaces, to our knowledge no investigation of the exciton dynamics has been performed using a method capable of accessing the dynamics specifically in the interfacial layer. The difficulty is that the interfacial layer thickness is on the order of 10 nm only. Techniques, which allow for an exceptionally high depth resolution, are therefore required.

Marsh et al.$^{101}$ have recently reported their study of exciton dynamics in situ in a prototypical P3HT-only diode (P3HT film sandwiched between ITO and an aluminum electrode). To the best of our knowledge this work is the only example where the exciton dynamics was studied in the presence of a metal contact using femtosecond spectroscopy.
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These authors observed that the exciton dynamics are not affected neither when the metal electrode is present nor when the ITO glass electrode is coated with a conducting polymer (PEDOT:PSS) contact. We would like to point out that these authors aimed to investigate exciton dynamics in situ (in a typical electronic device), but did not specifically aim to address the exciton dynamics at the metal contact itself. Our results will demonstrate that these authors have observed only bulk excitons by using a far-field spectroscopic technique, since the highly spatially confined information is lost in the (diffraction-limited) far-field detection due to spatial averaging.

So far the exciton dynamics in organic semiconductors has been studied using time resolved spectroscopy with microscopic techniques, which are diffraction-limited.\textsuperscript{19,20} Therefore, this approach is unable to provide details about local dynamics with spatial resolution on the order of the exciton diffusion length of $\approx 10\ \text{nm}$ as we find e.g. for the P3HT semiconductor. The use of scanning near-field microscopy can considerably improve the lateral and axial resolution. Noteworthy, only very few works have been published about the combination of femtosecond time-resolved spectroscopy with SNOM because of the technical complexity of this technique.\textsuperscript{84,99,114-118} Generally, spatial resolution in SNOM is realized using either a fiber tip with an aperture size below diffraction limit (like in the experiment presented above)\textsuperscript{84} or with an apertureless metal tip of few nanometers in size. In the latter case, a local field enhancement at the tip is used to increase the spectral response in a spatially restricted volume.\textsuperscript{114,115} This “tip-enhancement” results in an even higher lateral and axial resolution due to the near-field characteristics. In our experiment, we have combined both techniques. We use a fiber SNOM tip with an aperture big enough to collect sufficient light. The reduced depth
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field resolution is compensated by a gold coating applied to the glass fiber tip, which results in a local field enhancement reaching less than 150 nm into axial direction as we will describe in chapter 6. In this other study of P3HT thin films, we have used the combination of SNOM (with the “tip-enhancement” contribution) with CARS (coherent anti-Stokes Raman scattering). Investigating nanostructures on the surface, a particularly increased height resolution of the P3HT surface could be observed experimentally.

For the study presented in this section, we have employed femtosecond time-resolved pump-probe spectroscopy in combination with scanning near-field optical microscopy (PP-SNOM) to study the exciton dynamics in P3HT and at the Au-P3HT interfaces.

5.2.2 Sample preparation

Sample (P3HT/Au contact) preparation. Poly-3-hexylthiophene-2,5-diyl purchased from Rieke Metals (P3HT, RMI-002EE) was dissolved in chlorobenzene to obtain a solution of 35 mg/ml. The solution was stirred overnight at a temperature of about 60 °C. Glass substrates were cut in the size of 25 mm x 25 mm and cleaned thoroughly with acetone, isopropanol and DI-water successively. For a final cleaning process, the substrates were treated in an ozone cleaner for 10 minutes. The cleaned substrates were immediately spin-coated with the prepared P3HT solution at 1000 rpm for 30 seconds at room temperature. The thickness of the obtained P3HT layer was 170 nm, as measured with a Dektak surface profilometer. The coated substrate was annealed at 100 °C for 2 minutes to remove residual solvent from the layer. Then, a patterned metal contact with the P3HT layer was made by depositing a gold film of 10 nm thickness on the P3HT-coated substrate via a shadow mask in a sputter coater (Quorum Q150T S) to obtain a sample
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field with alternating neat P3HT and Au-P3HT regions, as depicted in figure 5.2.1. All the sample preparation and treatment took place inside a clean room.

![Figure 5.2.1 Top view of sample (Au-P3HT contact)](image)

Figure 5.2.1 Top view of sample (Au-P3HT contact)

The far-and near-field experimental setup has been already described in chapter 4 in detail.

5.2.3 Results and discussion

In order to understand the effect of gold contacting on P3HT, the exciton dynamics in P3HT were investigated on neat P3HT and at the Au-P3HT interface first in the far-field using a standard microscope technique and then in the near field using the SNOM technique described below. In our experiment, the early exciton dynamics were studied within the delay time window of -5,000 to 15,000 fs between the pump (520 nm) and the probe (650 nm) pulse. The obtained results are depicted in figures 5.2.2 and 5.2.3 and the proposed interpretation is illustrated in figure 5.2.4.

Panel (a) of figure 5.2.3 shows and compares the normalized differential transmission ($\Delta T/T$) of the probe pulse as a function of time delay measured in the far field on neat P3HT and at the Au-P3HT interface (where $\Delta T/T$ is the intensity difference of the transmitted probe pulse when the pump pulse is on or off, divided by the transmitted...
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field probe pulse intensity when the pump pulse is off). At the probe wavelength of 650 nm, P3HT shows a photo-induced absorption; this excited state absorption can be attributed to instantaneously photo generated charge pairs (electron-hole pair) that quickly recombine, in agreement with previous observations.\textsuperscript{20,101,103} The mono-exponentially fitted profiles of the average probe transmission in the far-field reveal nearly the same exciton dynamics for neat P3HT and Au-P3HT interface, yielding a time constant of about 1.8 ps. As we have discussed above, the exciton dynamics can vary even within the excited sample spot. Note however, that for the observations discussed above higher powers of the incident pump pulses were used, where due to the higher density of generated excitons, exciton-exciton annihilation could not be neglected. A series of measurement with different pulse energies in the energy range applied in the present work did not yield a change of the dynamics pointing to a contribution of annihilation effects. The transients recorded in the far-field yield averaged information, where light is collected from a micrometer size region. As a consequence, subtle differences, if any, in the exciton dynamics between neat P3HT and Au-P3HT interface cannot be seen in panel (a) of figure 5.2.3. i.e. diffraction-limited microscopy cannot specifically access the interfacial contribution to the exciton dynamics. Therefore, PP-SNOM has been used in order to obtain more detailed insights into the exciton dynamics in P3HT, which can be influenced not only by the surface roughness of P3HT, but more importantly also by the coupling interaction at the interface between the P3HT surface and the metal contact. As was already pointed out above, the SNOM tip with an aperture of approx. 200 nm in diameter will collect the probe signal from only a nanometer-sized region in the center of the illuminated sample spot instead of collecting
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the signal from a micrometer-sized region as is usually the case in far-field microscopic studies. More importantly, the local field enhancement drastically increases the depth resolution. This tip-enhancement effect can be easily demonstrated by choosing laser pulse energies, which in the far-field microscopy experiment do not yet damage the sample. Approaching the tip to few nanometers distance then results in a highly localized damage of the surface. Therefore, the upper limit of the useful laser powers was defined by the SNOM experiment and not the optical microscope setup.

We first have investigated the performance of PP-SNOM vs. conventional SNOM (i.e. without the initial pump pulse) by recording the transmitted probe pulse intensity in order to build 128×128 pixels images of both the neat P3HT and the Au-P3HT interface region of the sample at a probe delay time of 500 fs for the PP-SNOM experiment and with 100 ms integration time per pixel for both measurements. For comparison, an AFM image of the same region was also recorded using only the SNOM tip (no laser interaction). Note that the AFM resolution is rather limited due to the relatively big size of the fiber tip compared to standard AFM tips.
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Figure 5.2.2  Pump-probe SNOM images based on the transmission of the 650 nm probe pulse, (a) without and (b) with the initial 520 nm pump excitation (at the probe pulse delay time of 500 fs relative to the initial pump pulse) of both the neat P3HT and Au-P3HT interface regions (a 170 nm P3HT film with 10 nm thick gold contacts), and (c) the corresponding AFM topographical image. The color code of the transmitted probe intensity scale of the SNOM images is shown on the top left: blue = lowest intensity; red = highest intensity. In panel (e), the probe pulse transmission profile along the black horizontal line in the image (b) of the P3HT and Au-P3HT interface regions with initial pump excitation is displayed showing the varying transmission due to the gold layer and to the different dynamics in the different regions of the sample. The corresponding transients recorded at several points on the Au-P3HT side are shown in panel (d) and those obtained at different points on the neat P3HT side are displayed in panel (f).

In the PP-SNOM images in panels (a) and (b) of figure 5.2.2, the left side in each image is the gold-plated region (on top) of P3HT and the right side is neat P3HT. The color code shows the variation in the transmitted probe pulse intensity, with blue and red being used for the lowest and the highest intensity, respectively. Note that the metal contact on the P3HT film has a net shielding effect resulting in the relatively reduced optical
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field transmission in the region of P3HT coated with gold in the PP-SNOM images. This information can be used to correct for the shielding effect when evaluating the pump-probe results. Indeed the shielding effect can be removed by presenting the pump-probe data in the form of differential probe pulse transmission, which also helps to remove any eventual background absorption of the probe pulse that may happen in the absence of the pump pulse. Unlike the image obtained without the pump pulse (showing greater probe pulse transmission), the PP-SNOM image with initial pump shows an excited state absorption and is therefore yielding an instant visualization of the exciton population in the P3HT film. Therefore, the PP-SNOM imaging provides a chemical contrast, as compared to AFM imaging, which was performed only with the SNOM tip (panel (c) of figure 5.2.2) when both pump and probe beams were blocked and provides pure topography information. The AFM image clearly shows the surface roughness in the range 30-40 nm, which can introduce a point-to-point variation in the transmitted power density on the micro to nanometer scale. Changes in the local incident optical power (and hence in the exciton population density) due to sample morphology (thickness and roughness), but also the surface roughness by itself can influence the material response and the exciton dynamics. This is clearly indicated by the fact that PP-SNOM transients recorded at different points in both the regions of neat P3HT (see panel (f) of figure 5.2.2) and Au-P3HT interface (see panel (d) of figure 5.2.2) show small variations in the observed exciton dynamics. The obtained time constant values vary between approx. 1700 and 2000 fs, and 1000 and 1200 fs for the neat P3HT and the Au-P3HT regions, respectively. This observation already points to the higher potential of the PP-SNOM
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field technique. The detected lateral variation reflects the local details of the dynamics of the excitons that were formed optically.

It is clear from above that the PP-SNOM technique is very sensitive to local details. While this is of a great advantage, it also comes with challenges, especially because we aim to detect subtle characteristic changes across the sample surface, in particular between the region of neat P3HT and the region of the interface between P3HT and the gold contact. In order to establish that the observed difference in exciton dynamics time constants between neat P3HT and Au-P3HT interface is not due to the topographical fine structures seen in the near-field experiment, we have averaged many transients taken in either the neat P3HT or the Au-P3HT interface region of the sample performing a series of measurements along a line within the region of interest. The data have been transformed and presented as differential probe pulse transmission as mentioned above, either as normalized or non-normalized data (insets). The results are shown in figure 5.2.3, which compares the average transients of the differential probe pulse transmission \((\Delta T/T)\) of neat P3HT and Au-P3HT interface in panels (a) and (c) respectively in the far field and neat P3HT and Au-P3HT interface in panels (b) and (d) respectively in the near field. The insets in panels (b) and (d) depict non-normalized \(\Delta T/T\) transients and show drastic changes in optical density (OD) between the far- and near-field observations. This is an important result, showing the capability of the near-field experiment. The mono-exponentially fitted average probe signal reveals clearly faster dynamics of excitons in P3HT when it is in contact with gold, with a time constant of 1.10 ps, as compared to neat P3HT with about 1.9 ps decay time constant. This observation is particularly important because a faster dynamics at the metal-organic interface can significantly
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field influence the properties of organic electronic devices. Moreover, by comparing the intensity recovery levels of the probe transients in figure 5.2.3, we estimate about 80% and 70% exciton relaxation in neat P3HT and Au-P3HT interface, respectively, within our observation time window. The incomplete exciton relaxation points to the formation of long-lived trapped states, as clearly indicated in the respective probe time profiles by the slow decay components at longer time scales.

![Figure 5.2.3](image)

*Figure 5.2.3 Normalized time profiles of the probe pulse differential transmission ($\Delta T/T$) at 650 nm as a function of delay time after exciton preparation by the pump laser pulse (520 nm). The exciton dynamics in neat P3HT are shown in panel (a) for the far-field and in panel (b) for the near field experiment. Panels (c) and (d) show the exciton dynamics observed at the Au-P3HT interface in the far field and near field, respectively. The insets in panels (b) and (d) depict non normalized $\Delta T/T$ and show drastic changes in optical density when going from far field near field conditions.*
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field

Recalling the P3HT exciton dynamics in the far-field and in the near-field measurements (see figure 5.2.3), key observations emerge, which are worth to be emphasized as follows:

(i) In the far-field, we have observed approximately the same time constants for exciton relaxation in neat P3HT and in the Au-coated part. A similar time constant is observed in the near-field for neat P3HT (see panels (a) (b) and (c) of figure 5.2.3), but not for the Au-P3HT interface (see panel (d) of figure 5.2.3). As was mentioned above, a significant difference in the time constants of the exciton relaxation between neat P3HT (1.9 ps) and Au-P3HT interface (1.1 ps) has been observed in the near-field (panels (b) and (d) of figure 5.2.3). This clearly indicates that in the near-field investigation, we are able to detect the interfacial exciton dynamics, whereas in the far-field experiment the bulk P3HT contribution dominates the observed transient absorption dynamics. Additionally, there is no clear difference between the exciton dynamics in bulk (as observed by far-field measurements) and the P3HT-air surface layer (seen by the PP-SNOM approach).

(ii) As compared to the far-field measurements, we see a significantly higher photo-induced optical density (transient probe pulse absorption) in the near-field measurements as depicted by the insets in panels (b) and (d) of figure 5.2.3. The rather small change in differential probe pulse transmission in the far-field is due to the collection of signal averaged over regions of high to low or even negligible transient absorption on the illuminated sample spot (the pump-pulse excitation intensity is maximum in the center of the focal spot and decreases towards the edges of the micrometer-sized focal area produced by the microscope objective). However,
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in the case of near-field detection, the signal is collected from a small area of only about 200 nm diameter (equivalent to the aperture size of the SNOM tip) within the illuminated spot, where the excitation density is maximal and hence a big change in the probe pulse differential transmission is seen. Obviously in this case, the observation of more specific information can be assumed.

(iii) A significant difference in the recovered probe signal level between neat P3HT and Au-P3HT interface has been observed in the near-field as seen in panels (b) and (d) of figure 5.2.3. The same observation can be made when comparing the transient for Au-P3HT interface in the far-field to that in the near-field (see panel (c) of figure 5.2.3). The far-field experiment obviously is dominated by the bulk P3HT signal. Indeed, beyond ~ 4ps within our measurement time window (see panel (d) of figure 5.2.3), we can still estimate up to 10% more exciton population for the Au-P3HT interface as compared to neat P3HT on the basis of the PP-SNOM technique, what the far-field technique is unable to reveal.

In the following discussion, we attempt to clarify firstly, why the near-field experiment is capable of accessing the dynamics of the molecular layers close to the metal-semiconductor interface. Secondly, we discuss why the characteristic dynamics are different at the Au-P3HT interface, as revealed by the near-field investigation, in comparison to the P3HT bulk.

In both the far- and near-field experiments, the pump and probe laser pulses travel through the P3HT layer towards the Au-P3HT interface and then are detected above the Au layer. While the SNOM is known to detect with a very good spatial resolution (near-field), one would still expect the dynamics of the bulk excitons contributing to the
observed signal since the probe laser is traversing the complete P3HT layer. Nevertheless, the signal observed obviously arises from the near-field range of the SNOM tip as we also have observed for pump-probe (see above) and coherent anti-Stokes Raman (CARS; see below) experiments.\textsuperscript{99,116} There, we have made a very important observation. We have found that as soon as the SNOM tip is brought into near-field contact with the sample, the photodamage threshold is much lower as compared to the situation in the far-field (as was already mentioned above). Hence, the experimental settings (incident pump and probe pulse energies, focusing objective, etc.) for both standard pump-probe (far-field measurement) and PP-SNOM had to be adequately chosen high enough to achieve signal strengths, which still could be detected, but low enough so that photo damage of the sample was avoided. In our experiments we are using a 10x objective to focus pump and probe laser pulses onto the sample. Femtosecond laser pulse energies just below the photo damage threshold for the far-field have to be adjusted to lower energies in order to avoid highly localized surface damage on the sample surface when the SNOM fiber tip is in the near-field range. The explanation for this is given by the well-known tip-enhancement effect, here caused by the metal coating of the tip (0.2 μm thick Au coating), which increases the field strength in the near-field.\textsuperscript{94,116} The enhancement of the pump laser field in the near-field results in an efficient exciton preparation in a nanometer range only. Therefore, a transient absorption of the probe laser mainly happens there. Only based on this effect, it is possible to explain why even with the very small collection cross section of the nanometer-sized fiber tip we still detect much higher signal changes as compared with those detected in the far-field (the rather high OD in SNOM is depicted in the insets of panels (b) and (d) of figure 5.2.3). As we
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already had pointed out earlier, besides the very high lateral resolution, here, especially the extremely high axial resolution makes the SNOM technique (combined with the inherent tip-enhancement effect) a very powerful investigation method in the nanometer range.

In this work, excitons at the metal-polymer interface (Au-P3HT in this case) are observed to behave differently as compared to the bare polymer. In fact, the metal (Au) work function is known to decrease when in contact with P3HT. This then results in the alignment of the metal Fermi level with the polymer chemical potential at the equilibrium and thus allows charge transfer into the metal, which can influence the exciton dynamics at the interface.

In our experiments, the above band gap excitation leads to the formation of hot excitons, which can quickly relax to Frenkel excitons or states (FS) after ultrafast thermalization (< 100 fs) as depicted in panels (d) and (e) of figure 5.2.4. For our near-field measurements in the case of P3HT bulk, the majority of these Frenkel excitons (up to 80%) relax within about 2 ps, while a small proportion (less than 20%) convert into long-lived self-trapped excitons or states (STS), which do not show any trend of relaxation within our observation time window.

However, at the Au-P3HT interface in comparison to P3HT bulk, both hot excitons and Frenkel excitons can follow other relaxation channels (see panel (e) of figure 5.2.4) because of the coupling of the electronic systems of P3HT and metal. Both Coulomb attraction (for the hole) and the aforementioned energy level alignment (for the electron) at the metal-polymer interface provide a direct recombination pathway for Frenkel excitons as well as hot excitons, which are close enough to the metal contact. Therefore,
while the photophysics remains unchanged in molecular layers deeper into the P3HT bulk, it is expected to be different at the interface with the Au contact. This is reflected by our experimental findings, which reveal (see panels (b) and (d) of figure 5.2.3) that the exciton dynamics at Au-P3HT interface is in fact faster due to the direct recombination path via the metal. This concept is only valid for those P3HT layers within a distance of about the exciton diffusion length to the interface with the metal, which is just around 10 nm. While the axial resolution of a diffraction-limited optical microscope cannot selectively probe this range of molecular layers, the near-field technique is restricting the detection nearly exclusively to this part of the sample, where changes in the sample are predominant due to the aforementioned local field enhancement caused by the Au-coated SNOM tip. In addition, as mentioned in point (iii) above, up to 10% less exciton relaxation beyond 4 ps within our observation time window is observed with SNOM at the Au-P3HT interface as compared to neat P3HT (see panels (b) and (d) of figure 5.2.3). This corresponds to an additional increase in the overall exciton population at the interface.

After about 70% signal recovery, the measured PP-SNOM transient for the Au-P3HT interface is practically constant within our measurement time window, what indicates the formation of trapped states, which appear to be longer-lived states at the Au-P3HT interface than in neat P3HT.
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Figure 5.2.4 (a) Energy level diagram of Au, where $\phi_m$ and $E_{fm}$ are the work function and Fermi level of pure Au, respectively. (b) Energy level diagram of neat P3HT, where $\phi_p$, $E_F$, $E_v$ and $E_c$ are the work function, chemical potential, valance band and conduction band of P3HT, respectively. (c) Energy level alignment at the Au-P3HT interface (i.e. the Au-coated region of P3HT), where the Fermi levels are equal in equilibrium. (d) Exciton relaxation mechanisms in the neat P3HT region, where Frenkel exciton states are labeled by FS and self-trapped exciton states are labeled by STS (e) Exciton relaxation mechanisms in the Au-coated region of P3HT, showing an additional recombination path at the interface via the metal due to Coulomb attraction of the hole in the valence band and the fast decay of the high energy electron into the metal conduction band.

Note that in panels (d) and (e), the pump pulse at 520 nm is used for above band gap excitation of P3HT and the formed exciton wave packet is then probed at 650 nm.

In summary, femtosecond pump-probe transient absorption spectroscopy has been combined with a scanning near-field optical microscopy technique (PP-SNOM) to shed light onto the exciton quenching in P3HT when it is in contact with a thin gold layer. We have observed in the far-field approximately the same time constants for exciton
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field

relaxation in neat P3HT and at the Au-P3HT interface pointing to the fact that here the bulk contribution dominated the signal hiding the interface effect. However, the observations made in the near-field for neat P3HT and for the Au-P3HT interface have yielded a more detailed and specific information. Unlike far-field spectroscopic techniques, the PP-SNOM approach reveals that the exciton dynamics at the Au-P3HT interface are significantly different from those found for neat P3HT, both in terms of the relaxation time constant and the relaxation efficiency. The obtained information is confined within just a couple of molecular layers at the metal-polymer interface. Therefore, its selective observation requires the combination of extremely high axial resolution (~ 10 nm) and chemical contrast, which both is realized by the use of the PP-SNOM technique. Here, the chemical selectivity provided by the femtosecond transient absorption measurement is localized within a sub-diffraction limited range. A tip-enhancement effect of the metal coated SNOM fiber tip allows for the selective excitation and probing of dynamics within the near-field range and thus yields the very high axial resolution needed for the investigation of the thin interfacial layer. The observed change in the exciton dynamics time constant has been discussed in terms of known mechanisms, including Coulomb attraction and energy level alignment at the metal contact, which both provide a direct and faster decay channel for interfacial excitons. Also the nature of long-lived states was found to be different when comparing the interface results with those obtained from the P3HT bulk. The PP-SNOM transients point to longer-lived trapped states at the metal-semiconductor interface.

While the experiments are very demanding, they offer the possibility to access the dynamics on a femtosecond timescale with an extremely high lateral and (even more)
Time-resolved pump-probe spectroscopy of organic semiconductors in the near-field axial resolution. This work was triggered by a project, in which we study the interaction of the electronic systems of metal and adsorbed molecules, but the technique will be applied to other systems in near future where nanometer spatial resolution is required.
Chapter 6

CARS microscopy in the far- and near-field

Chapter 5 presented pump-probe experiments in the near-field for different systems. However, in pump-probe experiment the wavelengths always have to be in resonance with molecular transitions. In order to generate a coherent anti-Stokes Raman scattering (CARS) signal, any two wavelengths can be chosen in such a way that a vibrational resonance is achieved when the frequency difference fits the vibrational frequency of a molecular vibration. No electronic resonances are required as long as only ground state dynamics have to be accessed. The experimental setup for forward SNOM-CARS (F-SNOM-CARS) for transparent samples and Epi-SNOM-CARS (E-SNOM-CARS) for opaque samples is described below (also see introduction to the experimental details above). In case of a transparent sample, the focusing is preferably done by an objective from the bottom. The signal is transmitted through the sample and is collected at the top of the sample by the tip of the optical fiber, filtered using short pass edge filter and then detected by APD as shown in figure 6.1.1. In case of an opaque sample, the irradiation of the sample has to happen from above so that the tip can detect reflected light. A long working distance (LWD) objective has be used for focusing the laser pulses onto the sample in order to keep sufficient distance between the tip and the objective. The geometry shows the detection scheme for opaque samples in figure 6.1.2.
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Figure 6.1.1 SNOM-CARS for transparent sample. The Laser is focused from the bottom; laser light and signal propagate in forward direction.

Figure 6.1.2 SNOM–CARS for opaque sample, only long working distance objective (LWO) with NA 0.25

The resolution of the SNOM-CARS technique in either case depends on the size of the aperture of the SNOM tip.

In this chapter we describe the application of F-SNOM-CARS to the investigation of nanostructures of the organic semiconductor P3HT, the properties of which we already have discussed earlier in this thesis. For calibration and testing of the CARS microscope, we first have used polystyrene beads.
6.1 Micro-CARS of polystyrene beads and preliminary results

Coherent anti-Stokes Raman scattering (CARS), a member of the family of coherent Raman processes, is a third-order nonlinear technique that involves the interaction of four waves, including pump field at frequency (\(\omega_{pu}\)), Stokes field at frequency (\(\omega_S\)), probe field at frequency (\(\omega_{pr}\)) and anti-Stokes signal at frequency (\(\omega_{CARS}\)). A resonantly enhanced CARS signal is generated when the difference between pump and Stokes lasers is in resonance to one of the vibrational modes of the molecule, i.e., (\(\omega_{pu} - \omega_S\) = \(\omega_R\)) and thus can selectively image molecules with a high sensitivity.

The coupling of incident fields i.e. pump field, Stokes field (when the difference between pump and Stokes is tuned to the molecular vibrational mode) and probe field via wave mixing process can generate strong CARS signals following the same selection rules like spontaneous Raman scattering. This general type of CARS, which involves three different interacting laser fields, is called three-color CARS\(^{30,52,119}\) and the signal is generated at the anti-Stokes frequency given by \(\omega_{as} = \omega_{pu} - \omega_S + \omega_{pr} = \omega_R + \omega_{pr}\) (where \(\omega_S < \omega_{pu}\)). When the pump and the probe fields have the same frequency, i.e., \(\omega_{pu} = \omega_{pr}\), one calls the process two-color CARS or degenerate CARS, where the signal frequency is given by \(\omega_{as} = 2\omega_{pu} - \omega_S\). This is the technique applied in our experiments.

CARS microscopy was first reported in 1982 by Duncan et al. by employing non-collinear geometry, using picosecond dye lasers\(^{53}\) for generating chemical specific imaging of a sample. They recorded CARS images of onion skin cells; however, the image quality was poor due to non-collinear geometry. Later on in 1999 Zumbusch et al. replaced the complicated non-collinear geometry by a simple collinear geometry using a
CARS microscopy in the far- and near-field high numerical aperture objective to focus the beam tightly.\textsuperscript{27} After this improvement significant efforts were devoted to CARS microscopy by different research groups especially in lipids, metabolite, tumor identification and drug imaging, which could provide new exciting possibilities for biology and medicine.\textsuperscript{27,45,51,52,120}

To test and calibrate our micro-CARS system (described above), we have used polystyrene beads mainly because of their availability in many different diameters and their highly Raman-active vibrations in the range of 800-3000 cm\textsuperscript{-1}. For the experiments discussed here, we have used 3 µm beads. The experimental setup and the schematic diagram for the micro CARS technique was already discussed (figure 4.3) in chapter 4.

In this case, we employed a pump wavelength at 670 nm and the Stokes wavelength at 718 nm, i.e. the excitation was tuned to be in resonance with the ring breathing mode of the polystyrene beads at approx. 1000 cm\textsuperscript{-1}. The pump and Stokes beams were focused onto the sample by using the microscope objective (10x, NA 0.25) of the inverted microscope. The CARS signal generated from the polystyrene beads was collected by the microscope objective (10x, NA 0.25) of the upright microscope. A short pass edge filter (Semrock SP 632 nm) was used to remove the laser background (pump and Stokes) from the CARS signal before detection by an APD (STM1DAPD10, Amplification Technology, Inc. USA). The sample was raster-scanned and the signal was recorded at each (X,Y) position. The imaging was recorded very fast in order to avoid sample damages due to the laser interaction with the sample. The total scan area was 22 X 22 µm\textsuperscript{2} with 500 ms pixel dwell time. The total time for the scanning was \(\approx 5\) min. We found that the sample already showed small damages after recording the image.
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The image is shown in figure 6.1.3 (a) and a horizontal cross-section is displayed in panel (b). The cross section was taken at an arbitrary position highlighted as red line in panel (a) of the figure. It clearly shows the spatial CARS intensity distribution having a FWHM of approx. 3 µm.

![Figure 6.1.3](image.png)

*Figure 6.1.3*  (a) CARS image of polystyrene beads of approx. 3 μm diameter dried on a microscopy cover slip. (b) A horizontal section was taken along the red line shown in the image displayed in panel (a)

6.2 Far- and near-field CARS experiments of P3HT

The use of a high numerical aperture objective can improve the spatial resolution, which however still is limited by the diffraction limit. In order to increase the resolution beyond this limit, we have employed SNOM. The optical near-field technique in combination with ultrafast spectroscopy is an experimental approach, which provides images with chemical specificity, which can also be used for recording the localized dynamics on a nanometer scale.94,99

Due to the complexity of the involved techniques, the combination of CARS with SNOM is rather challenging and only very few scientific reports are available in this regard. Ichimura et al. reported tip-enhanced CARS microscopic images of the ring-breathing mode of diazole of adenine molecules, where the signal was enhanced at the tip apex by
CARS microscopy in the far- and near-field using aperture-less SNOM. Kyoung-Duck et al. also reported high spatial resolution in carbon nanotubes films by using tip enhanced Raman scattering. Kilmove et al. investigated the surface morphology of P3HT-PCBM for solar cell application by using scanning near-field optical microscopy (SNOM) and confocal Raman microscopy. P3HT has been chosen for the SNOM-CARS experiments because of the principal importance of this organic semiconductor material and also because of its high optical damage threshold, strong Raman-active modes and the simple access to thin films of varying thickness. The Raman mode of the C=C stretching frequency proved to be ideal for CARS imaging. To our knowledge our application of SNOM-CARS to P3HT is up to now the only reported attempt to obtain highly time-resolved Raman information with sub-diffraction-limited spatial resolution.

The main task of this work was not to improve the CARS imaging technique itself. Picosecond laser pulses with their narrower bandwidth are better suited for imaging. In addition, the destruction of the sample is less when using picosecond laser pulses as compared to femtosecond laser pulses. Our goal was to perform time-resolved CARS experiments in order to investigate the ultrafast local dynamics in the near-field. As described above, the SNOM tips used for our experiments were optical glass fiber tips coated with a thin metal film. This metal coating results in sharp edges, which as in the case of aperture-less SNOM, lead to a local field enhancement, which ultimately increases not only the lateral resolution but also the axial resolution as we have demonstrated in our investigation of the exciton dynamics at Au-P3HT interfaces above.

For the SNOM-CARS experiments, both thin and thick films of P3HT of various thicknesses were prepared. The solution of P3HT (16 mg/ml) in chlorobenzene was
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prepared and stirred for 3-4 hours at an elevated temperature of about 60 degrees. Microscopic slides of about 25 mm by 25 mm were cleaned thoroughly using acetone and isopropanol. After the cleaning, the slides were dried with a nitrogen gun. With an eppendorf pipette, 500µl of P3HT solution was applied for spin coating at 2000 rotations per minute for half a minute. The substrate was then heated at 100 °C for 1 minute. Before the SNOM-CARS experiments were performed, Raman spectra were taken. A typical spectrum is shown in figure 6.2.1.

![Figure 6.2.1 Raman spectrum of P3HT](image)

The strong peak at 1440 cm⁻¹ is assigned to the ring stretching mode of P3HT.

The experimental setup used for the SNOM-CARS experiment has already been explained in chapter 4 in detail.

Before obtaining the SNOM images with high resolution, firstly micro CARS images in the far-field were taken using the standard microscope detection scheme in order to be able to correlate the far-filed images with the near-field images. Due to our special design of the SPM, AFM topographic images can also be obtained using the SNOM tip. Since the SNOM aperture is coated with a metallic thin film of gold of thickness 200 nm to
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increase the collection efficiency and to reduce the leakage of light, the lateral resolution achieved in the AFM mode is relatively poor.

Figure 6.2.2 provides the experimental results obtained from the investigation of nanostructures on thin P3HT films. Panel (a) shows a micro CARS image (taken in far-field), panel (b) presents a SNOM-CARS image (taken in the near-field), panel (c) depicts the AFM topography of the scanned region, and panel (d) displays the CARS intensity profile along a horizontal section indicated in the images. The AFM topography of the P3HT thin film as shown in panel (c) of figure 6.2.2 was analyzed by using the WSXM software. For obtaining the SNOM-CARS image with sufficient signal intensity, a SNOM tip with an aperture of 300 nm was used. The resolution of the SNOM image is still better than that of an AFM image as was explained above.

For the CARS experiment, the pump pulse was set to 650 nm and the Stokes laser had a center wavelength of 717 nm. The difference between the pump and Stokes wavenumbers is almost equal to 1440 cm⁻¹, which fulfills the resonance condition for the ring stretching mode (C=C) of P3HT as shown in figure 6.2.1 and also mentioned by others. Femtosecond laser pulses have broad bandwidths (in our case approx. 100 cm⁻¹), thus the neighboring (and less intense) modes can also be excited. The non-resonant background can be reduced, when resonance CARS is used, i.e., when the laser wavelengths are chosen to be in resonance with an electronic transition within the molecule. Then, also the signal from the P3HT environment has a very small intensity as compared to the P3HT CARS signal.

Naturally, due to the small portion of the whole signal, which passes through the SNOM aperture tip of only 300 nm diameter, the far-field micro-CARS experiment yielded
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stronger signal intensities. Therefore, SNOM-CARS requires higher laser pulse energies. When choosing femtosecond laser pulse energies just below the photo damage threshold for the far-field, damages have been observed in the SNOM experiments. Thus, the pulse energies had to be adjusted to lower energies in order to avoid highly localized surface damage on the sample surface when the SNOM fiber tip was in the near-field range. The reason for this lowering of the damage threshold is the well-known tip-enhancement effect,\textsuperscript{114} here caused by the metal coating of the tip (0.2 μm thick Au coating), which increases the field strength in the near-field. For optimization of the SNOM-CARS experiment significant efforts had to be devoted to the selection of the right laser pulse energies. The signal strength had to be kept high enough for detection, but low enough not to destroy the sample. The overall pulse energy applied for the experiments shown above was approx. 0.75 nJ, which was focused onto the sample using the 10x objective; each pulse therefore contributed approx. 0.25 nJ. Increasing the energy above 1 nJ on the sample already caused an instantaneous damage of the sample; a similar observation was also reported by Wang et al.\textsuperscript{123}
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Figure 6.2.2 Experimental results obtained from nanostructures or P3HT. Panel (a) shows a micro-CARS image, panel (b) shows a SNOM-CARS image of the same sample area, and panel (c) shows the AFM topography. The height of the P3HT structure is approx. 145 nm. Panel (d) shows the CARS intensity profile, along a section shown as horizontal line in the CARS images.\textsuperscript{116}

The images obtained by far-field (micro-CARS) and near-field measurement (SNOM-CARS) were taken from the same location (area) of the sample surface. The CARS intensities were normalized, however the color code is chosen in such a way that it covers the entire range of intensity as can be seen in the images of panel (a) and panel (b) of figure 6.2.2. Comparing the SNOM-CARS image with the AFM image, it can be seen that the lateral resolution of the SNOM-CARS image is better than that of the AFM image. The explanation for this was already given in section 5.2 (metal rim of the glass fiber).
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Panel (d) of figure 6.2.2 shows the intensity profile for both far-field and near-field CARS, along a section in the horizontal direction of the 3x3 μm² area investigated. This section is indicated by a horizontal line in the CARS images. In the AFM image, as depicted in panel (c), a structure having a height of approx. 145 nm can be observed. The intensity profile for the far-field CARS experiment (shown by dashed line) is almost flat and cannot describe the surface features in detail, while the SNOM-CARS intensity profile (shown by solid line) can resolve the surface features of the sample with high resolution.

The change in CARS signal intensity occurs due to the variation in thickness of the nanostructure of the sample of interest. In order to monitor the variation in the CARS intensity as a function of structure height, we investigated a region in another sample of P3HT where the height of the P3HT nanostructure was approx. 1.5 μm. The experimental results are depicted in figure 6.2.3.

Panel (a) shows the far-field micro-CARS image, panel (b) the near-field SNOM-CARS image, panel (c) presents the AFM topographic image, and panel (d) again shows the CARS intensity profiles along a section indicated in the CARS images. All images were recorded on the same region of the sample. A higher lateral resolution in SNOM-CARS, as compared to micro-CARS, is confirmed by the intensity profiles displayed in panel (d) of figure 6.2.3, where the dashed line shows the far-field micro-CARS profile and the solid line that of the near-field SNOM-CARS profile. In addition, as opposed to panel (d) of figure 6.2.2, panel (d) of figure 6.2.3 shows the changes in the relative intensity both in the far-field as well as in the near-field due to the rather thick structure, which also yields a clear signal for the micro-CARS experiment.
CARS microscopy in the far- and near-field

Figure 6.2.3 Results obtained for a bigger P3HT surface structure. Panel (a) shows the micro-CARS image in the far-field, panel (b) the SNOM-CARS image in the near-field, and panel (c) shows the AFM topography of the same sample surface area. The feature clearly visible in the AFM image has a height of approximately 1.5 μm. Panel (d) shows the CARS intensity profiles along a section across the 20 x 20 μm² sample area for both micro-CARS and SNOM-CARS.

As was also demonstrated in the investigation of the Au-P3HT interface, the SNOM tip does not only yield a relatively high lateral resolution, but also a very high axial resolution, which is even increased when the enhancement of the laser fields in the near field due to the tip-enhancement effect of the sharp edges of the metal coating contributes.

The axial resolution of a microscope objective is given by

\[ \Delta z = \frac{1.5 \times n \times \lambda}{NA^2} \]
CARS microscopy in the far- and near-field

Now by using a high numerical aperture objective of 1.5, an index of refraction of 1.6, and a wavelength of 650 nm, one can estimate a theoretical value of 795 nm. Since, in our experiment we are using an objective only having a numerical aperture of \( NA = 0.25 \), the axial resolution is less, but still enough to resolve the 1.5 \( \mu \text{m} \) high structure. This is also due to the fact that the nonlinear interaction of the laser foci with the sample increases the resolution. However, the structure used for the first experiment cannot be resolved anymore. The high axial resolution of the SNOM tip combined with the tip-enhancement effect is estimated to be on the order of 10 nm as shown in the experiment on the Au-P3HT interface.

Due to the influence the metal-coated tip has on the laser fields, it was important to also compare the temporal resolution achieved with micro-CARS and SNOM-CARS. For this, we have measured the cross correlation between pump and Stokes pulses under both experimental conditions (see figure 6.2.4). The FWHM was found to be approx. 150fs for both far- and near-field experiment, i.e., the temporal resolution is not influenced by the SNOM tip.

In conclusion, we found that femtosecond time-resolved CARS experiment are possible in combination with SNOM both in vibrational and electronic resonance without sample destruction.

By using the CARS technique we were able to obtain highly spatially resolved images in combination with near-field microscopy. We demonstrated first results of femtosecond coherent anti-Stokes Raman scattering (fs-CARS) with sub-diffraction-limited resolution. For this, a scanning near-field microscope with fiber tips having apertures of 300 nm was used. Images of P3HT nano-structures have been obtained using the SNOM-CARS
CARS microscopy in the far- and near-field technique. A comparison between P3HT structures of different heights (145 nm and 1.5 µm) shows that especially the axial resolution obtained with SNOM-CARS clearly beats the resolution that can be obtained even with high NA objectives.

![Figure 6.2.4 Cross correlation between the pump and Stokes pulses determined using micro-CARS and SNOM-CARS setup. The far-field and near-field cross-correlation traces had a full width at half maximum (FWHM) of approx. 150 fs (instrument response time) for both far-field and near-field CARS.](image-url)
Chapter 7

Summary and Outlook

The thesis describes the application of a combination of two nonlinear spectroscopic techniques, transient absorption pump-probe and coherent anti-Stokes Raman scattering (CARS) spectroscopy, with scanning near-field microscopy for the investigation of vibrational dynamics and exciton dynamics of organic semiconductors.

Section 5.1 of chapter 5 presents results from pump-probe-SNOM experiments used for studying the exciton dynamics in the organic semiconductor 3,4,9,10-perylene tetra carboxylic dianhydride (PTCDA), which is an important model system that could help to gain information about the processes playing a role in organic electronic devices. We have investigated thin films formed by PTCDA nanocrystals. Comparing results obtained from transient absorption experiments with different spatial resolution from few micrometers down to sub-100-nanometer resolution, different lifetimes of the photo induced exciton states could be observed. A series of experiments has been performed, which yielded information about the dependence of the exciton dynamics on exciton density. We have demonstrated that the SNOM approach does not only help to avoid structural inhomogeneities, but also yields results with much more well-defined excitation intensity.

The intensity dependent exciton dynamics observed at exciton densities higher than $10^{19}$ cm$^{-3}$ is attributed to exciton-exciton annihilation. Interestingly a difference in exciton-exciton annihilation rate is observed in far-field and near-field measurements. The rate of exciton-exciton annihilation in the near-field is 23% less than that obtained from the far-
field measurement. The reason for this was the averaging over different pump intensities present across the focal area of the laser pulse, which correspond to different exciton densities in the sample, for the far-field experiment. The SNOM tip selectively probed different regions of the focal area and thus yielded results attributed to well-defined pump excitation intensities corresponding to well-defined exciton densities. Besides dynamics the PP-SNOM is also capable to record images with high spatial resolution beyond diffraction limit. SNOM images of 160 nm thin film of PTCDA were recorded using transient absorption in the near field. While AFM images only yield topographic information PP-SNOM images additionally give chemical information.

Section 5.2 of chapter 5 presents the experimental results of another organic semiconductor, P3HT (Poly(3-hexylthiophene). Here, we were interested in the interface between a gold electrode and the semiconductor. Photo-induced exciton dynamics are expected to be changed in a semiconductor in the proximity of a metal layer. The length scale of such interface induced modification is in the nanometer range and is defined by the exciton diffusion length. Up to now, a highly localized access has not been demonstrated and diffraction-limited micro spectroscopy did not detect a difference in the dynamics of interface and bulk. In our work, we have combined scanning near-field optical microscopy (SNOM) with tip enhancement from a metalized tip in order to improve the axial resolution to a range, which enabled us to study the interfacial dynamics of an Au-P3HT system. Femtosecond time-resolved transient absorption spectroscopy now yields the early exciton dynamics in P3HT. We demonstrate that the exciton relaxation is significantly faster at the Au-P3HT interface than in neat P3HT. Additionally, significant differences in the long-time behavior (picosecond range) are
Summary and Outlook

also observed comparing bulk and interface data, which is attributed to long-lived trap states.

We not only used P3HT for our PP-SNOM experiment, but we also have investigated this semiconductor material in an experiment, which for the first time demonstrated the combination of femtosecond CARS (fs-CARS) and SNOM for sub-diffraction limited resolution. These results are described in chapter 6. SNOM-CARS images of (P3HT) nano-structures have been obtained. A comparison between P3HT structures of different heights (145 nm and 1.5 μm) shows that especially the depth resolution obtained with SNOM-CARS clearly surpasses the resolution that can be obtained with microscope objectives. Both the nonlinear technique PP-SNOM and SNOM-CARS provide high lateral and axial resolutions.

For future work, time resolved CARS and pump- CARS experiments in the near-field are planned, which probe the vibrational dynamics with femtosecond time-resolution localized to nanoscale, and to see whether the local dynamics are changing when comparing near-field with far-field. An interesting candidate is a blend of P3HT with ZnO nanostructures, where the ZnO nanostructure vibrational Raman mode is far away from the P3HT C=C ring stretching mode and could provide high chemical contrast images. Highly localized dynamics in the near-field could demonstrate the influence of the ZnO nanoparticles on the P3HT exciton dynamics. Another interesting experiment would be the investigation of the Au-P3HT contact, when different external electric fields are applied. A variation of the exciton dynamics especially in the interfacial region can be expected.
Summary and Outlook

The combination of time-resolved spectroscopy with near-field microscopy remains a very challenging task. There are a number of problems and challenges, which have to be dealt with also in future:

1. The tight focusing of femtosecond pulses is always critical. The high peak power of the pulses can easily ionize the medium and optical break down of the sample happens.

2. The mechanisms of damage are not well understood. Pulse energies of < 1 nJ had to be applied in most cases in order to avoid damages. As we reduce the power of incident pulses, the signal is also reduced and even sensitive detection schemes (e.g. Avalanche photo diode) are at their limit when detecting signals from SNOM tips.

3. The repetition rate of the laser systems is another important factor in microscopy. High repetition rate systems are used in most of the works because the enable to do faster imaging. Also the pulse power can be decreased still yielding signals with good signal to noise ratio (e.g. making use of lock-in amplifier technique).

4. The peak power can be reduced by reducing the pulse width to few picoseconds. In Raman imaging this also gives good spectral resolution because most of the condensed matter systems have Raman line widths of few 10 cm\(^{-1}\). However, this will cause poor temporal resolution. We are interested in studying both the dynamics and imaging at the same time.

5. Using wavelengths near the IR region would help reducing damage due to electronic absorption. Unfortunately, when interested in excited state dynamics, this is not an option. Lasers in resonance with electronic transitions are required to excite and probe the ultrafast processes.
References


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86 WOLLENHAUPT, M. *et al.* FEMTOSECOND PUMP-PROBE PHOTOELECTRON-SPECTROSCOPY ON ELECTRONIC STATES OF NA2: A TOOL TO STUDY ULTRAFAST CONTROL OF CHEMICAL REACTIONS.


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List of Publications

- Pump-probe scanning near field optical microscopy: Sub-wavelength Resolution chemical imaging and ultrafast local dynamics
  

- Scanning near-field optical coherent anti-Stokes Raman microscopy (SNOM-CARS)
  

- Nonlinear Spectroscopy in the Near field: Time Resolved Spectroscopy and Sub wavelength Resolution Non-Invasive Imaging, Nano photonics. 2013 (Invited Review)
  
  **M. Namboodiri, T. Z. Khan, K. Karki, M. M. Kazemi, G. Flachenecker, V. Namboodiri and A. Materny,**

- Vibrational dynamics and energy transfer in imidazolium-based ionic liquids probed by femtosecond coherent anti-Stokes Raman scattering,
  

- Application of Coherent Anti-Stokes Raman Scattering- Probing Vibrational Hot State Dynamics and Non-Invasive Chemical Specific Imaging, DAE-BRNS National Laser Symposium (NLS-22), p 42

- Femtosecond Time-Resolved Spectroscopy with Sub-Diffraction-Limited Lateral and Ultrahigh Axial Resolution
  
  **Tahir Zeb Khan, Patrice Donfack, Mahesh Namboodiri,Mehdi Mohammad Kazemi, Sidhant Bom, Veit Wagner, and Arnulf Materny**

  *(Submitted for publication)*
List of Publications

- A Review on Time resolved exciton dynamics and Sub wavelength Resolution Non-Invasive Imaging of organic semiconductors in the near field. (In preparation)

  *Tahir Zeb Khan, Patrice Donfack, Mahesh Namboodiri, Mehdi Mohammad Kazemi, and Arnulf Materny*
Appendix

The Appendix describes all the publications listed, which are summarized in this thesis and other works, I contributed during the course of my PhD at Jacobs University Bremen.