Ultrafast nonlinear response of plasmonic nanoantennas

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1 Introduction

The influence of light on all aspects of human life is virtually unlimited. Electromagnetic waves fulfill a variety of purposes: nowadays more and more as carrier of information or as an instrument to obtain information. Of immense importance is the interaction of electromagnetic waves with matter. The objective of this work is to provide new insights into the physical concepts behind light-matter interaction, an important field combining the major disciplines optics and solid-state physics down to the atomic scale. This goal is achieved by exceeding the limits of the current understanding of light-matter interaction across multiple dimensions: mastering the reduction to the nanoscale at the same time as tracing ultrafast processes allows to observe effects that are not accessible under conventional conditions. Apart from this deeper insight into basic physical relations, the experiments and their results presented in this thesis also expand the scope of applications from routinely used tools as in computer technology up to highly sophisticated scientific methods in many experimental disciplines.

To capture this in more detail, it is necessary to address at first the main concepts of electromagnetic waves interacting with certain types of matter. It is of special interest to investigate the response of metals to optical excitations in the near infrared range (NIR): their free charge carriers are able to respond to the driving force - that is, the incident electric field - with collective oscillations. Thereby they give rise to a variety of effects, summarized under the keyword plasmonics. This promising field passed a rapid development over the last decades, revolutionizing many disciplines and emerging with novel applications constantly [Ozb06, Sch10, Hal10, Bar03].

The experiments performed within the scope of this thesis are dedicated to the investigation of the optical interaction with gold, a metal equipped with excellent plasmonic properties to suit this purpose. Its high value in the ordinary world is not very surprising in consideration of its superior physical characteristics (although they are a minor cause for the popularity of this noble metal). Apart from being chemically stable, which is in general a favorable characteristic in experiments, gold impresses with its optical properties in different spectral regimes. Being relevant for many purposes, the optical response is subject of diverse studies [Joh72, Boy14, Key01, Bla10, Olm12, Hao07, Hac88, Chr71, Gue75]. In particular, gold is of exceptional importance in plasmonic applications. As a conductor it provides the necessary free electrons, yet it exhibits interband transitions in the visible regime, providing it with a semi-conductor like optical behavior close to a “band gap” [Mar14].

In contrast to conventional usage of gold, plasmonic experiments benefit the most when the amount of this valuable noble metal is reduced to a minimum [Nov12]: restricting the plasmonic response spatially over several orders of magnitude down to the nanoscale gives rise to an altered interaction: in gold particles with dimensions comparable to the wavelength of the
incident light, evanescent fields inside the metal cannot be neglected anymore. Thus, the nanoparticles can support certain resonances in the collective oscillations. Firstly, this implies to achieve the transfer of the classical antenna concept of receiving and emitting electromagnetic radiation to spectral regimes not accessible before [Bha09, Bia12b, Nov11]. Secondly, the reduction of the transmitter size to the penetration depth of the electromagnetic radiation into the metal enables to overcome the diffraction limit [Sch10] and to provide enormous field enhancement via the lightning rod effect [Bha09, Sun05].

The spatial confinement and the resulting enhancement of electromagnet fields become even more interesting when combined with extremely short light pulses. Investigating ultrafast nanooptical processes itself opens up various possibilities. But additionally increasing the already high peak intensities of ultrashort optical pulses offers the possibility to leave the ordinary linear regime and observe nonlinear effects [Vas09, Han11, Ryb16, Kni15, Kni17, Kni18]. This powerful combination can be used to boost the scope of experimental investigations and to access phenomena in the ultrafast and nonlinear optical regime, as performed for this thesis. Moreover, both the coherent and incoherent nonlinear effects occurring in the nanostructures are investigated to gain insight into the internal electronic processes. Via third harmonic generation (THG) [Blo69], visible light is coherently emitted when the particles are illuminated in the near infrared regime. The mechanism is based on the frequency conversion of long-wave light to photons with the threefold amount of energy. The sharply defined THG emission is accompanied by broadband incoherent multi-photon photoluminescence (MPPL) [Bia12a, Sha13]. Both phenomena are exploited in many applications, such as microscopy [Bha09, Dur07], ultrafast pulse measurement [Tsa96, RO04, Hyy17b] or plasmonic mode mapping [Ghe08, Han12, Hua10]. They are used mostly separately and their concurrent occurrence is often lowering the efficiency of the respective targeted process. Hence it is important to fully understand all occurring effects and their influence on the optical response. This thesis highlights how complete control can be achieved and that in particular the combination of coherent and incoherent emission can be turned into an advantage.

Generating and detecting these nonlinear effects poses several experimental challenges due to the four-dimensional confinement: to give an order of magnitude, the ultrafast timescale requires a temporal resolution in the range of a few femtoseconds ($1 \text{ fs} = 10^{-15} \text{s}$), while at the same time, the spatial confinement to the nanoscale has to be mastered. The widespread utilization of nanostructures has propelled the search for advanced fabrication methods over the past decades, boosting resolution, flexibility, and efficiency enormously. Applications range from ultrafast nanooptics [Vas09], tunneling and quantum-mechanical experiments [Fit17, Ryb16], the generation of nonlinear emission [Vam17, Pfu13b, Pfu13a, Han12, Dan07], enhancement of nanomitters [Cur10, Pfe10, Reg16, Kin09, Hal10] sensory devices [Tan08, Liu10] to solar cells [Pil07] as well as (bio)-imaging and microscopy [Bha09]. The experiments presented in this thesis are performed on gold nanostructures with precisely controlled size parameters in addition to flexible adaption in shape and crystallinity. The standard fabrication technique to
meet these demands is based on electron beam lithography (EBL) [Che15], which enables to custom tailor nanostructures for almost any purpose at high precision. As a top-down process it is limited to polycrystalline gold, so in addition a scheme for the fabrication of single crystal nanoparticles with controllable size and shape parameters must be developed. For this thesis, the combination of a wet-chemical process to grow gold microplates [Rad12] and subsequent structure milling with a focused ion beam (FIB) is adapted to fit the desired purpose. Supporting simulations of the nanostructures’ expected optical response increase the efficiency of the fabrication procedure. The simulations are based on a boundary element method and performed with a MATLAB toolbox provided by Prof. Dr. Hohenester et al. [Hoh12, Wax15]. The computer-based results also assist with the analysis of the experimentally achieved data [Kni15].

The corresponding experimental implementation to provide few femtosecond light pulses in the NIR regime is based on fiber laser technology [Bri14, Ryb16]. One of its big advantages is the wide spectral range that can be covered, yielding wavelengths from 850 to 2200 nm. Apart from satisfying the necessity for ultrashort pulses, it allows tuning the excitation in the experiments and thus gives access to advanced spectroscopy. The generation, control, and compression of such pulses as well as the precise excitation of single nanostructures with them is all done in a comparably small and efficient tabletop setup. From the generation of the seed pulses up to the frequency converted optical response of the nanostructure, the long concatenation of exploited nonlinear effects demands perfect system stability while the overall nonlinear order of the nested processes increases.

With this experimental equipment, two major topics can be addressed at the same time: investigating nonlinear effects triggered by the plasmonic light-matter interaction in the nanostructures helps to understand the fundamental physical processes occurring on the electronic level. Furthermore, insight into the response of nanostructures in turn gains control over their behavior so that they conform to various requirements. To achieve this, the experiment is split into several subtasks focusing on different aspects. First, it is crucial to analyze the nonlinear response spectrally. Thereby, the aforementioned coherent and incoherent contributions can be separated to evaluate their dependence on geometry and material [Kni15]. The nonlinear character is addressed with a novel order analysis: it is performed spectrally resolved, in contrast to the approaches before based on integrated emission [Sch05, Mue05, Bia12a, Jia13, Bou05, Dem16, Eic07, Mej16]. With these aspects thoroughly investigated, the influence of the excitation wavelength is targeted as the next step. By separating the response in coherent and incoherent contributions linked to distinct nonlinear effects (THG vs. MPPL), it is possible to gain fundamental insight into the general nonlinear properties of gold while ruling out normally accompanying uncertainty factors [Kni17]. This is crucial since gold, as mentioned before, is widely favored as a plasmonic material especially in the visible and NIR regime, and furthermore exhibits an extremely high nonlinearity. Thus not only fundamental physics profits from the results, yet also advanced applications. Despite this
1 Introduction

importance, the literature lacks a comprehensive analysis of the nonlinear susceptibility and especially of its wavelength dependence. Instead a variety of values determined under different experimental conditions and for various parameters are reported [Boy14, Con12]. Having completed the spectral analysis from both the excitation and emission side, it remains to expand the full control towards the temporal properties. First of all, it is worth noting that many applications based on plasmonic excitations in nanostructures depend on their respective lifetime. Thus it is crucial to understand which properties influence the decay times on which scales [Han12, Sön02, And10]. Many studies tried to answer this question [Han09, Han11, Sön02, And10, Bos13, Kra16, Lam99], however most of them are restricted to specific models that require assumptions in advance and only give rough time constants as an estimate instead of the complete dynamic behavior. Having at hand the high temporal resolution thanks to the ultrashort pulses used for the optical sampling, this work aims to go one step further and challenges the conventional decay model by analyzing the full plasmonic response [Kni18]. Furthermore, it overcomes the restriction of former studies to polycrystalline materials. Since single crystals with their ordered inner structure are more promising for applications requiring long-lasting plasmonic support, they are investigated in comparison to their polycrystalline counterparts.

Hence, the concept of this work can be summarized: by literally shining light into darkness (darkness naturally protected by the diffraction limit), the same is achieved on a metaphoric level, extending our current knowledge of nanoplasmonic light-matter interaction.
2 Light-matter interaction at the nanoscale

Light-matter interaction can be described in a first approach by the interplay of linear optics and classical electrodynamics [Jac99, Hec02]. For higher light intensity, nonlinear effects must be taken into account, as illustrated in the next chapter. Here, we focus on the linear interaction, especially between light and metals, since plasmonic excitations in nanostructures form the fundamental basis of the experiments presented in this thesis. The transfer to the nanoscale requires some adaptions to account for all the effects observed in this regime, but the main principles can be described with linear optical interaction in metals. Details can be found for example in [Nov12].

2.1 Principles of light-matter interaction

The temporal and spatial evolution of electromagnetic fields obeys a set of partial differential equations. In the international system of units it is given by:

\[
\begin{align*}
\nabla \cdot \mathbf{D} &= \varrho \\
\nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} \\
\nabla \cdot \mathbf{B} &= 0 \\
\nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} + j
\end{align*}
\] (2.1.1)

This system is called Maxwell’s equations and completely accounts for the influence of matter, charges and currents if combined with the material equations:

\[
\begin{align*}
\mathbf{D} &= \varepsilon_0 \mathbf{E} + \mathbf{P} \\
\mathbf{B} &= \mu_0 \mathbf{H} + \mathbf{M}
\end{align*}
\] (2.1.2)

Here, \( \mathbf{E} \) denotes the electric field with the corresponding flux density \( \mathbf{D} \) and \( \mathbf{B} \) the magnetic field with its flux density \( \mathbf{H} \). The polarization \( \mathbf{P} \) and the magnetization \( \mathbf{M} \) form the link between these quantities, while \( \varrho \) stands for the electric charge density and \( j \) for the electric current density. The constants \( \varepsilon_0 = 8.854 \cdot 10^{-12} \text{As/(Vm)} \) and \( \mu_0 = 4\pi \cdot 10^{-7} \text{Vs/(Am)} \) are called the vacuum permittivity and permeability, respectively.

We assume linear interaction in a medium of susceptibility \( \chi = \varepsilon - 1 \), with the dielectric function \( \varepsilon \) describing the optical response. Incident electromagnetic fields induce an instantaneous polarization proportional to the electric field:

\[
\mathbf{P} = \varepsilon_0 \chi \mathbf{E}
\] (2.1.3)

For nonmagnetic materials without free charge carriers and currents, the inhomogeneous wave equation for linear optics can be derived from Maxwell’s equations 2.1.1 and the material equations 2.1.2:

\[
\nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \mathbf{P}}{\partial t^2}
\] (2.1.4)
The solutions of this partial differential equation have the oscillating character in common. One possible homogeneous solution is given by a transverse plane wave with frequency $\omega$ and amplitude $E_0$, propagating along the direction of its wave vector $k$:

$$E(r, t) = E_0 \exp(i(kr - \omega t))$$ (2.1.5)

For electromagnetic waves like this, the dielectric function $\varepsilon$ of a material generally depends on their frequency $\omega$. The optical response of a medium to oscillations at a certain frequency is determined by the dispersive behavior of $\varepsilon(\omega)$, e.g. via the index of refraction $n(\omega) = \sqrt{\varepsilon(\omega)}$ and the absorption coefficient which is related to the imaginary part of that generally complex quantity. Real and positive $\varepsilon(\omega)$ therefore is equivalent to a material which is transparent at this frequency. In the case of metals, the dielectric function is complex and strongly influenced by the quasifree charge carriers that exist in a conductor. The electrons in the half-filled conduction band form a so-called Fermi gas that behaves similarly to a plasma where the positive charge carriers are the fixed ion hulls. To understand the interaction of the free electron gas with electromagnetic waves, a modified Lorentz oscillator is applied, as derived in the next section.

### 2.2 Optical properties of gold

The focus lies now on metals, especially gold, as it is an ideal material for the plasmonic experiments performed in this thesis. Gold is inert under ambient conditions and has a high optical conductivity. It is of special importance for plasmonics, since the downscaling for gold nanoparticles to typical resonances in the visible regime stops at feasible sizes. Furthermore, the high nonlinearity can be exploited for a variety of effects, as will be discussed later. First, the linear properties are derived.

The electron dynamics in metals is described in the Drude-Sommerfeld model by a damped harmonic oscillator driven by the outer electric field $E$, but without a restoring force for the quasifree electrons in the bulk material. The displacement of the comparably heavy ion hulls is neglected. Their positive charge induces a restoring force via Coulomb interaction and is introduced later phenomenologically through the polarization, but actually requires quantum mechanical treatment. Absorption is also introduced phenomenologically via a damping term $\gamma = 1/\tau$, with $\tau$ denoting the mean free time between two electron scattering events. It is a cumulative quantity, taking into account all different interaction possibilities for the electrons oscillating in the potential landscape. In metals, scattering events between charge carriers contribute primarily to the damping (Ohmic losses). The equation of motion for the electrons is equivalent to the one of the Lorentz oscillator:

$$\ddot{x} + \gamma \dot{x} = -\frac{e}{m^*}E$$ (2.2.1)

where $x$ denotes the displacement of the electrons carrying the elementary charge $e$. Their effective mass $m^*$ accounts for the influence of the condensed matter, since they do not belong
Figure 2.1: Complex dielectric function of gold from various sample types and experiments, split in the negative real part (a) and the imaginary part (b) [Olm12]. Both parts are shown in dependence of photon energy (bottom axis) and corresponding wavelength (top axis). The dashed line reflects the behavior of the free electron model without the influence of interband transitions.

to a real free electron gas, but to the quasifree charge carriers of the conduction band. They behave like free electrons with the corresponding mass in an outer field. For gold \( m^* = 0.99 m_e \) with the electron mass \( m_e \) [Joh72]. The quantity is linked to the band curvature.

The solution of the equation of motion 2.2.1 combined with the electron density \( n \) yields the macroscopic polarization \( P = n e x \). With plane waves as driving force of the oscillation, the solution for \( x \) inserted in the polarization equation can be used to derive the dielectric function from Eq. 2.1.3.

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}
\] (2.2.2)

The so-called plasma frequency \( \omega_p \) corresponds to the eigenfrequency of the undamped harmonic oscillator, i.e. of the free charge carriers in the metal. It is defined by:

\[
\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m^*}}
\] (2.2.3)

As a consequence of the plasma frequency, the real part of the dielectric function \( \Re(\varepsilon) \) exhibits a zero-crossing that influences the optical response drastically: below their eigenfrequency \( \omega_p \), the electrons follow the oscillations of an incoming electric field easily and reflect the light. This results in the typical metallic shine. Above the plasma frequency which normally lies in the ultraviolet (UV) regime, the electrons respond too slow and the material becomes transparent.
2 Light-matter interaction at the nanoscale

In the following, we focus on the optical properties of gold (plasma frequency $\omega_p = 8.55$ eV [Bla10]), a case in which the behavior is more complex due to interband transitions in the visible regime.

These cause an additional contribution to the absorption, which is introduced via $\varepsilon_\infty$, including the relative permittivity of the screening field from the bound electrons:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

(2.2.4)

Figure 2.1 shows the results of different experimental studies that determined the dielectric function of various gold samples [Olm12]. The data show a strong variance, which is unfavorable especially for nanooptical device engineering, where it is crucial to know the dielectric surroundings in detail [Olm12]. This uncertainty directly affects the susceptibility $\chi = \varepsilon - 1$, which is determined in experiments with comparable variance, particularly affecting the nonlinear behavior [Boy14]. This will be addressed later in detail, see Sec. 3.1 and Chap. 6.

As a comparison to the experimental data, Fig. 2.1 sketches the free electron response, which does not predict the actual behavior of the electrons very well. At least for higher photon energies above, since it neglects the interband transitions that set in at 1.9 eV and strongly shape the optical response [Hao07]. A closer look at the band structure of gold reveals more details. Figure 2.2 (a) shows bands as they are reconstructed from a calculation based on plane waves (black) and linearly expanded plane waves (green) [Key01]. Several fully occupied $d$-bands below the Fermi level $E_F$ lie close together. The $sp$-type conduction band is partly filled and intraband transitions are possible therein [Hac88].

Furthermore, electrons may transfer from the $d$-bands to free states in the conduction band, as it is sketched in the zoom of the band structure near the $L$-point in Fig. 2.2 (b) (blue). Optically induced interband transitions leading to the absorption of a photon occur vertically in the $k$-space, since photons do not provide sufficient momentum for indirect transitions. Interband transitions are most likely to take place at the $L$ or $X$ symmetry points in the Brillouin zone, as the local density of states (DOS) is very high there due to van Hove singularities [Boy86]. The optical response is dominated by the band structure and enhances absorption of photons with sufficient energy to cross the “gap” of 2.4 eV ($L$-point) or 1.9 eV ($X$-point) [Chr71, Gue75]. This results in the characteristic color of gold in contrast to other metals, whose interband transitions set in only in the UV regime.

In general absorption of ultrashort intense light pulses as applied in this thesis, changes the Fermi-Dirac distribution of the electron population significantly via all possible channels. Hot electrons, i.e. electrons with higher energies and not in thermal equilibrium with the material, are generated [Mar14, Cla14].

Figure 2.2 (c) shows how the DOS is forced out of its initial position (left panel, gray) by the absorption process. The hot electrons relax on a picosecond timescale via interaction with the lattice, so that the out-of-equilibrium distribution (blue - - -) turns into a Fermi-Dirac distribution but with elevated temperature (right panel) [DV12]. Consequently, only sub-picosecond light
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Figure 2.2: (a) Gold band structure, calculated from a plane wave ansatz (black) and a linearly expanded ansatz (green) [Key01]. Energy is shifted by the Fermi-level $E_F$ and depicted versus the most relevant points in the $k$-space. The region around the $L$ symmetry point is magnified in panel (b), where the interband transition of a $d$-electron ($e^-$) to a free state above the Fermi level $E_F$ via photon absorption is sketched (blue), as well as the radiative recombination of an excited sp-electron with a $d$-vacancy under emission of PL (green). (c) Sketch of the density of occupied states in gold (gray) in dependence of the energy. The arrows depict the interband (—) and intraband (- -) photon absorptions, changing the Fermi-Dirac distribution around the Fermi level $E_F$. The resulting nonequilibrium distribution (blue) of hot electrons relaxes via scattering to a Fermi-Dirac statistic of elevated temperature. Excited electrons recombine radiatively with $d$-band vacancies, emitting PL. The hot electron distribution transfers energy to the cold lattice until the original distribution is reset.

pulses generate a significant hot electron contribution [Fal99]. The excited electrons from the polaritons generated via interband transitions in the sp-band lose most of their energy via scattering and thereby contribute also to the hot electron distribution [Bev03, Cla14]. They can recombine radiatively with a $d$-band hole, as demonstrated by the green transition in Fig. 2.2 (b). This emission is called photoluminescence (PL) and was observed in metals first by A. Mooradian [Moo69]. Its spectrum represents the convolution of the electronic joint DOS between the involved bands with the optical coupling efficiency due to the particular structure geometry [Bev03]. The exact calculation is described in [Moo69].

As the nonequilibrium $d$-hole population undergoes fast energy and momentum relaxation via intraband scattering (internally or with phonons [Sha13]), the holes move easily in the flat $d$-band, covering all $k$-vectors of excited electrons. This results in recombination over a wide area where the large slope of the sp-band leads to very broadband emission.

2.3 Plasmonic properties of nanostructures

As explained in the preceding section, the free electron gas can undergo collective oscillations triggered by an incident electromagnetic wave. At optical frequencies where metals do not behave as perfect conductors anymore, the electron motion is phase lagged with respect to the driving field [Bia12b]. The strong confinement in a nanostructure to regions much smaller than
the electrons’ delocalization length leads to a restoring force via Coulomb interaction between the displaced electrons and the fixed ion hulls, as well as between concentrated electrons near the boundaries. Thus, at these scales the light-matter interaction becomes quantized and discrete optical resonances occur [Nov11, Pue01]. The corresponding quantization of the collective electron oscillation is called “plasmon”. The plasmonic response determines the behavior of the nanostructure in the interaction with the light field, which is in principle very similar to the classical antenna concept, with particular resonance properties and impedance [Bha09, Nov11, Bia12b]. Ergo, a nanostructure can serve as an emitter and receiver of electromagnetic radiation simply by the restriction of free charge carrier oscillations to certain well defined regions of space [Bia12b]. Highlighting this property, they are very often referred to as “nanoantennas”: emitters and receivers working in the optical or the infrared (IR) regime. However, the very strong confinement in the nanostructure leads to effects unknown from classical antenna theory, as they are irrelevant in the radio frequency range. For instance, despite the high reflectivity of gold in the near infrared regime (NIR), it is possible that evanescent fields enter the metal several nanometers deep (about 24 nm at a wavelength of 1200 nm [Kle07]). In this spectral regime, the metal is not perfectly conducting anymore, so the aforementioned phase lag becomes relevant. The skin depth is just on the order of typical antenna dimensions as for example for a simple rod shape\(^1\) with a length of approximately half the resonance wavelength, for which the receiving and emitting concept is shown in Fig. 2.3 (a). Actually, the resonance parameters scale differently in the optical regime, too, due to the considerable electron inertia (causing the phase lag), so that an effective wavelength is applied [Nov07, Bha09]. Also the nonlinear behavior is affected by the strong confinement, see Sec. 3.1 and 3.3, such that multipole and intraband transitions become likely [Bha09]. However, particle sizes of a few 100 atoms are sufficient to ensure bulk behavior of the dielectric response \(\varepsilon\) [Bev03] and the band structure [Dul04].

When treating the nanostructures as resonators, it is convenient to look at the quality factor \(Q = \lambda_{\text{res}}/\Delta \lambda = E_{\text{res}}/\Gamma\) with the resonance wavelength \(\lambda_{\text{res}}\) and a resonance width at full width half maximum (FWHM) of \(\Delta \lambda\) and the corresponding values in terms of energy, \(E_{\text{res}}\) and \(\Gamma\) respectively. Despite modest \(Q\) values (10 - 100) sufficiently small metallic resonators can outperform dielectric cavities (\(Q \sim 10^6\)) by offering a broadband response and easy electrical access [Sch10]. Typical resonance spectra are presented in the next section.

On resonance, the big displacement of the charge carriers induces a strong associated field concentration and thus enormous field enhancement via the lightning rod effect. It is particularly prominent at sharp tips, as in the so-called bowtie structures shown in Fig. 2.3 (b). The figure further demonstrates the first order plasmonic mode that develops in such a double structure arranged around a feedgap. Panel (c) shows a higher order mode\(^2\). Both stem from simulations explained in detail in the next section. Two single structures brought close enough

\(^1\)An overview over more complex antenna geometries suitable for specific applications is given in [Bia12b].
\(^2\)The modes are visualized via surface charge gained from simulations, see Sec. 2.4.
Figure 2.3: (a) Antenna concept demonstrated at the nanoscaled analog of a half-wavelength rod: electromagnetic waves (red) are received and generate a collective electron oscillation - the plasmon (violet). As the charge carriers dephase, the converted energy stored in the plasmon is either dissipated into electron-hole pairs via intraband and interband transitions (left) or is reradiated into the far field again (right) as an electromagnetic wave (blue). (b) and (c) show two possible plasmonic modes at a certain phase angle (top) and a half cycle later (bottom), that can be excited in a bowtie type nanoantenna featuring a feedgap in which a nanoemitter (e.g. quantum dot or molecule) can be placed. The smaller the gap, the stronger the coupling of the plasmons in the single triangles, lowering the total energy. The coupling principle is sketched for double rods in the bottom of panel (c), forming antibonding and bonding patterns.

Together experience coupling between the respective plasmons, reducing the energy level in the so-called bonding mode, where the electrons of both single structures oscillate in phase (see sketch at the bottom of panel (c)). The reradiated emission is redshifted with respect to the single structures’ emission. Principally, also the antibonding mode can develop, although it corresponds to a higher energy level when the charge carriers oscillate symmetrically with respect to the feedgap. It is also referred to as “dark” mode since it does not reradiate energy into the far field, lacking the necessary dipole moment.

The field enhancement offers the outstanding possibility to force light concentration below the diffraction limit [Sch10]. Ergo it makes sense to place nanoemitters like quantum dots (QD), molecules, etc. there, see Fig. 2.3 (b), which are difficult to couple light into them due to their small dimensions. The field enhancement is reported with varying results in the literature, and values of up to 100 - 1000 [Sun05, Bha09], since it depends strongly on the particular antenna parameters like size, shape, material and dielectric environment [Cro03]. It definitely benefits from double structures featuring a feedgap. The enhancement is maximal inside the gaps, as

\[ \text{Furthermore, the references often do not specify if they treat the factor as the maximal value at one position (which?) or if they average over a region (where?). This complicates comparisons. The exact parameters should always be specified.} \]
demonstrated in Fig. 2.4 with simulation results (see next section for details) and can be as high as 40 (averaged over the $z$ dimension) [Ryb16]. This value is confirmed by other simulation techniques, as well as by experiments probing the maximum field enhancement via ultrafast photoemission [Rac17], although it is very sensitive to the specific (gap) dimensions [Sun05]. The intensity enhancement of a single antenna can be increased even further (by a factor of 1000) when it is embedded in a periodic array [Ko11]. These can reradiate the light emitted by their neighbors in addition to the incident illumination [Cro03]. The main disadvantage of arrays is the inhomogeneous broadening of the results and therefore only single antennas are used in this thesis. Although only nonlinear emission is investigated, single structures yield sufficient output at moderate excitation intensity due to their high field enhancement. This together with the strong confinement renders plasmonic nanodevices an outstanding tool for numerous applications. They serve directly in fundamental physics, for instance to investigate quantum effects [Fit17] or nonlinear light-matter interaction as in this thesis [Kni15, Kni17, Kni18]. Additionally, their ability to confine and enhance electromagnetic fields supports other experiments, like in ultrafast nanooptics [Vas09] and for tunneling experiments [Ryb16]. Their nonlinear behavior (details in the next chapter) is exploited in high harmonic generation (HHG) [Pfu13b, Pfu13a, Vam17] and frequency mixing [Dan07, Han12] and the strong fields can increase the energy density on single photon sources such as QDs [Cur10, Pfe10, Reg16], molecules [Kin09] and nanodiamonds [Sch09]. They improve the efficiency of sensory devices [Tan08, Liu10] and increase photoluminescence [Sha13] as well as the performance of biomarkers and solar cells [Pil07, Hal10]. Apart from the strong field enhancement especially their ability to overcome the limit of diffraction establishes them as irreplaceable tools in modern (bio)-imaging and microscopy [Bha09].

The basic concept of nanoantennas is to receive and convert or reemit electromagnetic waves, as sketched in Fig. 2.3 (a). The depicted scheme explains further conceptually, how the thereby excited collective oscillation of charge carriers develops over time and how the stored energy is transferred into the far field. The rather low $Q$ values already hint to a strong damping of the plasmon, which can also be described by a harmonic oscillator model amended with a damping component [Bos13]. Two loss channels give rise to the damping term: plasmons can lose energy via inelastic dissipation processes connected to the time constant $T_1$ as well as via loss of their coherent phase relation, a purely elastic interaction described by the time constant $T^\ast$. The latter includes elastic scattering process among the electrons or between electrons and the surface, defects or phonons. The two constants are combined to the plasmonic dephasing time $T_2$ [Sön02]:

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T^\ast}.$$

$T_2$ corresponds to the time when the field amplitude has decreased to a fraction of $1/e$ of its maximal value. It represents the whole damped harmonic oscillator model with Lorentzian lineshape condensed into the time constant of the related exponential decay in the temporal
domain. It should not be confused with the decay time $\tau = T_2/2$, which is connected to the decay of the oscillation energy to a fraction of $1/e$ of its maximum.

The dissipative processes can be distinguished into radiative and nonradiative channels. The first converts the energy into emitted photons and dominates for larger particles with dimensions above 40 nm [Wok82, Han11, Cla14], the latter is transacted via intraband and interband transitions (if they are energetically accessible, compare Sec. 2.2). This Landau damping [Kre95] causes the plasmon to dephase into single excited electron states by losing coherence of the collective oscillation via interaction with defects, walls etc. [Mar14, Hau15]. The single excited electrons dissipate their energy via scattering.

The coherence of the collective oscillation is lost through the discussed channels on a timescale of a few femtoseconds only. The remaining single excited electron states then relax back into the ground state over timescales of 100 fs via electron-electron scattering and over 1 - 10 ps via electron-phonon scattering, until the Fermi distribution is recovered. Remaining hot electrons can further lose energy via phonon-phonon interaction on the order of 100 ps [Cla14, Mar14, Hau15]. These timescales are all short versus the repetition rate of the laser used for experiments in this thesis, so that heating up the sample from cycle to cycle is negligible. However, the extremely short dephasing time $T_2$ challenges requirements concerning the ultrashort pulse length. It is therefore necessary to provide the shortest possible pulses. It is advantageous to investigate single nanostructures to determine $T_2$, so that no further inhomogeneous broadening is added to all the various decay channels [Kle05]. For the particle sizes used in the thesis, radiation damping dominates, as mentioned above. The spectral linewidth $\Gamma$ of the resonance therefore corresponds to the dephasing time via $\Gamma = \hbar T_2^{-1}$. This can be exploited in indirect measurements of $T_2$ [Sön02]. The broad antenna resonances are thus directly linked to the large damping, see Fig. 2.4 in the next section.

### 2.4 Simulation of light-matter interaction with Boundary Element Method

The relevant antenna properties such as field enhancement and resonance can be simulated with several methods. This helps to predict and compare the outcome of experiments, as well as to test theoretical models describing the electrooptical processes in the nanostructure. Simulations performed in advance of fabrication, determine the adequate parameters in terms of size, material and excitation for the desired application. Typical schemes are based on the finite difference time domain (FDTD) [Cro03, Sun05, Rac17] and finite element method (FEM) [Par10] or the discrete dipole approximation [Mer08]. In this thesis, a MATLAB® toolbox implementing the boundary element method (BEM) is applied [Hoh12, Wax15]. It is capable to simulate light-matter interaction in nanostructures by solving Maxwell's equations. In contrast to FEM, it restricts the task from the three-dimensional space to two dimensions, thereby reducing drastically the number of points in the discretization grid on which it is solved. Furthermore,
Figure 2.4: (a) Spatial map of the electromagnetic field at a gold bowtie antenna under NIR illumination from the \( z \) direction with plane waves polarized along the \( x \) direction, simulated with the BEM toolbox [Hoh12]. The inset shows a zoom in on the gap region. (b) Corresponding scattering cross section representing the resonance, for incident light with wavelength \( \lambda_{\text{exc}} \) polarized in parallel (red) and perpendicularly (blue) to the bowtie, whose surface triangulation is depicted in the corner. (c) Field enhancement close to the resonance wavelength of a similar bowtie as used with contacts in tunneling experiments [Ryb16], spatially resolved in the \( x-y \)-plane and averaged over the \( z \) values. Detailed information of the enhancement distribution in the gap is shown in the zoom.

The solution is calculated in the frequency space, not in the time domain as in FDTD. Actually, Maxwell’s equations are not only Fourier transformed for that purpose, but instead are transferred to another model of potential equations [GdA02, Kni12]. They are given by

\[
\begin{align*}
\triangle + k^2 \varepsilon & \ A = -h_s \\
\triangle + k^2 \varepsilon & \ \phi = -\sigma_s
\end{align*}
\]  

(2.4.1)

with the vector potential \( A \) and the scalar potential \( \phi \), as well as the surface charges \( \sigma_s \) and surface currents \( h_s \). The potentials are linked to the field quantities \( E \) and \( B \) via

\[
\begin{align*}
E &= ikA - \nabla \phi = \varrho \\
B &= \nabla \times A
\end{align*}
\]  

(2.4.2)

The surface charges and currents together with their particular boundary conditions at the interface between nanostructure and surrounding material form the key element. Since the potential equations can be solved straightforwardly within one material (either the metal inside the nanoparticle or the environment with their respective dielectric function) with the help of Green’s functions [GdA02, Kni12] the task is restricted to determine the surface conditions at
the two-dimensional (2D) interface. The resulting surface charges and currents can be used directly to visualize the plasmonic modes, as shown in Fig. 2.3 (b) and (c). Moreover, the full electromagnetic field can be calculated at any position inside and outside of the particle, as shown in Fig. 2.4 (a) for a gold bowtie antenna. Also the scattering cross section can easily be derived at any wavelength for which the dielectric functions are known. The bowtie from panel (a) yields the scattering cross section in panel (b), for incident light polarized in parallel (red) and perpendicularly (blue) to the long antenna axis. The maxima give a good estimate for the spectral position of the plasmonic resonance $\lambda_{\text{res}}$. The resonance width $\Delta \lambda$ is linked reciprocally to the dephasing time $T_2$. The inset shows the corresponding triangulation of the interface, which determines the points where the equations are solved directly. Knowledge of the resonance position in advance boosts the efficiency of the fabrication process because only the suitable size parameters need to be produced. Since for many applications the field enhancement is an important parameter, too, it makes sense to simulate it also in advance. This can be done spatially resolved at any point, starting from the surface charges. An example is given in Fig. 2.4 (c), for a bowtie antenna exploited in tunneling experiments [Ryb16]. There, ultrashort optical pulses bias the structure, so that single electrons tunnel from one triangle tip across the antenna gap to the other tip. Thus it is crucial to guarantee sufficiently high field enhancement to increase the tunneling probability. The zoom in on the gap region (bottom) shows field enhancement factors of up to more than 40 (averaged over the $z$ dimension of the feedgap region). The detailed simulation of such structures can be significantly reduced in costs by exploiting the inherent symmetry. In the case of the bowtie, only one quarter of the structure needs to be simulated.
3 Nonlinear light-matter interaction

For higher light intensities, the nonlinear behavior of light-matter interaction becomes relevant. To describe the response of a medium to intense electric fields, higher order terms are introduced. Consequently, the polarization does not respond linearly anymore: the Lorentz oscillator experiences larger displacement. The former parabolic potential is developed into a Taylor expansion. This results in a nonlinear equation and a variety of effects based on the interaction of the light field with itself while it propagates through the medium. New optical frequency components are generated directly in the near field by mixing the fundamental frequencies. This will be explained in more detail for a few special aspects that are particularly relevant in this thesis. For a general discussion see for instance [Boy92].

3.1 Nonlinear optical properties in gold

Developing the polarization $P$ (Eq. 2.1.3) into a Taylor expansion reveals its dependence on higher orders of the electric field [Boy92]:

$$P(t) = \varepsilon_0(\chi E(t) + \chi^{(2)} \otimes E(t)^2 + \chi^{(3)} \otimes E(t)^3 + \chi^{(4)} \otimes E(t)^4 + ...)$$ (3.1.1)

Here, $\chi^{(n)}$ denotes the nonlinear susceptibility of order $n$, a tensor of rank $n + 1$ linked via the tensor product $\otimes$ to the vectorial electric fields. It typically decreases in value for higher order terms, so that mostly second and third-order effects can be triggered at moderate intensities. Especially gold serves as a good basis to exploit its high $\chi^{(3)}$ [Blo69], yet it is challenging to determine it quantitatively. As described in the preceding chapter, the experimental data for the dielectric function of gold, linked to the susceptibility via $\chi(\omega) = \varepsilon(\omega) - 1$, exhibit a strong variety [Olm12]. The values of $\chi^{(3)}$ in gold differ even worse [Con12, Boy14]: the various studies addressing the topic investigate it under different experimental conditions, e.g. for various optical frequencies, although the susceptibility is like the dielectric function $\varepsilon(\omega)$ strongly dispersive in gold. Even more problematic, the studies exploit different nonlinear optical effects to determine $\chi^{(3)}$, without relating them to the specific contribution of this quantity. A more detailed analysis reveals that the $\chi^{(3)}$ has its origin in mainly three effects in gold [Hac88, Boy14]. First, there is the instantaneous “intraband” or “free-electron” contribution. Actually, the free electrons themselves do not directly give rise to a nonlinear term, simply because there is no restoring force that could be nonlinear. However, this becomes possible in nanostructures via the strong confinement [Lip05, Nov11, Boy14]. Ergo, this contribution is strongly size dependent. It is analyzed in detail in [Zhe95]. Instead, the so-called interband contribution is basically independent of size as it is linked to intrinsic properties of the gold band structure described in Sec. 2.2, allowing for interband transitions at certain frequencies [Hac88]. It is therefore highly dispersive [Con12]. The third contribution originates from the hot electron distribution. It is thus strongly influenced by
the electron temperature and relevant mostly for noninstantaneous effects on longer timescales [Hac88, Boy14].

In this thesis, the instantaneous and coherent contributions of the third-order susceptibility $\chi^{(3)}$ are exploited to drive nonlinear effects, as well as the noninstantaneous part. By relating the different effects, it is possible to highlight the strong dispersion of the $\chi^{(3)}$ as an intrinsic property of the gold, freed from the influence by the individual field enhancement of the nanostructures. Therefore it is necessary to drive the exploited nonlinear effects in the very same nanoemitter and separate their contributions, as demonstrated in Chap. 6. First, the relevant optical effects are introduced.

### 3.2 Coherent nonlinear emission

An interesting example for a coherent nonlinear effect is the expansion of the absorption process described in Sec. 2.2, when ultrashort light pulses illuminate a material which allows interband transitions: the high intensity leads to the simultaneous absorption of $n$ photons (multi photon absorption, MPA) with less energy than necessary to cross the “band gap” singly. This is indicated for two photons by the green arrows in Fig. 3.1 (a). It is absolutely necessary, that the photons are absorbed simultaneously, thereby guaranteeing coherence. Furthermore, real states in the band structure are obligatory. However, a similar coherent effect is possible also in transparent materials with sufficiently large nonlinearity, which does not require real states: the $n$ incident photons (red in Fig. 3.1 (a)) can be converted into one photon with $n$-fold energy (blue) that is instantaneously reemitted. This process is mediated via virtual states (dashed lines). In general, any $n + 1$ electromagnetic waves may be involved in such frequency conversion processes, and they can correspond to various frequencies, as e.g. in four-wave mixing (4WM) [Boy92]. In the special case of $n$ incident photons of the same energy, the scheme is called high harmonic generation (HHG) and requires extremely large intensities ($10^{13}$ W/cm$^2$) to observe high orders $n$ [Boy92]. Here we focus on the special cases depending on the nonlinear susceptibility up to the $\chi^{(2)}$ and $\chi^{(3)}$ terms.

#### 3.2.1 Second Harmonic Generation

When the Taylor expansion 3.1.1 is done until the quadratic term $P^{(2)}$ and an electric field oscillating at a frequency $\omega$ of the form

$$E(t) = E_0 \sin(\omega t)$$

is inserted, we can derive the following expression with the help of a trigonometric identity$^1$:

$$P^{(2)}(t) = \varepsilon_0 \chi^{(2)} E(t)^2 = \varepsilon_0 \chi^{(2)} E_0^2 \sin^2(\omega t) = \frac{1}{2} \varepsilon_0 \chi^{(2)} E_0^2 (1 - \cos(2\omega t))$$  

$^1$This derivation can be done analogously for short pulses.
Figure 3.1: (a) Coherent nonlinear processes sketched in a schematic metal band structure (gray). For MPA, the energy to transfer an electron \( \text{e}^- \) across the “band gap” into an available state above the Fermi level \( E_F \) in the \( sp \)-type conduction band is provided by the concurrent absorption of \( n \) photons (green). No real vacancies are necessary for SHG where virtual states (- -) mediate the frequency conversion of two incident photons (red) into one at the doubled frequency, which is instantaneously reemitted (blue). (b) Normalized spectra (intensity versus wavelength) of incident NIR laser light, fundamental (green - -) and influenced by the plasmonic response (red - -) of the nanoantenna on which the pulses are focused and whose scattering cross section \( C_{\text{sca}} \) is displayed (gray). Furthermore, the corresponding THG spectra (intensity versus THG wavelength) are shown: measured at the nanoantenna (blue) and calculated from the pure fundamental excitation (green — -) and the plasmonic response (red — -), respectively. The THG process is sketched in the middle.

Apart from a constant term, a contribution oscillating at a frequency of \( 2\omega \) is obtained. This process is called the second harmonic generation (SHG) and is a special case of sum frequency generation. The intensity \( I_{2\omega} \) of the SHG is proportional to the square of the incident fundamental intensity \( I_\omega \) and depends also strongly on the \( \chi^{(2)} \) term of the nonlinear susceptibility. In centrosymmetric materials, the sign of the electric field changes under spatial inversion, which is restored at even orders of the polarization. The equation is only fulfilled when the even orders of \( \chi^{(n)} \) vanish. However SHG may arise for a symmetry break, e.g. at the surface [Dad04]. For this reason we observe it also spuriously in gold nanostructures despite the fcc lattice. More important is its application in ultrashort pulse measurement, see Sec. 3.5, where nonlinear crystals with high second order nonlinearity are carefully chosen to gain as much SHG as possible: phase matching guarantees that the fundamental field propagating typically at a slower group velocity than the contributions oscillating at a frequency \( 2\omega \), is kept as long as possible in a coherent phase relation to the SHG [Bal99].

3.2.2 Third Harmonic Generation

The Taylor expansion 3.1.1 can also be derived until the cubic term \( P^{(3)} \), with the analog to the SHG being the third harmonic generation (THG), a special case of 4WM with three incident electric fields oscillating at the same frequency \( \omega \) and an emitted field converted to a frequency of \( 3\omega \). Its intensity \( I_{3\omega} \) scales with the cube of the incident intensity \( I_\omega \) and the third-order
nonlinear susceptibility $\chi^{(3)}$. In this thesis, the nonlinear optical effects are driven by broadband ultrashort laser pulses in gold nanoantennas. As the discussion in Sec. 3.1 revealed, the $\chi^{(3)}$ of gold originates from different sources, and for the THG as an instantaneous and coherent effect, only the corresponding instantaneous contributions by the free electrons and interband transitions are relevant.

Figure 3.1 (b) demonstrates how the broadband spectrum of the excitation $E_{\text{exc}}$ (green - - -) is reproduced in the spectrum of the THG (blue), as well as the influence of the plasmonic response of the nanoantenna: the gray graph is the simulated scattering cross section $C_{\text{sca}}$ of the gold bowtie antenna, that yields the red dashed spectrum $E_{\text{ant}} \propto C_{\text{sca}} E_{\text{exc}}$ when it is applied to the full laser pulse. For both spectra, the theoretical THG spectrum can be calculated (green and red, respectively) via a double convolution $E(\omega) \ast E(\omega) \ast E(\omega)$ with $E(\omega)$ being $E_{\text{exc}}$ or $E_{\text{ant}}$, respectively. The plasmonic resonance clearly affects the THG emission in the frequency domain, as the calculated spectrum fits the measured data better when $C_{\text{sca}}$ is multiplied to $E_{\text{exc}}(\omega)$ before the convolution, yielding $E_{\text{ant}}(\omega)$.

3.3 Incoherent nonlinear emission

Absorption of several photons can not only occur coherently, as described in Sec. 3.2, but also on noninstantaneous timescales via a cascade of single intraband steps. Electrons excited into higher levels of the conduction band through this channel emit incoherent radiation when they recombine with holes in the $d$-band. The process is called multi-photon photoluminescence (MPPL) for its nonlinear character. The specific scheme [Bia09, Bia12a] is explained in the following.

3.3.1 Multi-photon photoluminescence

As sketched in Fig. 3.2 (a) with curved arrows (I,II), incident photon can create vacancies in the $sp$-band below the Fermi level, which are filled with lower level electrons promoted by subsequent photons [Sha13]. Eventually, free states become available separated only by a short “band gap” from the $d$-electrons, so that even low energy photons are sufficient to induce interband transitions (III). The resulting hole population in Fig. 3.2 (b) is subject to fast scattering events in the flat $d$-bands. The holes can also recombine radiatively with excited electrons, emitting nonlinearly generated photoluminescence: MPPL. Mostly, the electrons relax under the generation of localized plasmons, which eventually can decay radiatively, thereby contributing to the MPPL later [Bia09, Bia12a]. Thus, the cascaded emission process is in contrast to the THG noninstantaneous and incoherent, and additionally bound to real states in the band structure. The sequential one-photon absorption steps depend on the lifetime of the intermediate states and the energy levels are strongly influenced by scattering events [Jia13]. In principle, any combination of interband and intraband steps can form the absorption channels which are
Figure 3.2: MPPL sketched in a schematic metal band structure (gray). (a) Sequential absorption steps consisting of an intraband transition (I) that lifts an electron $e^-$ above the Fermi level $E_F$ within the $sp$-band. The electron loses energy via scattering, but can also gain energy by further intraband absorptions (II), which can also fill the hole below $E_F$. This generates vacancies energetically closer to the $d$-band so that the NIR photon energy is sufficient for an interband transition of a $d$-electron (III). (b) As a result of these absorption cascades, an excited electron population is generated in the $sp$-band, while holes occur in the $d$-band. All charge carriers are dynamically redistributed due to scattering (dashed arrows), before they recombine radiatively (colored arrows), emitting broadband PL.

Additionally shaped by losses. Experiments investigating the MPPL dynamics show that it is most likely for four involved absorptions to consist of three (energetically overlapping) intraband sequences and a single-photon interband step instead of a combination of coherent multi-photon absorption [Bia12a]. This situation is sketched in Fig. 3.2.

In principle, intraband transitions are dipole forbidden, since their initial and final state have the same symmetry and additionally they are separated in $k$-space by a large momentum that photons cannot provide [Bev03]. However, the strong confinement in nanostructures increases the probability for higher order transitions and multipole modes, since the electromagnetic fields are not uniform over the dimensions of the subject and the photon momentum is not given anymore by its free space value [Nov11]. It can be increased by a factor of 100 in the optical near field [Bha09]. Due to the strong confinement, the dipole approximation is no longer legitimate. Instead, quadrupole mediated intraband transitions are likely to happen while obeying their selection rules [Bev03]. The interaction of the confined fields with the boundaries relaxes the momentum conservation requirements so that they can be overcome by the augmented $k$-vectors of the evanescent fields entering the structure [Mar14]. Altogether, the low quantum yield of MPPL is enhanced in nanoantennas [Eic07, Sha13].

3.4 Time domain aspects

As described in Sec. 2.3, the plasmonic dephasing time is the fundamental constant to describe the dynamics of the energy transferred via light-matter interaction generating a plasmon. The collective excitation can be described with a damped harmonic oscillator also when nonlinear effects come into play [Han11]. This is justified since the nonlinear behavior of the plasmonic oscillation, resulting for example in THG, is sufficiently small to not influence the temporal
The plasmon oscillation can be regarded as the source of the nonlinearity and the plasmonic dephasing time $T_2$ is a measure for the response time of the nonlinear susceptibility $\chi^{(3)}$ [Pue01, Kle05, Kra16]. In this thesis, it is determined via the detection of THG, with the analysis tools for ultrafast emission described in the next sections. However, since these require a purely instantaneous response whereas in our case it is mediated by the plasmon, some adaptions must be made, as described in Chap. 7.

The response time of the nonlinearity is on the order of a few femtoseconds only, however the triggered effects can persist on longer timescales: the dynamics of MPPL is governed by the lifetime of the intermediate states and typical decay times are on the order of a few picoseconds [Jia13, Dem16], depending on the hot electron distribution, see Sec. 2.3. Electrons with higher excitation energy above the Fermi level possess faster scattering rates [DV12].

### 3.5 Characterization of ultrashort light pulses

The investigation of physical effects on extremely short timescales at the best possible temporal resolution motivates the search for light sources generating ultrashort pulses. Accordingly, methods for the characterization of such pulses are developed. In principle, this requires a shorter event than the one under investigation. For the shortest possible laser pulses with durations of attoseconds to femtoseconds, all electric methods are out of question since they operate naturally on longer timescales. Therefore, the pulses are employed to gate themselves. Many different techniques apply this scheme and combine it with a nonlinear effect to enhance the sensitivity of the pulse characterization. An overview is given for example in [Gal00] and [Rho14]. The methods relevant for this thesis are explained in the following.

#### 3.5.1 Intensity autocorrelation

Performing an intensity autocorrelation (AC) is one of the fastest ways to estimate the temporal characteristics of ultrashort pulses [Sal80, Mes97]. The setup is based on a Michelson interferometer, as sketched in Fig. 3.3 (a), that splits the incident light at a beamsplitter (BS) into two identical replica

$$E(t) = A(t)e^{i\omega_0 t} =: E_t$$

with the complex amplitude $A(t)$ and $\omega_0$ as the central frequency\(^2\). Spatial dependence is neglected here. The replica propagate through different interferometer arms, of which one has an adjustable optical path length via a motor stage (MS). Thereby, one pulse can be delayed by

\[^2\text{Due to imperfections at the beamsplitters, the replica may be not perfectly identical, so that the pulses are actually split in two parts with amplitudes } \tilde{A}(t) \neq A(t). \text{ This discrimination is neglected in the following for better readability and has no significant consequences.}

Due to imperfections at the beamsplitters, the replica may be not perfectly identical, so that the pulses are actually split in two parts with amplitudes $\tilde{A}(t) \neq A(t)$. This discrimination is neglected in the following for better readability and has no significant consequences.

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a time \( t_d \) versus the other:

\[
E(t - t_d) = A(t - t_d)e^{i\omega_0(t - t_d)} =: E_{td}
\]  

(3.5.2)

A parabolic mirror focuses the pulses from both arms on a nonlinear optical element (NLE), for example a beta barium borate (BBO) crystal, where a frequency conversion process is exploited. Selected newly generated components are focused with a spherical mirror onto a photodiode (PD, path A in the figure), while the fundamental light is blocked by a short pass filter (SP). Depending on the applied nonlinear effect, several superfluous mixed frequencies are spatially filtered as well. Here, we focus on SHG as the method of choice, since it has many advantages such as a very high sensitivity, and therefore is exploited also very often in the technique described in the next section [DeL94, Kan99]. Nevertheless, there is a variety of alternatives, such as THG for example [Mes97]. For comparative details see [Tre97]. The signal field \( E_{sig}(t, t_d) \) at the crystal in the case of SHG is proportional to the square of the superimposed incident fields:

\[
E_{SHsig}(t, t_d) = (E_t + E_{td})^2 = E_t^2 + E_{td}^2 + 2E_tE_{td} \equiv \bar{E}_{sig}^{\text{blocked}}
\]  

(3.5.3)

Since the three contributions propagate in different directions, the SHG components of the single arms \( E_t^2 \) and \( E_{td}^2 \) can easily be filtered out spatially, while the integrated signal (proportional to the mixed component \( E_{sig}(t, t_d) = E_tE_{td} \)) is detected on the PD in dependence of the delay time \( t_d \) that is varied by moving the stage:

\[
I_{AC}^{SH}(t_d) \propto \int_{-\infty}^{\infty} \left| E_{sig}(t, t_d) \right|^2 dt = \int_{-\infty}^{\infty} \left| E_tE_{td} \right|^2 dt
\]  

(3.5.4)

The result of a typical AC measurement is depicted in Fig. 3.3 (b). The full width at half maximum can be used to extract from it a rough estimate of the pulse duration. Unfortunately, assumptions on the pulse shape are required as the direct pulse reconstruction corresponds mathematically to the ill-posed one-dimensional phase retrieval problem. This is a significant disadvantage of this in principle easy-to-implement scheme. It can be overcome with a quick adaption, adding a second dimension: acquiring the full spectrum of the nonlinear response at each position of the delay stage yields a data set including sufficient information to fully resolve the temporal shape (intensity and phase) of the original pulse. This technique is described in the next section.

3.5.2 Frequency resolved optical gating

An extension of the AC is the frequency resolved optical gating (FROG) which relies on an almost identical setup, depicted in Fig. 3.3 (a) as path B. The only difference is the detection of the full spectrum for each delay step on a spectrometer (S) instead of collecting the AC trace that is integrated over all wavelengths. Thereby, a two-dimensional (2D) spectrogram is recorded in
Figure 3.3: (a) Experimental setup for AC (A) and FROG (B). A beamsplitter (BS) separates the incident light pulses and sends them to two different arms of a Michelson interferometer of which one arm can be varied in length via a motor stage (MS) to control the delay time $t_d$ between the pulse trains. A parabolic mirror (PM) focuses the pulses on a nonlinear element (NLE). The sketch shows exemplarily all upconverted frequency components that arise when either SHG or THG (bottom) is exploited as nonlinear effect. Selected contributions are focused with a spherical mirror (SM) on a photodiode (PD) for AC or on a spectrometer (S) for FROG. Fundamental light is blocked by a short pass filter (SP). (b) Typical AC data $I_{SH}^{AC}(t_d)$ (intensity versus delay time $t_d$) for SHG and (c) SHG FROG spectrogram $I_{SH}^{FROG}(\lambda, t_d)$. The color-coded SHG intensity map is depicted in dependence of the delay time $t_d$ and the wavelength $\lambda$.

the frequency domain, see Fig. 3.3 (c), whose measured intensity is proportional to the Fourier transform of the signal field $\mathcal{F} \{ E_{sig}(t, t_d) \}$:

$$I_F(\omega, t_d) \propto |\mathcal{F} \{ E_{sig}(t, t_d) \}(\omega) |^2$$  \hspace{1cm} (3.5.5)

and which is directly linked to the AC via spectral integration, as can be seen when the Plancherel theorem is applied:

$$I_{AC}(t_d) \propto \int_{-\infty}^{\infty} |E_{sig}(t, t_d)|^2 dt = \int_{-\infty}^{\infty} |\mathcal{F} \{ E_{sig}(t, t_d) \}(\omega) |^2 d\omega \propto \int_{-\infty}^{\infty} I_F(\omega, t_d) d\omega$$  \hspace{1cm} (3.5.6)

The generated signal field $E_{sig}$ depends again on the selected nonlinear effect and the detected field on the setup geometry, which in the case of standard FROG modifies $E_{sig}$ to $\mathcal{F}^{\pm H} \{ E_{sig}(t, t_d) \}$ via spatial filtering, see Eq. 3.5.3 and 3.5.4. Correspondingly, for SHG FROG this yields

$$I_{F}^{SH}(\omega, t_d) \propto \mathcal{F} \{ \mathcal{F}^{\pm H} \{ E_{sig}(t, t_d) \} \}(\omega) |^2 = \left| \int_{-\infty}^{\infty} E_{t} E_{td} e^{-i\omega t} dt \right|^2$$  \hspace{1cm} (3.5.7)

The spatial filtering is displayed in Fig. 3.3 (a) additionally for the case when THG is exploited as the nonlinear effect for the FROG. Only the signal proportional to the component $E_{sig} = E_t^2 E_{td}$ of the full signal field

$$E_{sig}^{TH}(t, t_d) = (E_t + E_{td})^3 = E_t^3 + E_{td}^3 + E_t E_{td}^2 + \underbrace{E_t^2 E_{td}}_{\text{blocked}}$$  \hspace{1cm} (3.5.8)
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is detected, while the other mixed component \( E_t E_{td}^2 \) is blocked like the signals from single arms. The spectrogram for THG FROG can then be written as:

\[
I_{TH}^T (\omega, t_d) \propto \left| \int_{-\infty}^{\infty} E_t^2 E_{td} e^{-i\omega t} dt \right|^2
\]

Very often SHG is used as the nonlinear effect of choice, mostly due to its high sensitivity. However, the phase retrieval problem can be only solved except for an ambiguity in the direction of time [DeL94]. This can be overcome by using THG instead since these traces exhibit a certain asymmetry [Tsa96, RO04]. Furthermore, the short interaction length especially of surface-enhanced THG circumvents the challenging phase matching conditions for ultrashort pulses with broad spectra.

The 2D FROG traces contain all information required to solve the 2D phase retrieval problem and gain full insight in the temporal electric field profile [Tre93]. The extraction of the original pulse from the FROG spectrogram is not directly straightforward but can be solved with numerical algorithms, that even make use of the overdetermination in the 2D trace due to the redundant information content [Tre97]. A typical implementation is based on generalized projections [Kan98, Kan99]. It reconstructs the measured spectrogram by applying constraints given through the experimental conditions on an assumed pulse shape, then updates the assumptions so that the error to the measured trace is minimized. The algorithm can be additionally supported by external correction techniques for experimental challenges, such as a marginal correction [DeL94, Hyy17a], where the FROG trace is adjusted with a separately measured spectrum of the original pulse.

By these means, reliable results for the full temporal electric field with intensity and phase profile are found, as long as a few experimental criteria are met. For instance, when characterizing ultrashort pulses with equivalently broadband spectrum, it is crucial to guarantee for ideal phase matching conditions at the nonlinear element over the full spectral range, see Sec. 3.2.1. Extremely thin crystals like a 10-\( \mu \)m BBO for SHG, or even better, the use of the plasmonic nanoantennas which are the key of this thesis, solve this issue due to the short optical path, as long as they provide sufficient nonlinear signal. To optimize the conversion process, tight focusing and good overlap of the incident pulses \( E_t \) and \( E_{td} \) are improved, for example by controlling their polarization, which allows to use type I phase-matching [Bal99]. It is even more effective to change the setup geometry to a collinear arrangement, as the next section illustrates.

### 3.5.3 Interferometric frequency resolved optical gating

An adaption of the standard FROG setup implies the same technique in principle but in a collinear scheme. This is illustrated in Fig. 3.4 (a), where the pulses \( E_t \) and \( E_{td} \) propagate collinearly after the second beamsplitter. It allows for tighter focusing onto the nonlinear element and hence higher intensity of the upconverted signal and improved measuring sensitivity allowing to analyze weaker signals such as from THG [Hyy17b] than in the noncollinear version with its finite crossing angles where phase matching is even more crucial. Furthermore, the setup is
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Figure 3.4: (a) Experimental setup for FRAC (A) and IFROG (B), mainly identical to the one in Fig. 3.3 (a) except for the collinear alignment after the second BS. Consequently, blocking of spatially separated upconverted frequency components is not possible and the full signal field $E_{\text{sig}}$ is detected. (b) Typical FRAC data for THG intensity versus delay time $t_d$. The collinear setup causes the fringe structure, as well as in panel (c) in the typical THG IFROG spectrogram $I_{IF}^{\text{TH}}(\omega, t_d)$. The color-coded THG intensity map is depicted in dependence of the delay time $t_d$ and the wavelength $\lambda$.

Easier to align and prevents spatial distortions in the focus [Tie96, Han11] as well as it inherently avoids temporal smearing effects [Hyy17b].

The upconverted light generated at the nonlinear element propagates collinearly and is either detected on a PD as an integrated signal, or frequency resolved on a spectrometer, path A and B in Fig. 3.4 (a), respectively. The result is either a fringe-resolved autocorrelation (FRAC) [Die85], the interferometric analog to the AC, as shown in Fig. 3.4 (b) or an interferometric FROG (IFROG) [AR04, Sti05], yielding the 2D spectrogram depicted in Fig. 3.4 (c). In both cases, the collinear propagation of the full signal field does not allow spatial filtering, so that the different components interfere. This causes on the one hand the fringe structure in both data sets and on the other hand that the IFROG spectrogram contains even more redundant information than the FROG trace [Sti06]. This overdetermination can be exploited to generate more robust algorithms based on a differential evolution (DE) scheme [Hyy17a, Hyy17b]. The pulses can be reconstructed from several subsets of the measured data simultaneously, of which some are more sensitive to phase changes than the standard trace [Hyy17b]. The DE algorithm as a genetic search tool starts with a whole population of approximate solutions instead of just one initial guess as for example with generalized projections. In each iteration, new candidates are derived via crossing of earlier guesses and amended with simulated mutations. Only the fittest candidates are taken to next level.

To gain further insight, we analyze the recorded IFROG trace. It is given analogously to the FROG spectrogram 3.5.5, just that it is proportional to the full signal field $E_{\text{sig}}$, since no spatial filtering is applied. In the case of SHG, this means:

$$I_{IF}^{\text{SH}}(\omega, t_d) \propto \left| \mathcal{F} \left[ E_{\text{sig}}(t, t_d) \right] (\omega) \right|^2 = \left| \int_{-\infty}^{\infty} \left( E_t + E_{td} \right)^2 e^{-i\omega t} dt \right|^2 \quad (3.5.10)$$
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Figure 3.5: (a) Measured THG FROG spectrogram $I_{IF}^{TH}(\omega, t_d)$ as color-coded THG intensity map depicted in dependence of the delay time $t_d$ and the frequency $\omega$ and (b) its integral over $\omega$, yielding the corresponding FRAC (THG intensity versus delay time $t_d$). (c) Fourier transformation along the delay time $t_d$ of the trace in panel (a). The x-axis is transformed into the corresponding delay frequency. The components modulated at $\omega_0$, $2\omega_0$ and $3\omega_0$ are clearly separated. The white lines mark the cutoff for the filtering. Reverse Fourier transformation yields the trace in panel (d), with the DC baseband that is subtracted to generate the fully filtered spectrogram $I_{IF}^{TH}$ in panel (e). Integration over $\omega$ leads to the analog of an AC $I_{IFAC}^{TH}$ (THG intensity versus delay time) in panel (f).

The reconstruction for $E(t)$ can be done directly from this fringe resolved trace with the algorithm described in [Hyy17a]. Alternatively, this spectrogram contains the noncollinear SHG FROG as well (Eq. 3.5.7) and can be traced back to it via retrospective filtering in the Fourier domain of the delay time [Sti06]. Then, standard FROG algorithms can be applied to solve the 2D phase retrieval problem. However, as described in the preceding section, these are commonly based on a generalized projections approach, which is outperformed by the DE algorithm, especially because the DE does not get stuck so easily and is more robust to noise [Hyy17a]. The filtering procedure is explained in the following for the case of THG IFROG, since a more complex term structure arises there. However, measuring the THG has the advantage that it can be done at all dielectric interfaces and has a short interaction length [Hyy17b]. Thus, the upconverted fields are free of geometrical distortions and allow for a broad phase matching bandwidth. In this thesis, we observe strong THG from nanoantennas, so they are exploited as the nonlinear element themselves. The THG IFROG trace is given by:

$$I_{IF}^{TH}(\omega, t_d) \propto \left| FT \left[ E_{sig}(t, t_d) \right](\omega) \right|^2 = \left| \int_{-\infty}^{\infty} (E_t + E_{td})^3 e^{-i\omega t} dt \right|^2$$

(3.5.11)
Inserting the expressions 3.5.1 and 3.5.2 for $E_{t,t_d}$ and performing the expansion of the cubic term as in Eq. 3.5.8, yields

$$I_{IF}^{TH}(\omega, t_d) \propto \left| E^{TH}(\Delta \omega) \left[ 1 + e^{-i(\Delta \omega + 3\omega_0)t_d} \right] + E_F^{TH}(\omega_d, t_d)e^{-i\omega_0 t_d} + E_F^{TH}(\Delta \omega, -t_d) e^{-i(\Delta \omega + 2\omega_0)t_d} \right|^2$$

(3.5.12)

as demonstrated in [Hyy13]. Here, $\Delta \omega = \omega - 3\omega_0$ and $E^{TH}(\Delta \omega) = \int_{-\infty}^{\infty} A^3(t) \exp(-i\Delta \omega t) \, dt$ corresponds to the THG of a single pulse. The noncollinear THG FROG trace 3.5.9 appears as well, via $|E_F^{TH}(\Delta \omega, t_d)|^2 = I_{IF}^{TH}(\Delta \omega, t_d)$. Unfortunately, we cannot assume invariance to time inversion $E_F^{TH}(\Delta \omega, t_d) = E_F^{TH}(\Delta \omega, -t_d)$ as in [Hyy13], because of chirp [Pol10]. By applying these definitions and a few complex trigonometric identities, the following terms can be identified in Eq. 3.5.11:

$$I_{IF}^{TH}(\omega, t_d) \propto$$

\[ \begin{aligned}
2|E^{TH}(\Delta \omega)|^2 & \quad \text{independent of } t_d \\
+ 9|E_F^{TH}(\Delta \omega, t_d)|^2 & + 9|E_F^{TH}(\Delta \omega, -t_d)|^2 & \quad \text{unmodulated} \\
+ 6 \cos(\omega_0 t_d) \Re\{E^{TH\ast}(\Delta \omega)[E_F^{TH}(\Delta \omega, t_d) + E_F^{TH}(\Delta \omega, -t_d)]\} & \quad \text{modulated at } \omega_0 \\
+ 6 \sin(\omega_0 t_d) \Im\{E^{TH\ast}(\Delta \omega)[E_F^{TH}(\Delta \omega, t_d) - E_F^{TH}(\Delta \omega, -t_d)]\} & \\
+ 18 \cos((\Delta \omega + \omega_0) t_d) \Re\{E^{TH\ast}(\Delta \omega)[E_F^{TH}(\Delta \omega, t_d) + E_F^{TH}(\Delta \omega, -t_d)]\} & \quad \text{modulated at } 2\omega_0 \\
+ 18 \sin((\Delta \omega + \omega_0) t_d) \Im\{E^{TH\ast}(\Delta \omega)[E_F^{TH}(\Delta \omega, t_d) - E_F^{TH}(\Delta \omega, -t_d)]\} & \\
+ 6 \cos((\Delta \omega + 2\omega_0) t_d) \Re\{E^{TH}(\Delta \omega)[E_F^{TH}(\Delta \omega, t_d) + E_F^{TH}(\Delta \omega, -t_d)]\} & \quad \text{modulated at } 3\omega_0 \\
+ 6 \sin((\Delta \omega + 2\omega_0) t_d) \Im\{E^{TH}(\Delta \omega)[E_F^{TH}(\Delta \omega, t_d) - E_F^{TH}(\Delta \omega, -t_d)]\} & \\
+ 2 \cos((\Delta \omega + 3\omega_0) t_d) |E^{TH}(\Delta \omega)|^2 & \\
\end{aligned} \]

(3.5.13)

Here, * denotes the complex conjugate. In the first line, we can identify a DC component independent of $t_d$ and in the second line, we find a superposition of two noncollinear FROG traces. All other lines contain contributions modulated at multiples of the carrier frequency $\omega_0$. We can filter all of them by Fourier transforming along the delay time $t_d$ and then cutting off all contributions that appear at frequencies $\omega_0$, $2\omega_0$ and $3\omega_0$. This is demonstrated in Fig. 3.5: panel (a) contains the measured IFROG trace corrected for the transmission of the optical components with the fringe structure due to the modulation and panel (b) the corresponding FRAC. Fourier transformation along $t_d$ reveals the modulated components in panel (c). The white lines indicate where the cutoff for the filtering is set. Frequency components beyond are removed by a faded step function and thus are not taken into account in the reverse transformation shown in Fig. 3.5 (d). The fringe structure is now removed and only the DC baseband covers the noncollinear FROG traces. Since it is independent of $t_d$ it can easily be subtracted. The fully filtered result $I_{IF}^{TH}$ is depicted in panel (e) and contains only the contributions in line 2 of
Eq. 3.5.13:
\[ I_{TH}^{TH}(\omega, t_d) \propto I_{F \star}^{TH}(\Delta \omega, t_d) + I_{F}^{TH}(\Delta \omega, -t_d) \]  

(3.5.14)

The superposition of the two noncollinear FROG spectrograms in this sum excludes the application of a common FROG algorithm to the filtered trace as in the SHG case, although this has been commonly done [Han09, KD11, KD14]. However, either the direct reconstruction via the DE algorithm or, as described in Chap. 7, several other methods can be applied to extract information about the original pulse. For example by investigating the analog of a common THG AC trace, which in this case, is also a superposition of two components that would be spatially separated and filtered in the noncollinear case, see Fig. 3.3 (a). It corresponds to the integral over \( \omega \) of Eq. 3.5.14:

\[
I_{IAC}^{TH}(t_d) = \int_{-\infty}^{\infty} F^T[E^2_t E_{td}](\omega)^2 \, d\omega + \int_{-\infty}^{\infty} F^T[E^2_2 E_{td}](\omega)^2 \, d\omega
\]

Plancherel

\[
= \int_{-\infty}^{\infty} |E^2_t E_{td}|^2 \, dt + \int_{-\infty}^{\infty} |E^2_2 E_{td}|^2 \, dt
\]

(3.5.15)

Here, \( \star \) denotes a convolution and \( \otimes \) a correlation function. This superimposed THG IAC is shown Fig. 3.5 (f).

3.5.4 Two dimensional spectral shearing interferometry

An alternative approach to ultrashort pulse characterization is based on spectral shearing interferometry. The most common is the SPIDER technique (Spectral Phase Interferometry for Direct Electric field Reconstruction) [Gal99]. It applies frequency modulation instead of amplitude modulation as in the indirect FROG schemes and therefore has direct access to the spectral phase. It is especially useful for a complex phase over a particularly broad spectral range and stands out for its insensitivity to noise [Bir06]. For a detailed comparison of the FROG and SPIDER technique see [Gal00].

The main idea of this scheme is the use of a pair of frequency sheared pulses in an interferometric concept. A special realization of SPIDER is the 2DSI (2 Dimensional Spectral shearing Interferometry) [Bir06, Bir10]: a portion of the original pulse is sent through a
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dispersive medium and split in a Michelson interferometer into two identical replica. The strongly chirped pulses are each frequency mixed in a nonlinear element (e.g. a BBO crystal) with the original short pulse. The upconverted pulses are sheared spectrally and the spectrum is measured as a function of the phase delay of one of the chirped pulses. This results in a 2D intensity map, a direct interferogram of the spectral phase. In contrast to the original method, 2DSI uses no delay in the two sheared pulses and a collinear interferometric setup. This masters the challenges of SPIDER with the highly accurate setting of the delay time as well as distortions of the sheared pulses when they are split, due to dispersion over their broad spectral range [Bir06]. The collinear method further encodes the interferometric fringe structure over time, not space.

The exact realization of the setup used for this thesis is described in [Sch13]. Further details on the spectral shearing method can be found in [Bir06, Bir10].
4 Fabrication of metallic nanostructures

The fabrication of metallic nanostructures is of great importance for a variety of often interdisciplinary subjects which investigate or exploit fundamental properties at the nanoscale, such as: (bio-)imaging, sensory devices, fundamental physics, plasmonics, photovoltaics, chemical applications and many more profit from advanced methods in nanofabrication [Hal10, Sch10, Nov11, Bia12b, Cla14, Mar14]. At the same time, all these application areas demand different requirements in terms of material, design, resolution, reproducibility and substrates. In general, the quality of a method depends a lot on its flexibility, speed and convenience. The objective in this work is the production of gold nanoantennas of different shapes, with well defined resonance in the NIR regime, entailing dimensions of a few tens to hundreds of nanometers. Additionally, the crystallinity of the metal is controlled, which is not commonly done as most of the publications on nanoantennas deal with polycrystalline metals [Bou03, Cro03, Ghe08, Sch05, Kin09, Ko11] instead of single crystals. A comparison of both types as in this work is rarely done. Naturally, the fabrication of polycrystalline structures has obvious advantages: studies on surface plasmonics for instance require only metal films. Then, evaporation is a quick and easy method to gain user-defined film thicknesses of an arbitrary metal on basically any substrate. The same applies to nanostructuring: with the technically mature electron beam lithography (EBL) and subsequent evaporation, polycrystalline structures of all kinds of designs can be fabricated fast [Bha09, Nov11, Bia12b, Che15]. In contrast, conventional methods to directly grow single crystal particles are limited in geometry and size, thus are less controllable. However, the fabrication of monocrystalline films and subsequent milling with a focused ion beam (FIB) provides flexibility in the structuring, though it is bound to specific substrates due to the required lattice matching during growth. The effort pays since monocrystalline structures yield more homogeneous results as they suffer less from imperfections and have smoother surfaces in contrast to polycrystalline films with grain sizes of 15 - 50 nm [Sot03, Hua10], which lead to scattering and unknown influence of the varying crystal orientation [Bia12b, Mej16]. Moreover, this work demonstrates also faster and more flexible methods than epitaxial growth. A well defined crystallinity further allows to determine the dependence on crystal orientation in experiments, as proposed for instance by [Hua10]. The mentioned differences of the respective poly- and monocrystalline metallic structures lead to different physical results, for example in terms of optical and plasmonic properties and electron dynamics [Asp80, Kut08, Che10, Olm12, Kni15, Mej16]. Ideally, fabrication methods for both types of crystallinity are at hand, so that they can be compared.
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Electron beam lithography (EBL) is a standard method for the easy, flexible and fast fabrication of metallic nanostructures [Bia12b, Che15]. A mask is defined with a scanning electron microscope (SEM) in an electron-sensitive resist. Its boundaries determine the desired structures, which are subsequently filled with a polycrystalline metallic film via evaporation. The mask and excessive metal are removed in a lift-off process. The details of the complete method are described below, with the single steps shown schematically in Fig. 4.1.

1. Cleaning of the substrate
   The substrates, mostly fused silica discs with a thickness of 150 µm and a diameter of 25.4 mm, are cleaned in acetone twice and isopropanol once, each time for 10 minutes in an ultrasonic bath. Afterwards they are dried in a flow of dry air.

2. Spincoating of the resist
   100 µL of a electron-sensitive resist (950K PMMA A2, MicroChem Corp.) are spincoated on the clean substrates at 3000 rpm for 90 s, yielding a polymer layer of approximately 26 nm thickness. Before and after the spincoating, the substrates can optionally be placed on a hotplate set at a temperature of 120°C. The resist is hardened by baking it in an oven for 30 minutes at a temperature of 170°C.

3. Evaporation of a conductive layer
   Since the substrate is isolating, an additional conductive layer is needed to prevent the accumulation of charges which deflect the electron beam that writes the mask in the next step. On that account, 8 - 10 nm of aluminum are evaporated onto the substrates.

4. Exposure to the electron beam
   The writing of the mask into the polymer layer is performed with an SEM at the minimum step size of 2 nm. The electron column is operated at a voltage of 10 kV with a 10 µm aperture, yielding a current of 27 pA. To obtain optimal resolution, several masks are defined with different dwell times of the electron beam [Zus07], which is carefully focused onto the surface.
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5. **Removal of the conductive layer**
   A 0.5 molar solution of sodium hydroxide (NaOH) etches off the conductive layer in approximately 12 s. The etching process is stopped with purified water.

6. **Development of the mask**
   By developing the sample for 25 s the resist can be removed in the very areas exposed to the electron beam before, since there the polymer chains broke and are now sensitive to the developer. The developer consists of methyl isobutyl ketone (MIBK) and isopropanol in a ratio of 1:3 plus 1.5% of methyl ethyl ketone (MEK). The temperature is kept at 2 - 4°C to improve the resolution [Hu04]. Rinsing the sample for 5 minutes in isopropanol stops the development.

7. **Evaporation of the metal**
   The desired metal is evaporated onto the ready mask, up to approximately the thickness of the polymer layer which is 30 nm in our case. In the case of gold, an additional adhesion layer of 2 nm of chromium (Cr) is evaporated in advance.

8. **Removal of the resist**
   In the lift-off process the mask and excessive metal is removed with acetone at a temperature of 60°C. Since high resolution requires very thin resist layers [Che15] sonication might be necessary.

Figure 4.2 shows SEM micrographs of nanoantennas fabricated with EBL. Panel (a) and (b) display a simple rod geometry, resonant at different spectral regions of the broadband laser excitation (see Sec. 5.1.1 and 6.1). Their comparison (note the identical scale bars) illustrates the enormous scalability of EBL in combination with high resolution at all scales. This is exploited also in the array of bowtie antennas shown in panel (c), with varying parameters like resonance length and gap size from line to line and column to column, respectively. The distance between the individual devices is chosen larger than the laser spot size used for excitation, thus they can be addressed singly. The marker structures help to locate the desired antenna since they are visible with an optical microscope.

Figure 4.2 (d) displays a SEM micrograph of a contacted bowtie antenna and on the right side a zoom in on the tiny feedgap region [Ryb16]. The high resolution of EBL facilitates gap widths of only 8 nm which is crucial for the tunneling experiments these contacted antennas are used for. Furthermore, the large scalability is again beneficial since the leads starting at the antenna eventually need to end in macroscopic contacts. Panel (e) shows how the leads are guided to the contact section next in size.

One of the main advantages of EBL is the rapid fabrication of the mask, independent of its complexity. Writing a 50 µm by 50 µm array as displayed in Fig. 4.2 (c) with the electron beam takes only about one minute. This tremendous rapidity, combined with very high resolution and the independence of the other process steps on the number of written structures, allows producing densely packed arrays of nanoantennas over large areas, as demonstrated in Fig. 4.3.
Many optical experiments excite complete arrays of identical antennas instead of single devices \cite{Cro03, Sch05, Ko11, Siv13, Pfu13b, Pfu13a}. The high fidelity of EBL in reproducing identical structures minimizes effects like inhomogeneous broadening. For example inherently weak HHG profits enormously from the excitation of as many structures as possible, such that dense packing over the full spot size is a big advantage \cite{Kni11, Pfu13b, Pfu13a}.

### 4.2 Monocrystalline gold nanoantennas via focused ion beam milling

As mentioned in the introduction of this chapter, the growth of monocrystalline gold is often time-consuming. Typical methods to obtain films that can be structured in a top-down approach are epitaxial growth by evaporation, sputtering and molecular beam epitaxy \cite{Pas56, Cam64}. Unfortunately, one requirement for all these methods is to match the substrate’s crystal lattice. This limits choices of supporting materials severely, as for gold films with [111] oriented surface to substrates with hexagonal symmetry like mica with its high index of refraction. Alternatively, the

![SEM micrographs of polycrystalline gold nanoantennas.](image)

**Figure 4.2:** SEM micrographs of polycrystalline gold nanoantennas. (a) and (b) display objects in double rod geometry resonant at different wavelengths: 2200 and 1200 nm, respectively. (c) Array of bowtie nanoantennas with varying dimensions and resonance lengths. (d) Contacted bowtie antenna exploited for tunneling experiments \cite{Ryb16} with a zoom in on its tiny gap area (right panel). (e) Bowtie with leads as a nanoscopic part in a macroscopic circuit.
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Figure 4.3: SEM micrographs of large and densely packed arrays of polycrystalline rod (a) and bowtie (b) gold antennas, fabricated with EBL for high harmonic generation [Kni11].

wet-chemical growth of monocrystalline gold can be exploited to fabricate nanoparticles directly [Bru94, Bus03, Wan08]. A critical disadvantage is the severe limitation in size and geometry of such particles. Adapted recipes that generate extremely large microplates [Guo06, Hua10] serving as monocrystalline basis in which the structures are milled afterward via FIB [Bia12b] resolve this issue, especially if the microplates are substrate grown instead of in dispersion [Rad10, Wu15].

4.2.1 Wet-chemical growth of monocrystalline gold microplates

Here, a method to grow monocrystalline gold microplates directly on substrates is presented. It is adapted from a precursor recipe [Bru94] and a thermolysis step [Rad10]. During the thermolysis, the gold in the precursor on the basis of chloroauric acid is reduced from Au(III) to Au(I) and then to Au(0) [Rad11]. Small nuclei of reduced gold initiate the growth into monocrystalline microplates, first perpendicular to the substrate until they fall over and lie flat but movable [Rad11]. The precursor itself is hydrogen tetrachloroaurate (AuCl$_4^-$) stabilized by tetraoctylammonium bromide (ToABr) in toluene, shortly named Au-ToABr. The ToABr serves as a phase transfer agent, assisting to transfer (AuCl$_4^-$) ions from aqueous solution to toluene [Rad11]. The production of the precursor is described in detail in the recipe below, together with the other steps to fabricate monocrystalline gold nanoantennas as sketched in Fig. 4.4.

1. Cleaning of the substrate
   Substrates and cleaning procedure correspond to EBL, see Sec. 4.1.

2. (Optional) evaporation of a supportive layer
   Our experiments with different substrates and their pre-treatment show a slightly better performance of microplate growth when 2 - 3 nm of chromium are evaporated beforehand. Additionally, this serves as a conductive layer during the nanostructuring, anticipating this step after the thermolysis. Since bare fused silica substrates feature sufficient microplate growth, this step is optional.
3. **Dropcoating of the precursor**
   The precursor $\text{Au-ToABr}$ with an ideal gold concentration of 20 mmol is gained from a mixture of aqueous solution of hydrogen tetrachloroaurate (12.56 mg in 1.6 ml of purified water) and 109.3 mg tetraoctylammonium bromide in 4 ml of toluene. This two-phase mixture has to be stirred vigorously until the yellow aqueous solution at the bottom turns colorless and the organic solution on top becomes red. The top layer is carefully extracted with a pipette, yielding a few milliliters of $\text{Au-ToABr}$ precursor. Two times 20 µl of it are dropcoated onto the circular substrate with a diameter of 25.4 mm and are dispensed with the pipette tip. The rest of the precursor can be stored in a vial and used up to weeks later.

4. **Thermolysis**
   A temperature-stabilized hotplate with an aluminum block atop serves as a heat source for the thermolysis. The samples reside for approximately 24 - 28 h on the block that minimizes fluctuations of the temperature set to 132°C. The exact time is determined by the distribution of sufficiently large microplates which can easily be monitored constantly with the bare eye. Even after checking their sizes with a microscope quickly, thermolysis can be resumed for further growth. Figure 4.5 (a) shows the gold microplates in a drop of precursor. Evidently, the thermolysis does not consume all of the precursor, so residues have to be removed.

5. **Removal of the educts**
   The samples are carefully rinsed successively with toluene, purified water and acetone. Each liquid is added slowly with a pipette until the substrate is fully covered and then removed in the same way. The microplates might float in the solvents, causing their relocation when the liquid is withdrawn.

6. **Plasma cleaning**
   Figure 4.5 (b) shows the microplates from panel (a) after the washing process. The drop of precursor is removed, but black precipitate remains. 20 minutes of treatment in an oxygen plasma eliminate it, as demonstrated in Fig. 4.5 (c).

7. **(Optional) reactive ion etching**
   If the microplates are considered too thick, reactive ion etching (RIE) can thin them by
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a desired amount. Since their thicknesses vary from a few tens of nanometers to 1 or 2 microns, this might remove thinner microplates completely. There is no defined correlation between area and thickness [Rad10, Wu15], but by trend microplates with larger areas tend to be thicker. Consequently, sacrificing thin plates to the RIE yields more formerly thick microplates that possess now the desired height over a larger area. The RIE recipe is based on an argon flow of 16 sccm and chlorine flow of 8 sccm, resulting in an etching rate of 170 nm/min for gold. It was operated for 3 - 5 minutes as required.

8. **Evaporation of a conductive layer**
A conductive layer provides better conditions for the upcoming FIB milling step. Therefore, 2 - 3 nm of chromium are evaporated onto the sample if this has not been done already in step 2 or if this layer was removed by the RIE.

9. **Nanostructuring via focused ion beam milling**
The prepared microplates serve now as a monocrystalline basis of gold to mill the desired nanostructures with a FIB. The details of this method are explained in the next section.

Figure 4.5 (c) shows the fully cleaned monocrystalline gold microplates before they undergo further treatment such as nanostructuring. They can have an immense area while being extremely thin at the same time, thus they appear like gold foil as the SEM micrograph in panel (d) demonstrates. Furthermore, this graph points out how the microplates start growing perpendicularly to the substrate until they fall over and proceed their growth horizontally, thereby maybe covering another plate. As mentioned above, there is no correlation between area and thickness, as in the case of the two displayed triangles that differ significantly in their aspect ratio. By trend, larger area comes along with larger thickness. With our modified recipe that uses a gold concentration of only 20 mmol and thermolysis for just 24 h, we achieve areas ranging from $10^3$ to $10^5 \text{m}^2$. Thereby we excel the results from the original method [Rad10, Rad12], although there it was reported that higher concentration would enhance the microplate area, which was proven false by our own parameter study. Even for moderate thicknesses such as 120 nm that do not require RIE polishing we yield areas as high as $24 \cdot 10^3 \text{ m}^2$, see Fig. 4.6 (a). This result also renders

**Figure 4.5:** Microscope images of monocrystalline gold microplates grown on substrate, (a) right after the thermolysis, (b) after the wet cleaning process and (c) after treatment in the oxygen plasma. (d) SEM micrograph with a close-up of an extremely flat gold triangle that has fallen on top of a smaller and thicker one during the growth process.
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Figure 4.6: SEM micrographs of (a) a giant gold microplate with an area as large as $24 \cdot 10^3 \mu m^2$ at a thickness of only 110 nm (top view), (b) a naturally thin microplate (thickness 56 nm) with a close-up of its perfectly smooth surface and sharp edge in the inset and a sketch of the crystal orientation in the [111] plane with hexagonal dense packing at the plate surface and how it is oriented in the gold fcc lattice unit cell. (c) Edge of a formerly $1 \mu m$ thick microplate (indicated by the yellow bar) polished down to a thickness of 120 nm. Its surface smoothness is unaffected by the RIE, yet it resides now on a fused silica pedestal (blue bar) due to etching of the substrate. (d) Grain boundaries in a thermally evaporated, thus polycrystalline gold film, visualized with a SEM.

our method superior to the recipe reported by Guo et al. [Guo06, Hua10], which yields areas of barely $10^2$ to $10^3 \mu m^2$. Moreover, our recipe is chemically less demanding and thereby faster and does not require indium tin oxide (ITO) substrates which have an unfavorably high index of refraction.

Though the presented method produces microplates with a broad distribution of thicknesses, basically all of them support nanostructuring. Either they are naturally thin while sufficiently large as the examples in Fig. 4.5 (d) and 4.6 (a) and (b) illustrate. Or they are polished with RIE and thereby thinned down to the desired height. Polishing only fulfills the purpose of thinning, since the surfaces are perfectly flat thanks to the controlled monocrystallinity, as Fig. 4.6 (b) and the inset demonstrate. Panel (c) proves that the etching process preserves the surface smoothness of the depicted microplate that was polished from a thickness of nearly $1 \mu m$ down to a thickness of approximately 120 nm and now resides on a fused silica pedestal. To contrast the excellent smoothness, the polycrystalline surface of an evaporated gold film is shown in the SEM micrograph in panel (d). The boundaries of the grains with radii of up to 20 nm mentioned in the introduction are clearly visible. Scans with an atomic force microscope (AFM) find elevations of only $\pm 2$ nm on the monocrystalline counterpart, as confirmed by optical profilometry with irregularities in thickness of $\pm 1$ nm [Rad10].

Apart from the ultrasmooth surface, the monocrystallinity also induces the typical geometrical shapes of the microplates. As can be seen from Fig. 4.5 and 4.6, their surfaces appear only as triangles and truncated triangles, i.e. hexagons. This reflects the fact that the crystals are oriented in the [111] plane with their horizontal surface, triggering a 6-fold symmetry for the gold face-centered-cubic (fcc) lattice, see sketch in Fig. 4.6 (b). X-ray diffraction patterns prove the high purity of the sample, with a relative intensity of the [111] peak to the [200] peak of 100:0.02,
4 Fabrication of metallic nanostructures

Figure 4.7: (a) Microscope image of the giant gold microplate presented in Fig. 4.6 (a) after nanostructuring. One of the milled antenna arrays (blue box) is magnified by SEM in panel (b), and partly even further in panel (c). There, the blue shaded area indicates the region to be milled first, the yellow subsequently. The lines and dots demonstrate how the FIB is guided for polishing cuts at the edges and gap. (d) AFM scan (color-coded height map) of the area indicated in the left panel.

thus much lower than for bulk gold with 100:52 [Rad11] and also lower as 100:0.049 from the recipe by Guo et al. [Guo06].

4.2.2 Focused ion beam milling

The prepared monocrystalline microplates serve as a base material for further nanostructuring with a FIB. A controlled beam of gallium ions mills the gold in the determined areas, excavating the desired nanoantennas. In contrast to EBL with PMMA as a positive resist, in this case the negative is defined. The procedure requires careful alignment of the ion beam as well as a sophisticated strategy for the order of milling steps [Bia12b].

The ion gun is operated at a voltage of 30kV and the current and scanning step size set to the lowest values of 1 pA and 2 nm, respectively, guaranteeing a high resolution. Arrays in the size of 25 µm by 25 µm are milled in 3 to 5 hours. The giant yet thin microplate from Fig. 4.6 (a) has a capacity of 30 arrays (i.e. more than 3500 antennas), as can be seen in the microscope image in Fig. 4.7 (a). Panel (b) shows one of the arrays magnified with the SEM. It contains marker structures for the precise localization of each of the 117 antennas. Panel (c) and (d) zoom in further, via SEM and AFM, respectively, demonstrating the high resolution of the gaps (c) and of the sharp edges (d). The hexagonal geometry of the microplates facilitates the orientation of the antennas: if they are aligned in parallel to an edge of the plate it is guaranteed that they all are oriented in the same way with respect to the crystal structure.

For the high resolution, it is crucial to set the beam dwell time according to dose tests that must be carried out singly for each microplate. The dose test also yields the appropriate number of loops (i.e. milling repetitions) necessary to remove the gold down to the substrate for a given dwell time. In principle, one loop at a longer time would be sufficient to mill the gold completely, but the resolution improves a lot when 3 - 5 repetitions are applied at lower dwell time. To
minimize the influence of the lateral drift of the system, we engineered a sophisticated ring geometry indicated by the shading in Fig. 4.7 (c). Splitting the mask into such substructures ensures the rapid milling of all loops of the inner parts (that require the highest resolution) in a few seconds, thus they are not affected by the drift. Long-time drift might leave behind walls between the antennas. This can be compensated by an overlap of neighboring rings, visible as grooves in the AFM scan in Fig. 4.7 (d). Polishing cuts as indicated by the pink lines and dots in panel (c) help to prepare sharp edges and small gaps, especially if milled material deposits. These important areas can be re-treated selectively, after checking the results in the SEM. This is a great advantage over EBL, which allows no monitoring during the process. Also pure imaging with the FIB can be applied afterward for further polishing of the milled structures.

Figures 4.8 (a) and (b) exemplify the high resolution of single nanoantennas with different geometry by AFM scan and SEM image, respectively. Sharp edges and bowtie tips with feedgaps of only 8 nm are feasible.

For the structuring, microplates with a thickness between 40 and 150 nm are adequate, though thicker plates undergo additional FIB polishing first which thins them down. A FIB current of 5 pA at a step size of 4 nm yields milling rates of approximately 2 nm/min on an area of 25 by 25 µm. The low current and step size preserve the smooth surface, as illustrated by the AFM scan in Fig. 4.8 (c) and the cross section in panel (d). The scan also shows that the milling of the antennas removes another layer of gold from atop, reducing their thickness by another 30 nm (approximately, depending on the total milled height) with respect to the thickness of the polished microplate. Furthermore, this erases the chromium layer, so in contrast to the method by Huang et al. [Hua10] we avoid the negative influence from an adhesion layer [Bia12b, Mej16] without the disadvantages of an ITO substrate.

The implantation of gallium ions could also influence the antenna behavior. However, we performed energy-dispersive X-ray spectroscopy (EDX) revealing that no gallium is deposited by the milling and also chromium was removed completely. The gallium peak yielded only 0.28 atomic % in the EDX spectrum, which is confirmed in [Hua10].
5 Nonlinear spectroscopy of single plasmonic nanostructures

Many applications benefit from the ability of plasmonic nanostructures to strongly enhance and confine electromagnetic fields, as described in Sec. 2.3. Of special interest is the interaction between plasmonic devices and nanoemitters, like quantum dots [Cur10, Pfe10] or molecules [Kin09, Loh12]. However, since the local field enhancement enables to drive several nonlinear processes such as THG and MPPL, their emission might spectrally overlap and interfere with the coupling regime [Kni15]. Nonlinear spectroscopy of the nanostructures’ response as described in the following helps to better understand the spectral behavior of the nonlinear emission and therefore enables to control it. This is particularly crucial because these structures not only allow driving certain nonlinear, and in that case detrimental processes, but even enhance them strongly under specific conditions [Moh00, Bev03, Far05, Rop07]. Deeper insight into these mechanisms also paves the way to improve applications that actually exploit these by-products like MPPL themselves, as for example in bioimaging and microscopy [Dur07, Ghe08, Hua10]. Hence, to make better use of it or (where required), suppress it, it is important to investigate the origin of this parasitic multi-step effect [Bia09, Bia12a], see Sec. 3.3, as it is done in the second half of this chapter with an analysis of the involved nonlinear orders.

5.1 Experimental setup for nonlinear spectroscopy of nanoantennas

Spectroscopy with nanoantennas is performed on the basis of the antenna’s nonlinear response that is detected spectrally resolved. The NIR laser source with the white light continuum (WLC) generation that produces this nonlinear output in the visible regime is based on a fiber-laser technique, which is described elaborately in [Sel09, Kra10, Bri14] together with the physical background of the exploited optical processes. Details on the specific setup used in this work, modifications of it and further applications can be found in [Han11, Kni11, Fis13, Ven15]. A short overview of the general arrangement and the most important components is presented in the following.

5.1.1 Generation of ultrashort pulses tunable in the near infrared regime

We use an Er: fiber-laser system (EDF) in combination with a highly nonlinear fiber (HNF) to generate ultrashort pulses in the NIR regime. The laser consists of an oscillator (OSC) and an amplifier (AMP) stage made out of telecom fiber, partly doped with $\text{Er}^{3+}$ ions, see Fig. 5.1 (a), Sec. I and II. Both are pumped with laser diodes (LD) at a wavelength of 980 nm.
Figure 5.1: (a) Setup for nonlinear spectroscopy of nanostructures with tunable pulses in the NIR regime. Abbreviations see main text. The insets show a FROG spectrogram (color-coded SHG intensity versus delay time $t_d$ and wavelength) and a zoom sketching the excitation of a nanorod. (b) Fundamental spectrum of the fiber oscillator (blue) and amplifier (red). (c) WLC intensity over wavelength after the HNF for different settings of the Si PC. The broadest dispersive spectrum (gray) is displayed also in panel (d) (blue) with its reconstruction from a FROG measurement (intensity red, phase green) and the temporal trace on the right side. (e) Typical nonlinear response of a nanorod (SEM image in the inset) illuminated with the NIR laser.

The oscillator operates at a repetition rate of 39.6 MHz, while mode-locking is facilitated by a saturable absorber mirror (SAM). The seed pulses at a central wavelength of 1.55 µm with a pulse energy of 66 pJ are amplified in the next stage to 8.9 nJ via further pumping with laser diodes. In a side effect, this spectrally broadens them due to self-phase modulation in

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the fiber [Sel09], as the comparison in Fig. 5.1 (b) shows, yielding a pulse duration as short as 112 fs. Their actual temporal length is controlled in a silicon prism compressor in Brewster angle configuration (Si PC in Fig. 5.1 (a) Sec. III) right after the pulses leave the amplifier and are focused on the mirror at the end of the prism sequence. Adjusting the pulse duration and thereby the peak intensity regulates the WLC generation in the HNF which the compressed pulses pass now. It consists of a piece of standard fiber (length 125 mm) spliced to a 10-mm-long fiber of type GF4a, whose other end is protected by a 150-μm-long piece of coreless fiber. These specifications are selected on the basis of simulations [Bri14], that predict the spectral shift of the WLC generated by self-phase modulation: the incoming pulses centered around a wavelength of 1.55 μm both broaden and split up spectrally, resulting in a redshifted part with solitonic character and a blueshifted part that experiences dispersion. These new components form the basis for the spectroscopy and are referred to in the following as solitonic wave and dispersive wave. Figure 5.1 (c) shows a selection of shifted spectra, achievable by tuning the material passage in the second Si prism, i.e. the pulse duration and thereby peak intensity entering the HNF. The pulse energies vary between 0.2 - 0.3 nJ for the dispersive wave and 0.3 - 0.5 nJ for the soliton. After parallelizing the light behind the HNF with a parabolic mirror, both spectral parts are sent to a customized prism compressor sequence in Brewster angle configuration. Each is set up with the respective ideal specifications for pulse compression and spectral shaping (see Fig. 5.1 (a) Sec. IV). For excitation with the soliton, a spherical mirror sends the pulses through a pair of SF10 prisms with a tip-to-tip distance of 50 mm to precompensate chirp. Before reflection at the end mirror, the fundamental light and the dispersive wave are blocked by razor blades in the Fourier plane. In contrast, the soliton is blocked when compressing the dispersive part in the therefore customized prism sequence made of F2 glass and a tip-to-tip distance of 265 mm.

The described procedure allows us to tune pulses over more than one octave of central wavelengths from 1200 to 2100 nm and compress them to durations as short as 7.9 fs when for example the full dispersive wave is used, as a FROG analysis in Fig. 5.1 (d) proves. This and other detailed characterization of the pulses is possible with the tools depicted in Sec. V in Fig. 5.1 (a): a powermeter (P), an optical spectrum analyzer (OSA) and the setup to determine the pulse duration with SHG FROG as explained in Sec. 3.5.2. Up to here, the light polarization is parallel to the general beam plane and is also preserved in all fibers. Only at the entrance to the FROG interferometer a periscope (PS) rotates it by 90°, so that ideal type I phase-matching [Bal99] conditions are guaranteed in the 10-μm-thin BBO crystal that serves as nonlinear element. The beamsplitters (BS) consist of Inconel, a nickel-chromium based super alloy, on a fused silica substrate (thickness 150 μm). A shortpass filter (SP) blocks the fundamental light before the SHG enters the spectrometer (SM) where the FROG traces, as shown in the inset in Sec. V, are recorded. Figure 5.1 (d) presents the spectral (left panel) and temporal (right panel) reconstruction of a FROG spectrogram acquired from a pulse with one of the broadest dispersive spectra, marked gray in Fig. 5.1 (c).

To avoid damage of the nanostructures by the light focused on them, its power is controlled with
5 Nonlinear spectroscopy of single plasmonic nanostructures

a neutral density filter (NDF). Alternatively, the pulses can pass a spatial light modulator (SPM) which controls intensity as well as phase, thus the complete temporal and spectral pulse shape. For details of that setup see [Ven15].

5.1.2 Excitation and characterization of the nonlinear response

Sections VI and VII in Fig. 5.1 (a) demonstrate the excitation and collection of the nonlinear response of the nanostructures, as sketched in the zoomed inset. After passing the NDF, whose dispersion is already compensated by the prism compressor, only reflecting optics are used. Thus the characteristics like pulse duration and chirp of the NIR light are preserved. Two spherical mirrors form a Galilei telescope (GT) to expand the beam and fully illuminate the Cassegrain objective (CG) (NA 0.65, Ealing X52), which focuses the light onto the nanoantennas oriented with their long axis in parallel to the incident electric field polarization. The sample resides on a piezo positioner (PP) to perfectly move the selected nanoantenna into the focus with a diameter of circa 2 μm FWHM. The antennas are separated sufficiently to ensure that only one is excited. The objective for NIR excitation is alternatively interchangeable with an AFM device to perform surface scans on the sample. Meanwhile, the antennas can be imaged from the other side with a dark-field objective (DF) (NA 0.95, Zeiss EC Epiplan Apochromat) under white light illumination (WL) on a CCD camera (CCD1). When NIR excitation is applied, the nonlinear response of the nanoantenna is collected by the same objective without illumination. Sample positioner and objective are part of a commercial inverted microscope (IM, Zeiss Axiovert 200), but to analyze the nonlinear response, an external tube lens (TL) focuses the visible light onto the slit of a grating monochromator (GM, 150 grooves/mm, blazed for a wavelength of 500 nm). The fundamental NIR light is blocked by a shortpass filter (SP) and can optionally be filtered with a linear polarizer (PO). The spectrally resolved response is detected with a CCD camera (CCD2) for an integration time of 180 s and excitation pulse energies between 50 and 175 pJ. It is corrected for the transmission of the setup, which consists of the spectral influence on the transmitted light from the single components and in this setup is optimized for broad coverage of the visible spectral range. For details see Fig. 7.3 in Section 7.

5.1.3 Sample geometry

The nanostructures have the form of single rectangular rods as the SEM micrograph in the inset of Fig. 5.1 (e) demonstrates. This averts influence of more complicated shapes like bowties with sharp tips whose features are prone to a large variance, reflected in the individual field enhancement [Cro03]. Single rods lack the additional enhancement increase of coupled double structures, but thereby they circumvent the sensitive dependence on the exact gap size, whose precise control is challenging [Fro04, Mue05, Sch05, Sun05]. The structures are fabricated from monocrystalline as well as polycrystalline gold on fused silica substrates with the methods described in Chap. 4. Their plasmonic resonance is custom-tailored to fit the center wavelength
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Figure 5.2: Nonlinear emission spectra of polycrystalline (blue) and monocrystalline (red) gold nanorods (SEM micrographs in the inset) under NIR excitation at a center wavelength $\lambda_{\text{exc}}$ of 1560 nm (a) and 2000 nm (b), respectively. The pronounced THG peaks are cut off to highlight the spectral structure of the MPPL background.

of the excitation in the range of 1260 nm to 2050 nm by varying the rod length (150 to 380 nm for monocrystalline antennas and 230 to 480 nm for polycrystalline ones$^1$). The height and width are kept at 30 nm and 40 to 60 nm, respectively.

5.2 Spectral shape of the incoherent emission

The typical nonlinear response of a gold nanorod under NIR excitation consists mainly of coherent THG and incoherent MPPL, as explained in Sec. 3.2 and 3.3. We observe THG as a sharp peak and MPPL as broadband emission, covering the full visible range, see Fig. 5.1 (e). SHG might occur in addition as a smaller peak, if it spectrally overlaps with the detection window between 350 and 850 nm. We want to focus now on the substructure of the MPPL background.

5.2.1 Dependence on crystallinity

A closer look at the broadband PL emission reveals a peak structure: Fig. 5.2 illustrates this for poly- (blue) and monocrystalline (red) nanorods (shown in the SEM micrographs at the bottom) exemplarily at different excitation wavelengths $\lambda_{\text{exc}}$ of 1560 nm (a) and 2000 nm (b). The respective THG peaks as observed before in Fig. 5.1 (e) are here cut off to zoom in on and highlight the photoluminescence’ spectral shape. Their shift in accordance with the position of $\lambda_{\text{exc}}$ is still clearly visible when comparing panel (a) with (b). MPPL instead remains at its spectral position, always exhibiting a peak centered around a wavelength of approximately 570 nm.

$^1$The length difference is explained later with the help of the experimental results, see Sec. 5.2.2
In contrast, only polycrystalline antennas feature a second PL peak: at a wavelength of 730 nm in Fig. 5.2 (a) and 760 nm in (b), as the blue graphs show. Since the observed peak positions of 570 nm and around 750 nm corresponds to visible light that appears to the human eye in the color of green and red, respectively, we distinguish the two local maxima now by referring to them as the “green” and the “red” peak. In principle, the presented findings hold true for antennas resonant at other excitation wavelengths. Slight variations in the peak position occur, though, especially for the red peak between 710 and 790 nm, as well as for the relative peak intensity. The presented substructure has been reported before and was attributed to increased electron-hole recombination rates at the corresponding energies since they fit to the “band gap” at the X and L symmetry points in the gold band structure with a high density of states [Moo69, Boy86, Bev03, Bou05, Imu05], see Sec. 2.2. However, this should account for both types of crystallinity, which is contradicted by the missing red peak in the monocrystalline MPPL spectra. In order to find the origin of the peak structure, we now analyze the polarization of the nonlinearly emitted light.

Therefore, it has to pass a linear polarizer (PO) before it enters the detection unit, see Sec. VII in Fig. 5.1 (a). The filter transmits only light polarized either in parallel or perpendicularly to the long rod axis of the antenna, depending on the setting, as indicated by the sketch in the inset of Fig. 5.3 (a). Panel (a) to (c) compare unfiltered spectra from monocrystalline and polycrystalline rods illuminated at different wavelengths $\lambda_{exc}$ (blue) to their respective portions of light polarized in parallel (red) or perpendicularly (green). In all cases, the polarization analysis isolates the peaks: the polycrystalline red peak and of course the THG are polarized like the excitation pulses. In contrast, the green peak exhibits polarization in the orthogonal direction. This holds true for all excitation wavelengths.

An explanation for this behavior is found by investigating the scattering cross sections of the exemplary rods from which the data in Fig. 5.3 (a) and (b) was acquired and which are shown in panel (d) as solid and dashed lines. The cross sections were calculated with BEM, see Sec. 2.4, and for illumination polarized in parallel (red) and perpendicularly (green) to the nanorods. The exact particle size is obtained from SEM micrographs to generate the triangulations shown in the figure. The simulations performed on the basis of those particle boundaries illustrate that the plasmonic resonances in the NIR regime are custom-tailored to overlap with the excitation spectra. Their center wavelengths $\lambda_{exc}$ are indicated by the dotted line. The inset shows a zoom of the visible region, where the orthogonal resonance has its main peak at a center wavelength of around 575 nm, perfectly in accordance with the position of the green peak in the MPPL spectra. This means that the nonlinearly generated light is emitted preferentially in the direction of the linear resonance, which is typically in the visible regime for antenna dimensions of a few tens of nanometers [Kni12]. Here, the rod widths lie roughly between 40 and 60 nm, explaining the slightly varying positions of the green peak.
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Figure 5.3: (a) Nonlinear emission spectrum (blue) of a single polycrystalline gold nanorod illuminated at a center wavelength $\lambda_{exc} = 1560$ nm and its respective portions with polarization parallel (red) and perpendicular (green) to the long antenna axis, as sketched in the SEM micrograph of the rod. (b) Comparable data from a monocrystalline rod and (c) for excitation at a wavelength of 2000 nm. (d) Scattering cross section in dependence of the excitation wavelength from BEM simulation for the nanorods from which the data in panel (a) (—) and (b) (- -) is obtained. The excitation is modeled as plane waves with their polarization either set in parallel (red) or perpendicularly (green) to the rods, whose surface triangulations are depicted as well. The main resonance is in good accordance with the excitation wavelength $\lambda_{exc}$ as used in the experiment (···). The inset shows a zoom of the visible region, confirming the resonances found in the acquired data.

The red peaks for polycrystalline rods are reproduced, too, by the simulation as a second-order resonance at a wavelength of 710 nm in Fig. 5.3 (d). Consistently, a less pronounced peak is found also as second-order resonance for the monocrystalline rod. Apparently, the simulation cannot resolve this discrepancy, as the only distinction between the simulated specimens is their rod length (compare the triangulations). To understand this, further experiments are necessary.

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2The length difference when exhibiting the same plasmonic resonance is entered phenomenologically since the experiments document this effect. The naive model alone cannot predict it.
5 Nonlinear spectroscopy of single plasmonic nanostructures

Figure 5.4: Dark-field scattering spectra (—) from a polycrystalline (a) and a monocrystalline (b) gold nanorod, respectively, under illumination with an unpolarized white light source. The complete scattered light is depicted (blue), as well as its portions polarized in parallel (red) and perpendicularly (green) to the rod axis. For the purpose of comparison, panel (a) exhibits the nonlinear MPPL spectra (—) taken under illumination with ultrashort NIR laser pulses, resolved for the particular polarization.

The fact that a difference between mono- and polycrystalline specimens exists, combined with the polarization analysis and the simulations hinting at the origin of the peaks, already indicates that not the electronic band structure of gold but instead the geometry of the nanoantennas is decisive. Additionally, the resonances are reproduced not only by simulations but by direct linear measurements of the scattering spectra in the visible regime. The measurements have been carried out in dark-field mode under unpolarized white light illumination and the spectra (blue —) are shown in Fig. 5.4 (a) and (b) for the respective types of crystallinity. When the polarization filter is applied either the light polarized in parallel (red) or orthogonally (green) to the antenna axis is detected. The resonances predicted by the simulation are in principle reproduced, although the data is acquired from different specimens than modeled for the calculation. The monocrystalline rod from panel (b) has an exceptionally broader width of 90 nm. This redshifts the green peak with orthogonal polarization to a wavelength of 670 nm, illustrating nicely the dependence of the perpendicular plasmonic resonance on the structure dimensions. In contrast, the nanorod corresponding to the data in panel (a) has a typical width of 60 nm. Its resonances in the linear dark-field scattering spectra (—) are in perfect overlap with the peaks of the nonlinear PL emission (—) and show identical polarization.

The polarization distribution observed here has been found before [Bou05] and was assigned to the crystal structure at different facets and sides of the polycrystalline rods [Imu05]. We rule out any influence of the crystal orientation by exploiting our monocrystalline flakes, into which we can easily mill nanoantennas with FIB at different angles, see Sec. 4.2.2. The flat

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3The white light source emits only weakly at blue wavelengths. Consequently, only faint scattering is observed in the dark-field spectra in this regime.
single crystals are oriented in the [111] plane, thus by etching one rod in parallel to an edge of the hexagonal flake and another one rotated by 30°, see sketch in Fig. 5.5 (a), they differ in their internal crystal orientation. Rod A is parallel to the [101] axis and rod B to the [112] axis. Their mainly identical nonlinear emission spectra are depicted in Fig. 5.5 (a) in blue and red, respectively. The inset shows SEM images of the specimens. Thus, no influence of the crystal orientation is identified. Only the general crystallinity of the structure determines the spectral shape of the MPPL. To exclude an influence of the various production methods used to fabricate the respective antenna types, Fig. 5.5 (b) shows nonlinear emission spectra obtained for different polarizer settings from a nanorod that was milled with FIB into a thermally evaporated gold film. The spectra exhibit exactly the same behavior as all polycrystalline samples with an additional peak at a wavelength of 730 nm and longitudinal polarization. This verifies the independence of the fabrication method and points out that the spectral differences stem from the crystalline characteristics. Ergo, this fact as well as the mentioned length difference of poly- and monocristalline rods that experimentally prove to have the same plasmonic resonance, must be explained with the internal nanoscopic structure.

For this sample a quartz substrate was used exceptionally. It has a higher refractive index ($n = 1.53$ [Gho99] at a wavelength of 2000 nm) than fused silica ($n = 1.44$ [Mal65]). This redshifts the resonances and explains why the green peak is situated around a wavelength of 610 nm.

As for the sample in panel a) of Fig. 5.5, also in this case a quartz substrate was used. This redshifts the green peak to a wavelength of 630 nm and explains the shorter rod length that compensates the shift of the main resonance.

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**Figure 5.5:** (a) Nonlinear emission spectra of gold nanorods (shown in the SEM micrograph in the inset) with different crystal orientation. The sketch depicts how they are cut from a single-crystal flake: either in the [101] (blue) or [112] (red) direction. (b) Nonlinear emission spectrum (blue) from a polycrystalline nanorod fabricated via FIB milling and the respective portions of the emission polarized in parallel (red) or perpendicularly (green) to the rod axis.
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Figure 5.6: (a) Nonlinear emission spectra of polycrystalline gold nanorods shown as SEM micrographs in the inset. Their external dimensions are hardly distinguishable, especially for rod A and B which were also illuminated under exactly identical conditions. Yet the relative peak intensities in the MPPL features deviate significantly from each other due to the different internal structure. (b) Scattering cross section simulated with BEM for the rods that provided the data in panel (a), under illumination with light at different wavelengths, polarized in parallel (—) and perpendicularly (---) to the antenna axis. The inset shows a zoom in on the visible regime (marked gray) and how the simulation cannot grasp the influence of the internal structure since it predicts the same behavior for all rods. The center wavelength of the excitation $\lambda_{\text{exc}}$ is marked as dotted line.

5.2.2 Influence of the nanoscopic structure

The presented data clarify the fundamental origin of the peak structure in the MPPL, yet the simulations can neither resolve why the second order resonance is in practice so strongly enhanced only for the polycrystalline nanorods nor why they need to be about 60 to 120 nm longer than their monocrystalline counterparts when featuring the same plasmonic resonance. Of course, the shorter single-crystal length in turn shifts and reduces the intensity of the second order resonance peak, as the simulations in Fig. 5.3 (d) verify, but this explains only partly the difference between the two types of crystallinity and the immense variety within the data obtained from polycrystalline structures.

The variance is demonstrated in Fig. 5.6 (a) by nonlinear emission spectra acquired from geometrically nearly identical nanorods. The SEM micrographs in the inset show their similar external appearance and dimensions. Rod A and B were also illuminated under exactly the same conditions with identical environment, settings and pulse characteristics. Yet their relative peak intensities in the MPPL spectral structure differ. The respective simulated scattering cross sections for these experimental parameters are depicted in Fig. 5.6 (b) with a zoom in on the visible regime (marked gray) in the inset. The peak positions are predicted nicely in comparison

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Data from nanorod C was obtained another day with a slightly narrower spectrum for excitation.
to the data in panel (a), yet the relative peak intensities are not reproduced. The slight width variance does not affect the green peak, neither in the calculation nor in the experimental data. The slight length variance does not sufficiently influence the second order resonance. Instead, the internal grain structure has to be taken into account [Nov11].

As shown in Chap. 4 the thermally evaporated gold forms a grain structure with diameters of 20 - 50 nm. So particles with dimensions of a few hundreds of nanometers are arbitrarily crossed by grain boundaries. Figure 5.7 (a) illustrates how the nanorods from Fig. 5.6 are individually subdivided into several sections, each of which is presumably monocrystalline with random orientation. The size of the single grains scales their linear plasmonic resonance in the red visible regime, so they enhance preferentially the second order resonance of the nanorod which they build up [Kni12]. This coupling to form a gold rod of lower density than in a single crystal explains the length difference to the monocrystalline counterparts [Mer08]. To imitate the grainy structure, the nanorods are modeled with dented triangulations. Figure 5.7 (b) shows examples with different substructures. None affects the main longitudinal resonance, as it becomes evident when simulating the scattering cross section. The presented spectral window depicts only the visible regime, though, and thereby highlights their identical orthogonal resonances, in accordance with our experimental findings. However, the dents enhance the second order resonance (green, blue, turquoise lines) in contrast to the monocrystalline case (red line), especially when they overlap with the second order mode (blue).

The strong influence of the arbitrary internal structure that contributes via extremely sensitive coupling [Mer08] induces the huge variance in relative intensity and position of the peaks.
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Figure 5.8: (a) Nonlinear emission spectra from a rod-shaped (red) and a bowtie-shaped (blue) gold nanoantenna as depicted in the SEM micrograph in the inset. For the bowtie, emission polarized in parallel (cyan) and perpendicularly (green) to the antenna axis is shown. (b) Scattering cross sections of the nanorod (red) and bowtie (blue) from the left panel, simulated with BEM and excitation polarization set in parallel (—) and perpendicularly (- -) to the antenna axis. The inset shows the triangulations performed on particles with the dimensions of the specimens from the experiment.

Instead, even stronger influence with more control is given by the external geometry, as is demonstrated in the next section.

5.2.3 Influence of the external geometry

The dependence of the spectral MPPL peak positions on linear resonances points out the strong influence of the external geometry. Thus, by switching to a completely different geometry we change the incoherent nonlinear output drastically. The effect is demonstrated by the comparison of a rod-shaped antenna and a bowtie: their respective nonlinear emission spectra obtained under comparable illumination is depicted in Fig. 5.8 (a). The inset shows SEM micrographs of the completely different shapes that still exhibit identical plasmonic resonance positions, as proven by the simulation of the respective scattering cross sections for longitudinally polarized illumination, see solid lines in Fig. 5.8 (b). Of course the resonances differ strongly in their spectral width.

The experimental data in panel (a) reveal a pronounced redshift of the incoherent bowtie emission versus the rod emission. The spectrum is not very structured apart from an increase towards the NIR regime. Resolving the output into perpendicularly (green) and in parallel (cyan) polarized light (with respect to the bowtie antenna axis) therefore shows similar trends for both parts. This behavior is in accordance with the predicted scattering cross section for orthogonal polarization, see dashed blue line in Fig. 5.8 (b). The wider and tapered triangular geometry
has less defined resonances and its strongest emission is located outside the visible regime. In conclusion, the presented results prove that the linear resonances defined by the geometrical properties of the antenna determine the nonlinear behavior as well. Not only the microscopic geometry but also the nanoscopic internal crystal geometry influences the spectral shape of the nonlinear emission. This motivates the use of monocrystalline antennas since they have a well controlled internal structure and promise more reproducible and homogeneous results. In contrast to former interpretations which link the spectral features to intrinsic properties of the gold [Moo69, Boy86, Bev03, Bou05, Imu05] and which have been proven false by the results in this chapter, the findings here pave the way for more control over the antenna radiation by carefully tuning crystallinity and geometry. Adequate antenna parameters can now be determined for the desired application, especially when combined with the results presented in Chap. 6 where further investigations demonstrate how to enhance or suppress the coherent and incoherent nonlinear emission. But before, it is necessary to analyze the generation process of the observed emission, which actually turns out to be characterized only by intrinsic properties of the gold band structure instead of external parameters.

5.3 Spectrally resolved nonlinear order

Analyzing the spectral shape of the nonlinear emission reveals significant output down to wavelengths of 380 nm, i.e. photon energies of up to 3.3 eV, as the preceding figures in this chapter prove. The energy is provided by the NIR laser pulses whose center wavelengths vary between 1200 and 2050 nm, corresponding to photons energies of only 0.6 to 1 eV. The nonlinear multi-step process described in Sec. 3.3 thereby converts the NIR light into the broadband emission covering the full visible range. The energy difference indicates that 3 to 5 excitation photons are involved in the absorption cascade. This is still a naive assumption of a nondissipative procedure. The effective number of involved photons is expected to be higher since losses must be taken into account: at each sequential step, the excited electrons may lose energy due to electron-electron and electron-lattice scattering [Sun94, Fal99, DF00, Dem16]. Experimentally determining the nonlinear order will help to understand the origin of the MPPL and estimate the effective number of absorption steps. Since a multitude of applications relies on nonlinear effects as described in Chap. 3 many studies targeted the analysis of the involved orders, but in contrast to peaked HHG emission, the broadband MPPL requires a treatment that accounts for the enormous bandwidth. So far, only the nonlinear order of the integrated emission was investigated [Boy86, Bev03, Bou05, Far05, Mue05, Sch05, Eic07, Bia09, Bia12a, Jia13, Dem16, Mej16], or only specific wavelengths were compared [Ko11]. In this work, a detailed analysis of the nonlinear order is presented with spectral resolution over the full MPPL emission range.
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Figure 5.9: (a) Nonlinear emission spectra obtained from a monocrystalline nanorod for increasing excitation power $P$ at a center wavelength $\lambda_{exc}$ of 2000 nm. The vertical lines mark the spectral positions ($\lambda_1$ to $\lambda_3$) for which the there emitted intensity is plotted versus the particular excitation power $P$ (symbols) in panel (b). The lines in this double-logarithmic plot follow a power law $I(P) \propto P^n(\lambda)$ fitted to the data, from which the nonlinear order $n(\lambda)$ is extracted as a fit parameter for all spectral positions and displayed versus the wavelength in panel (c) as crosses. For orientation, a spectrum is shown in the background (gray).

To do so we follow the procedure presented in [Kni17]: several spectra are obtained consecutively from one nanorod for increasing excitation power, see Fig. 5.9 (a), while all other parameters are kept constant. The MPPL intensity ascends nonlinearly. To determine at which order, its increase is compared to the increase of the excitation power. Doing this for each emission wavelength in combination with an appropriate fit model allows to extract the spectrally resolved nonlinear order $n(\lambda)$.

At the three vertical lines in panel (a), the increase of the intensity $I$ is marked for three exemplary emission wavelengths $\lambda_1$ – $\lambda_3$. The intensity data $I$ are plotted (symbols) versus the excitation power $P$ in panel (b) on a double-logarithmic scale, together with the best fit results (lines) based on a power law $I(P) = a(\lambda) P^{n(\lambda)}$. Thus, the nonlinear order can be extracted and is displayed as crosses for each emission wavelength $\lambda$ in Fig. 5.9 (c)\(^7\).

\(^7\)The spectral resolution of the order equals the one at which the spectra were taken. It is determined by the grating in the spectrometer to 0.5 nm. The spectra are smoothed by a moving average with a width of 2 nm before the analysis. Only fit results with $n(\lambda)$ inside a 95% confidence interval are taken into account.
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![Graphs showing nonlinear spectroscopy of single plasmonic nanostructures.](image)

Figure 5.10: Spectrally resolved power dependence (symbols) of the nonlinear emission: (a) obtained from a monocrystalline (red) and a polycrystalline (blue) gold nanorod and (b) from the latter one (blue), with additional data for nonlinear emission polarized in parallel (red) and perpendicularly (green) to the antenna axis. The associated emission spectra are depicted at the bottom. The bottom axis in panel (a) is given in wavelength, the top axis in photon energy. The green line marks elastic reemission, i.e. the expected order for emission at the respective photon energies for excitation with photons of fixed energy: $n_{el} = E/E_{exc}$. In order to facilitate the estimation of the shift towards the MPPL nonlinear order as a measure for the dissipated energy, the elastic reemission $n_{el}$ is plotted continuously and not only for integer numbers.

The spectrum shown in the background demonstrates that the order is exactly 3 only at the THG spectral range, whereas everywhere else higher orders appear: pure MPPL emission involves at least 3 to 4 photons and increases smoothly up to 6 towards the UV regime. The cited studies [Boy86, Bev03, Bou05, Far05, Mue05, Sch05, Eic07, Bia09, Ko11, Bia12a, Jia13, Dem16, Mej16] all used titanium-sapphire based techniques to generate excitation pulses between 780 and 830 nm (≈ 1.5 eV) only. Thus, emission in the visible regime requires only about 2 photons for elastic emission in the blue regime (≈ 3 eV), but due to dissipation maximum orders of $n = 4$ are found [Mue05, Bia12a, Dem16]). However, with the advantageous fiber laser technology we can drive and observe conversion processes that transact more photons. So in contrast to THG, MPPL is of higher nonlinear order and its emitted energy is less than the summed energy of the $n$ expended photons. While THG is emitted exactly with the energy of 3 excitation photons ($E = E_{THG} = 3E_{exc}$), the incoherent and noninstantaneous MPPL transfers the energy of up to almost 1 photon (0.6 eV) to the electronic system which is not reradiated. This transfer is possible since the electrons are excited into real states in the electronic band structure, where they lose part of their energy via scattering mechanisms [Sun94, Fal99, DF00, Dem16]. The amount of dissipated energy can be estimated by comparing the data to the green line in Fig. 5.10 (a). It marks elastic emission $E = n_{el} \cdot E_{exc}$, so the emitted photon energy equals
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Figure 5.11: Spectrally resolved power dependence (crosses) of the nonlinear emission obtained from polycrystalline nanorods resonant at the different excitation wavelengths $\lambda_{\text{exc}}$ varying from panel (a) to (c). The associated emission spectra are depicted in gray. The bottom axes are given in wavelength, the top axes in photon energy. The colored lines mark elastic reemission, i.e. the expected order for emission at the respective photon energies for excitation with photons of fixed energy: $n_{\text{el}} = E/E_{\text{exc}}$. In order to facilitate the estimation of the shift towards the MPPL nonlinear order as a measure for the dissipated energy, the elastic reemission $n_{\text{el}}$ is plotted continuously and not only for integer numbers.

Exactly the $n_{\text{el}}$-fold excitation energy$^8$. It stays below the nonlinear order of the MPPL emission (crosses) at $E = E_{\text{MPPL}} < n_{\text{el}} \cdot E_{\text{exc}}$ determined by the experiment for a monocrystalline (red) and a polycrystalline (blue) nanorod (except for the regime dominated by elastic THG output). The identical behavior of both sample types proves that the generation of MPPL does not depend on the crystal structure. Furthermore, it is independent of the polarization, and thus (as described in the preceding section) also of the geometry: Fig. 5.10 (b) shows the same trend for the nonlinear order of MPPL emitted with polarization parallel (red) or perpendicular (green) to the antenna axis.

In summary, we find that the origin of the MPPL depends exclusively on the electronic band structure, thus enabling the high nonlinear orders. They can be as large as 6, for recombination of highly excited electrons from the tail of the Fermi-Dirac distribution with holes in the $d$-band, since above 2.4 eV the joint density of states in gold changes significantly with the electronic temperature [Lae81, Dem16, Kni17]. Moreover, this explains why the process is not influenced by the crystallinity or geometry, but instead by the smearing of the hot electrons: it is not possible to determine an exact sequence of absorption steps since the probability of creating a hole in the $d$-band is related to the global nonequilibrium distribution in the conduction band [Boy86, DV12, Con12, Kni17], see Sec. 3.3. Thus, the nonlinear order $n(\lambda)$ must be understood as an effective number averaged over the involved photons from all possible channels and is therefore fractional. This has been found before when integrated emission was investigated [Bou05, Dem16, Eic07, Mej16]. Here, the spectrally resolved analysis highlights in addition the

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$^8$Physically, only integer orders $n_{\text{el}}$ make sense for elastic reemission of course, but to facilitate the estimation of the shift towards the MPPL order, $n_{\text{el}}$ is depicted continuously.
smooth increase of the effective noninteger order with the emission wavelength.

In order to investigate the correlation with the excitation wavelength $\lambda_{\text{exc}}$, Fig. 5.11 compares the power dependence of the visible MPPL emission generated with pulses of different NIR photon energies. The crosses denote the nonlinear order determined from the MPPL of nanorods resonantly excited at (a) 1300 nm ($\approx 0.9$ eV), (b) 1700 nm ($\approx 0.7$ eV) and (c) 2000 nm ($\approx 0.6$ eV). The associated spectra are depicted in the background (gray), the colored lines illustrate the elastic emission. The higher the excitation energy $E_{\text{exc}}$, the less photons are needed to generate visible emission, as can be seen from panel (a), though the orders are still higher than for the nondissipative THG. The fundamental photons have an energy of $E_{\text{exc}} \approx 0.9$ eV and the nonlinear order of the MPPL varies between 3 and 4. Panel (b) and (c) indicate not only an increase of involved photons for $E_{\text{exc}} = 0.7$ eV and 0.6 eV, but also that the spread of occurring orders broadens, as the gray areas mark. So the amount of possible absorption sequences that rises with the number of involved photons influences strongly the nonlinear MPPL process. Apart from the variance of the effective order, the photon energy of the excitation also influences the MPPL intensity. Naively, we expect increased intensity for the lower-order MPPL process triggered by excitation photons of higher energy. However, the spectra in Fig. 5.11 hint to the opposite. The following chapter addresses a quantitative analysis of this effect.
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The preceding chapter gave a better understanding of the conversion mechanism which triggers the incoherent photoluminescence and how its emission is influenced. This is now contrasted with the behavior of the coherent THG. Instead of focusing on the emitted spectrum, now the dependence on the illuminating wavelengths is targeted. Thereby, we can gain access to the dispersion of the nonlinear effects and thus also to the dispersion of their origin, which is governed by the strong nonlinear susceptibility of gold [Kni17]. Assessment of this quantity is challenging [Boy14]: many studies evaluate the complex $\chi^3$ by different means, exploiting either THG [Bur71], 4WM [Ren10] or Z-Scan [Lee06, Rot07]. These methods are performed with varying optical parameters and for different spectral regimes. Consequently, the results are contradictory and hard to compare [Hac88, Con12, Boy14, Haj15]. None of the characterizations is complete since the choice of the optical effect inherently limits the access to the associated subcontributions of the susceptibility, see Sec. 3.1.

Another challenge is posed by the local field enhancement that highly influences the nonlinear effects [Dem16, Boy86]. Its determination by experimental and simulation techniques is difficult with high precision [Boy86, Bou03, Cro03, Bou05, Sun05, Sch05, Ko11] since it depends strongly on the local environment and nanoscopic geometrical properties of each individual structure. Here, we resolve this issue and exploit the simultaneous occurrence of instantaneous and noninstantaneous effects: contrasting THG to MPPL emission acquired at the very same nanoantenna rules out the structure’s individual field enhancement. This allows comparing many individual antennas as long as equivalent experimental conditions are guaranteed.

6.1 Nonlinear emission for excitation tuned in the near infrared range

Essentially, the experimental setup described in Sec. 5.1 is used to trigger visible emission from single nanorods with custom-tailored plasmonic resonance. The observed effects scale nonlinearly with the excitation power, ergo it is crucial to fully control the illuminating NIR pulses. While tuning over an enormous wavelength range, the incident intensity and therefore the pulse duration and spectral width need to be adjusted.

The center wavelengths of the excitation spectra vary from $\lambda_{\text{exc}} \approx 1200$ to 2000 nm, as the selection in Fig. 6.1 (a) illustrates. The fundamental laser emission at $\lambda_{\text{exc}} = 1550 \text{ nm} \pm 50 \text{ nm}$ must be spared out because the nonlinear conversion processes exploited to generate the WLC in the fiber laser system spectrally modulate the driving frequency. The structuring causes long pulse pedestals in the time domain. Thus, noninstantaneous emission depending on the ther-
Figure 6.1: (a) Selected excitation spectra with tuned center wavelengths $\lambda_{\text{exc}}$ used to investigate the dispersion of nonlinear processes in gold. One of them is compared in panel (b) to the spectral intensity (---) and phase (···) reconstructed from an SHG FROG measurement. (c) Corresponding temporal profile (intensity (—) and phase (···) versus time) from the spectrum in panel (b) (green) as well as for pulses centered at $\lambda_{\text{exc}} = 1400$ nm (blue) and 2000 nm (red), determined with SHG FROG. $\Delta t$ denotes the pulse length (FWHM).

The fully controlled pulses with well behaved phase resonantly excite single nanorods at different wavelengths and the respective nonlinear emission spectra are collected. Figure 6.2 displays a selection. The spectra are normalized to their THG peak to highlight how the broadband MPPL intensity increases relative to the instantaneous emission when excitation is tuned towards the IR regime. A quantitative comparison of the absolute energy content in the coherent and incoherent emission reveals further details.
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6.2 Dispersion of the incoherent and coherent emission

For the quantitative analysis a cubic spline is fitted to each spectrum, such that it excludes the THG peak and if necessary also the SHG. This allows to integrate the instantaneous and noninstantaneous contributions separately. For integration, the respective photon energy is taken into account. Figure 6.3 illustrates the procedure for three examples. Note that the spectra are not normalized to their THG peak, hinting to a strong dispersion in absolute THG intensity.

6.2.1 Absolute coherent and incoherent output

The described procedure is repeated for different excitation spectra and the separately integrated emission is plotted versus the particular center wavelengths $\lambda_{\text{exc}}$ in Fig. 6.4 (a) for the THG and in (b) for the MPPL, respectively. Each data point stems from one measurement at a single antenna. The results from the three examples in Fig. 6.3 are marked gray. Nanoscopic defects in the antenna geometry which affect the local field enhancement and thus the con-

Figure 6.3: Nonlinear emission spectra obtained from three gold nanorods resonantly excited at center wavelengths $\lambda_{\text{exc}} = 1300$ nm (a), 1700 nm (b) and 2000 nm (c), respectively. Fitting a cubic spline (green) separates the coherent THG (blue) from the incoherent MPPL (red) for individual integration.
version efficiency of the nonlinear effects, lead to a large variability in the experimental data. In spite of that, two distinct trends are evident: while MPPL intensity increases towards the IR regime, THG is strongly enhanced when tuning the excitation towards the visible. The opposite behavior of the effects is counterintuitive, as the antenna volume expands with longer resonance wavelengths. This is expected to be advantageous for both effects since it increases the field enhancement [Dem16]. MPPL even benefits from this despite the higher nonlinear orders which become relevant for lower energy of the excitation photons $E_{\text{exc}}$, see Sec. 3.3.

Furthermore, the extreme confinement in smaller particles which relaxes the momentum requirements for electron-hole-recombination, is discussed as a reason for stronger emission towards the visible, although on the contrary, larger particles have larger field enhancement [Hac88, Far05, Bou05, Boy14]. Yet, MPPL increases with excitation tuned towards the IR regime, as it has been found before by Boyd et al. [Boy86]. They attribute the behavior to surface resonances but also argue that uncertainties in the population distribution and the various local field enhancement complicate the interpretation. By comparing the incoherent and coherent emission we master this challenge and prove what the counterintuitive results already indicate: instead of the MPPL, it is the THG that is strongly influenced by a pronounced dispersion of the $\chi^3$ nonlinearity in gold [Boy86, Con12, Boy14].

### 6.2.2 Dispersion independent of the field enhancement

Instead of the absolute integrated emission, Fig. 6.5 (a) displays the ratio of coherent THG within the totally emitted radiation in dependence of the excitation wavelength $\lambda_{\text{exc}}$ and associated photon energy $E_{\text{exc}}$. We observe strong dispersion as a consequence of the now combined opposite trends of the absolute THG and MPPL intensities. THG output is almost 100% at the
expense of incoherent MPPL when going to higher incident photon energies $E_{\text{exc}}$, whereas this ratio is nearly reversed at the other end of the spectrum. The relative comparison of the two effects rules out an increased local field confinement at the smaller nanorods as the reason for the observed trends [Far05, Bou05]. Instead, we have direct insight into the dispersion of the origin of the THG: the instantaneous contributions of the third-order nonlinear susceptibility $\chi_3$. Its strong wavelength dependence can be explained with the optical response of gold below the plasma frequency which is shaped by the interband transitions that also influence the nonlinear behavior [Bla10, Boy14], see Sec. 2.2 and 3.1. The closer the excitation energy $E_{\text{exc}}$ approaches $\frac{1}{3}E_g$ with the interband transition energy $E_g = 2.4$ eV at the L point in gold [Chr71, Gue75], the more the THG is resonantly enhanced [Hac88, Con12, Haj15]. This is illustrated in the corresponding section of the gold band structure in Fig. 6.5 (b), where possible THG processes for different excitation wavelengths $\lambda_{\text{exc}}$ are sketched. Only photons with the highest energy $E_{\text{exc}} = 0.95$ eV of the three marked examples are sufficient to cross the “band gap” to the free states in the conduction band. Generally, the THG does not require real states in the electronic band structure, nevertheless it can experience strong resonance enhancement when free states are available. Of course, this quenches the MPPL emission. The enhancement increases for excitation energies $E_{\text{exc}}$ towards $\frac{1}{3}E_g$, yet it is not restricted to meet this value exactly, since a variety of transitions between the sp-band around the Fermi level and the various d-bands set in [Moo69, Hac88]. Thus the THG increases further towards the visible.

### 6.2.3 Estimation of the effective nonlinear coefficient

The quantitative analysis of the integrated THG and MPPL intensity $I_{\text{THG}}$ and $I_{\text{PL}}$, respectively, provide qualitative insight into the dispersion of the coherent nonlinear response of gold. For a rough quantitative estimation, we apply our knowledge of the conversion mechanisms behind the observed effects: while THG intensity is proportional to

$$I_{\text{THG}} \propto |d^{(3)}(\lambda_{\text{exc}})|^2$$

with the nonlinear coefficient $d^{(3)}(\lambda_{\text{exc}})$ and the local electric field $E_{\text{loc}}$ at the nanostructure, for MPPL we find

$$I_{\text{PL}} \propto |E_{\text{loc}}|^2$$

where $n$ is the nonlinear order\(^1\). By combining both relations we can circumvent knowledge of $E_{\text{loc}}$ and thereby roughly estimate the nonlinear coefficient $d^{(3)}(\lambda_{\text{exc}})$ as a quantity associated to the coherent third-order susceptibility:

$$d^{(3)}(\lambda_{\text{exc}}) \propto \sqrt{\frac{I_{\text{THG}}}{I_{\text{PL}}}}^{\frac{3}{2n}}$$

\(^1\)Influence of the nonlinear coefficients linked to the MPPL process is neglected: they can be taken as proportionality constants since their dispersion is expected to be small [Boy14].
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Figure 6.5: (a) Ratio between the coherent THG emission and the total nonlinear output of single nanoemitters (black symbols). Each data point corresponds to an individual measurement from a single gold nanorod. The dotted line serves as guide to the eye. The colored results are exploited to estimate the dispersion of the nonlinear coefficient $d^{(3)}(\lambda_{\text{exc}})$ (gray). (b) Section of the gold band structure at the $L$ symmetry point. The arrows indicate the THG process for the three photon energies $E_{\text{exc}}$ selected for the estimation of $d^{(3)}(\lambda_{\text{exc}})$. Only for $E_{\text{exc}} = 0.95$ eV (blue) the THG is resonantly enhanced, since then the energy is sufficient to reach the free states (dashed part) in the sp-band. In the other cases virtual states (⋯) mediate the process.

We exploit the three examples from Fig. 6.3, whose results for $I_{\text{THG}}$ and $I_{\text{PL}}$ are marked gray in Fig. 6.4 and 6.5, as for them we can also resort to the analysis of the involved nonlinear orders $n(\lambda)$ of the MPPL: from the same specimens the data in Fig. 5.11 was acquired. Reasonably, $n(\lambda)$ is obtained there in dependence of the emission wavelength $\lambda$. However, since we deal now with integrated intensities, we introduce a mean nonlinear order $\bar{n}$. It is given by an average over all data points in the respective shaded areas in Fig. 5.11 (a) to (c), weighted with the associated emission spectrum. The analysis yields the results for $d^{(3)}$ shown in Table 6.1 and Fig. 6.5 (b).

In this way, we can roughly estimate that the nonlinear coefficient of the instantaneous third order susceptibility increases by a factor of about 6 when tuning the excitation wavelength $\lambda_{\text{exc}}$ from 2000 nm to 1200 nm. This is mainly attributed to the enormous enhancement of the THG emission of a factor of 50 over the observed wavelength range. It should be noted that this increase, along with all other observations, holds true for mono- and polycrystalline specimens, as it is caused by an intrinsic property of gold. This behavior is reflected in the data. However, absolute THG intensities reach much higher values (up to 10-fold) for polycrystalline gold than for single crystals. This can be attributed to higher field enhancement at its structured surface [Boy86].
In conclusion, we gain direct insight into the dispersion of an intrinsic property of gold: the coherent contribution to the nonlinear susceptibility \( \chi_3 \). Field enhancement effects are ruled out by comparing two concurrently occurring effects from the very same plasmonic emitter. As a practical aspect for implementation, the ability to suppress or enhance certain types of emission yields together with the results from Chap. 5 full control over the nonlinear output, so that custom-tailored solutions can be offered for the many different applications.
7 Ultrafast dynamics in single plasmonic nanostructures

The dynamical properties of plasmonic nanodevices are subject of many investigations [Wok82, Lam99, Sön02, Han09, And10, Han11, Bos13, Kra16], aiming for deeper insight into two fundamentally important fields: firstly, the dynamics of the general nonlinear behavior is directly linked to the plasmonic dephasing time, mediated via the third-order nonlinear susceptibility $\chi^3$ [Pue01, Kle05]. Hence, analyzing the influences on the dephasing time provides a better understanding of the various damping mechanisms and electronic processes occurring in the metal, as described in Sec. 2.3 and 3.4. Secondly, control of the plasmonic dephasing time and the dynamic properties completes the achievements of the preceding chapters and gains full insight and control of the relevant structure properties to custom-tailor them for the many specific purposes. Very often, it is relevant to guarantee a dephasing time as short as possible [Sön02], as for example in the aforementioned tunneling experiments [Ryb16, Ryb18], compare Sec. 2.4. There, laser pulses trigger single electron tunneling across the feedgap of a metal nanostructure embedded in a circuit. To enable this process, it is extremely important to maintain the ultrashort pulse duration of the light throughout the entire light-matter interaction. Hence, the plasmonic transmitter may not retard the pulses and thereby decrease the high peak intensity of the pulses with a long dephasing time. This would result in the reduction of tunneling probability. A fast response instead preserves the pulse characteristics. In contrast, other applications benefit from longer dephasing times and a consequently increased field enhancement [And10]. Thus, it is necessary to minimize radiation damping [Wok82]. In any case it is crucial to investigate the different dephasing mechanisms mentioned in Sec. 2.3 and understand on which particle properties they depend: larger particles (dimensions approximately above 100 nm), for example, are mainly radiation damped [Wok82, Sön01, Han11]. For monocrystalline structures we expect longer dephasing times, as the collective electron oscillation would not be hindered by scattering at internal grain boundaries [Kut08, Che10, Sch12]. Among the general insight into the dynamic characteristics, the influence of the crystallinity is specifically investigated in the present chapter, together with the suitability of gold bowtie structures for the tunneling experiments. This is directly achieved via the determination of the plasmonic dephasing time $T_2$. Other approaches rely on indirect measurements: for instance may the spectral width of the resonance serve as a rough estimate for $T_2$ when Fourier transformation is applied [Sön02]. In general, the widely used dark-field scattering techniques suffer from the lack of phase information [And10]. Also electron energy loss spectroscopy (EELS) is performed to compare the dephasing of symmetrically shaped gold rods with irregular structures and to determine the dependence on the plasmon energy [Bos13]. However, the method is affected by large instrumental broadening. Similarly, experiments acquiring data from ensembles of particles
instead of individual devices are disturbed by inhomogeneous broadening [Kle05]. Lamprech et al. applied 4WM with the help of ensembles of nanoparticles and then compared the third-order autocorrelation to simulated results based on a damped harmonic oscillator model [Lam99]. Their results for an inhomogeneously broadened ensemble (\(T_2 = 12\) fs for arrays of gold disks) tend to be longer than the dephasing times determined with a similar scheme from single gold nanoantennas: in [Han09, Han12], fitting the measured THG FRAC taken from double antennas under the assumption that the plasmon is described by a harmonic oscillator with exponential damping time and perturbative third-order nonlinearity is demonstrated. The method yields a dephasing time of \(T_2 = 4\) fs for elliptical disks and up to \(T_2 = 12\) fs for other geometries. For comparison, the instantaneous response is taken from the THG at the substrate, which is not plasmon mediated. Another approach instead uses nonlocal excitation to perform 4WM at gold tips [Kra16]. Autocorrelation analysis is of course not restricted to 4WM and is for example also performed with incoherent two-photon photoluminescence (2PPL) from gold nanorods, however determining significantly longer dephasing times between 15 and 30 fs [Nis15, Zha16].

Not only the variety of methods and the dependence on the material, size, geometry, technical aspects and spectral range make it difficult to compare the many results for dephasing times reported in the literature [Sön02, And10]. Additionally, various assumptions (e.g. Lorentzian lineshape) and models enter in most schemes for the determination of \(T_2\). A superior approach aims to gain all encoded information from the nonlinear response and to avoid as many assumptions as possible. This can be achieved with the measurement of IFROG spectrograms from single nanostructures and their full reconstruction, compare Sec. 3.5.3. The full plasmonically retarded pulse shape \(E_{pl}(t) = E_{exc}(t) \ast R(t)\) including the phase information, can be extracted from the data. Via Fourier transformation, the convolution of the separately determined incident field \(E_{exc}(t)\) with the response function \(R(t)\) can be resolved to a multiplication, as demonstrated by Anderson et al. with SHG at conical gold nanotips [And10]. Thus, no requirements have to be posed to \(R(t)\), such as modeling it with an exponential decay.

For this thesis, THG IFROG is performed on single gold bowtie nanoantennas of fixed resonance in the NIR regime. This avoids inhomogeneous broadening and tests the dephasing conditions specifically for the tunneling experiments described in [Ryb16, Ryb18]. The fixed resonance is achieved via controlled size parameters, thereby also ruling out volume and shape influences. The IFROG scheme enables to extract the complete pulse information and the collinear tight focusing enhances nonlinear emission so that sufficient third harmonic light is generated. THG is less constrained by symmetry effects, so that in principle also non-centrosymmetric structures can be studied [Lam99, Kra16]. Moreover, the influence of monocrystalline and polycrystalline gold is investigated.

The results of this chapter were analyzed in cooperation with M.Sc. Janne Hyyti and Prof. Dr. Günther Steinmeyer from the Max Born Institute in Berlin. Kindly they carried out the full reconstruction of the measured IFROG spectrograms presented in the following.
7.1 Experimental setup for the characterization of plasmonic dephasing times

In principle, the experimental setup to characterize the plasmonic dephasing times relies on the same techniques as the setup for the spectroscopy of nanoantennas, see Sec. 5.1. It consists of an Er:fiber-laser system and WLC generation followed by precise detection of the nonlinear response of the excited nanostructures. However, some adaptations need to be implemented to provide the necessary temporal resolution. This is achieved by recording FROG spectrograms of the response interferometrically, instead of acquiring single spectra. Thus, in place of the wide tunability, the broad spectral range becomes relevant when compressed in the time domain. Furthermore, the detection has to be highly sensitive over the full spectral range of the coherent nonlinear response, in order to guarantee perfect conditions for the phase retrieval algorithm employed to analyze the data. The implementation suiting these requirements is explained in the following.

7.1.1 Generation of phase-locked ultrashort light pulses

The Er:fiber-laser system utilized for the following experiments is explained in detail in [Ryb18]. Its main difference compared to the system presented in Sec. 5.1.1 is its additional stage to generate carrier-envelope-phase-stable pulses, which is obligatory for the tunneling experiments described in [Ryb16]. While the phase stability is not necessary for the purpose of this work, the availability of extremely ultrashort pulses however is of great importance. For this reason, the quality of the pulse compression is also improved. Figure 7.1 gives an overview of
all relevant setup components.
The oscillator and amplifier stage (OSC and AMP in Sec. I and II in Fig. 7.1) are very similar to the ones in Sec. 5.1.1, aside from that the oscillator is operated at a higher repetition rate of 80 MHz and the amplifier is pumped with four instead of three laser diodes (LD), yielding a pulse energy of 7.8 nJ (corresponding to an average power of 620 mW). The WLC (Sec. III) is generated in an HNF with slightly different specifications since it is necessary to provide in the first stage a dispersive and solitonic wave that qualify outstandingly to perform difference frequency generation (DFG). This is exploited to provide the stability of the carrier-envelope phase (CEP) over an extremely long pulse train [Ryb18]. It enables direct control of the electric field and guarantees exactly the same conditions for all consecutive pulses.

Before the DFG in periodically poled lithium niobate (PPLN) doped with MgO, an SF10 prism sequence (Sec. IV PC) compresses the dispersive wave. The soliton is clipped after the first prism and sent back without dispersion correction, whereas the fundamental light must be blocked. The two spectral parts have now almost the same pulse length of approximately 30 fs which sets ideal conditions for the DFG (Sec. V). It yields a power of 1 - 2 mW after the pulses are focused onto the nonlinear crystal (MgO:LiNbO3) which is stabilized at a temperature of 343 K. The CEP of the now phase-stable frequency-mixed pulses may be set afterward by the insertion of fused silica wedges.

Another amplification stage consisting of an Er:fiber-based pre-amplifier and amplifier (Sec. VI PRE/AMP) pumped with one and four LD, respectively, enhances the output power to 555 mW. Subsequently, the pulses are sent through the second WLC generation setup (Sec. VII WLC2). The HNF there generates the final spectrum, again composed of dispersive and solitonic wave. With the enormous available bandwidth and a sophisticated compression setup, pulse durations as short as 4 fs are now achievable [Ryb18]. In contrast to the two separate prism compressors (PC) described in Sec. 5.1.1 for soliton and dispersive wave, here one sequence built out of three prisms (Sec. VIII 3PC) covers the dispersion control necessary to flatten the phase over the full spectral pulse bandwidth. The soliton is clipped after the first prism and is retarded in a silicon wafer. The dispersive wave, however, is split at a wavelength of 1040 nm into a part containing the short wavelengths and a part with long wavelengths. Both are sent through different restoring prisms, so that material passage can be controlled individually, allowing to compensate chirp even for the short-edge wavelengths. The end mirror positions of the PCs are adjusted with piezo positioners (PP) to perfectly overlap the different spectral parts in the time domain. The fundamental spectrum is blocked in the Fourier plane. For the experiments presented in this chapter, the soliton is blocked likewise, since the dispersive bandwidth is sufficient. As aforementioned, the CEP stability is also not obligatory, but in case it becomes relevant it can be checked with an $f - 2 - f$-setup (Sec. IX). It makes use of the more than one-octave-spanning bandwidth to guarantee the CEP stability, for details see [Ryb18]. In addition to the FROG setup described in Sec. 3.5.2 and 5.1.1, also a setup for 2DSI measurements (Sec. X in Fig. 7.1) is now available to characterize the exact temporal and spectral pulse shape.
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Figure 7.2: (a) Spectrum of the dispersive wave generated, compressed and analyzed with the setup described here, measured with the OSA (red) and reconstructed from SHG FROG (blue). The temporal profile (intensity over time) is depicted in (b) with the corresponding retrieved phase (green). Pulse duration is 7.5 fs (FWHM).

and phase, compare Sec. 3.5.4.

A typical pulse spectrum used in the experiments for excitation is shown in Fig. 7.2 (a), as it is detected with the OSA (red) and reconstructed from an SHG FROG measurement (blue). The corresponding temporal intensity profile with the associated phase (green) is shown in panel (b). The pulse length (FWHM) is typically set to 7.5 (± 0.1) fs and the central wavelength $\lambda_{exc}$ to around 1200 nm. The dip in the spectrum in Fig. 7.2 (a) results from the three prism compressor which splits the dispersive wave in two parts for individual compression.

7.1.2 Characterization of the ultrafast plasmonic response

To measure IFROG spectrograms of the plasmonic response, a Michelson interferometer splits the pulse train for the excitation into two separate trains and delays one set with respect to the other (Sec. XI in Fig. 7.1). The principle is explained in detail in Sec. 3.5.3. The beamsplitters are custom-made from 150-μm-thin fused silica substrates. 7.5 nm of gold are deposited on them, subsequent to a 0.4-nm-Cr adhesion layer. The nanoantennas serve as nonlinear elements themselves by generating third harmonic output when the two pulse trains are focused onto a single structure (Sec. XII). The excitation of the nanoantennas and the detection of their nonlinear response is in principle the same as described in Sec. 5.1.2, with the main difference that one spectrum is recorded now at each delay step of the excitation pulse train, yielding spectrograms as shown in the inset of Fig. 7.1.

Apart from that, the setup is optimized to provide a spectrally broader detection range towards the UV: down to one-third of all excitation wavelengths so that the THG is recorded in full range. This measure is absolutely crucial since for the IFROG reconstruction, all spectral components are relevant and need to enter in the algorithm to guarantee correct results. The adaptions are illustrated in Fig. 7.3, where panel (a) shows the transmission spectra of the optical components
Figure 7.3: Transmission spectra of the most dispersive components in the detection units of both the spectroscopy setup (a) optimized for broadband PL in the visible range (compare Chap. 5) and the setup for dynamical investigations (b) optimized towards the UV range. All shown components, i.e. the respective filters (turquoise), objectives (red) and the gratings (blue), except for the CCD chip (green) are replaced in the course of the setup adaptions from (a) to (b). Ergo the combined transmission (black), the product of the components, is shifted significantly towards the UV, providing additional detection sensitivity (panel (b): green area) compared to the former total transmission from panel (a) (gray in (b)), thereby covering the full THG range (gray - - -). The gray IR area depicts the edge of the fundamental laser excitation.

used in the spectroscopy setup in Sec. 5.1.2 and panel (b) the ones of the new components that were introduced for better performance towards the UV range. The black lines denote the total transmission over the spectral detection range when the influence of all relevant components is combined. In panel (b), a measured THG spectrum (gray - - -) illustrates that the detection range needs to be expanded well below the former limit (gray –), which is successfully achieved by the replacement of certain components, so that the green shaded area is gained and the THG emission range is fully covered by the total transmission (black). Therefore, several replacements are necessary for the updated setup: since most glasses are not transparent below 400 nm, the dark-field objective (in Fig. 7.3 (a), red) and the optical components of the inverted microscope are exchanged. A Cassegrain objective (CGd in Fig. 7.1, in Fig. 7.3 (b), red) with the same geometry as for the focusing (CGc, NA 0.65, Ealing X52) is used now, but with UV-enhanced aluminum coating instead of gold mirrors. Additionally, aluminum mirrors instead of silver coated ones then guide the light through a better suitable short pass filter (SP2, 5-mm-thick HA03, HEBO, turquoise) and a tube lens (TL) with UV-specialized coating into the monochromator. A good choice of the filter is very important since this component is responsible for the complete clipping of the fundamental light, ranging down to a wavelength of about 850 nm (gray area). If this requirement is not met, the fundamental light appears via higher orders on the CCD2 chip at

1Components with very flat transmission spectra, i.e. mostly wavelength independent, as the aluminum mirrors for example, are not taken into account since they reduce transmission - if at all significantly - only spectrally uniform.
around a wavelength of 400 nm. However, most filters that block the IR light from a wavelength of 800 nm upwards unfortunately also shut down in the blue and UV range, thus hindering the THG. A thick HA03 color glass (actually a heat absorber) is the best compromise, since interference filters with dielectric layers do not span more than one octave with their transmission range. Unfortunately, color glasses do not feature sharp cut-off edges as interference filters (compare to the SP842 short pass used in the spectroscopy setup, in panel (a) turquoise). Yet a custom-tailored thicker version of the HA03 serves as a good alternative, since the THG signal is strong enough even for further reduced transmission. The grating in the monochromator (GM) is substituted by another one blazed for a wavelength of 300 nm with 300 grooves/mm (blue), thus giving additionally higher spectral resolution. This limits the total width of the detection range in contrast to the 150-grooves/mm-grating\(^2\) (blazed for a wavelength of 500 nm) previously used, see Fig. 7.3 (a), but as an advantage shifts it right over the THG spectrum, see Fig. 7.3 (b). The CCD2 chip (green) is the same as before, since it does not limit the detection range severely.

### 7.2 Time measurement on the femtosecond scale

The analysis of physical effects on ultrafast timescales via FROG and IFROG as performed for this work relies in principle on the instantaneous response of the nonlinear medium employed in the specific scheme [Tre93, DeL95]. The light-matter interaction of the ultrashort NIR laser pulses with metallic nanostructures, however, is mediated via plasmons and the focus of the investigations presented here lies specifically on the thereby induced retardation. In order to estimate the corresponding time scales of the retardation, for example by extracting the plasmonic dephasing time \(T_2\), see Sec. 2.3, it is therefore necessary to compare the retarded reaction with an instantaneous response. This has been done before with THG from the glass substrate, which is not mediated plasmonically [Han09, Han11] or with separate FROG or IFROG measurements at a nonlinear crystal [And10]. The substrate signal however is weak, so here another approach is used: the reconstruction from the THG IFROG spectrograms yields the retarded response \(E_{\text{ret}}(t)\) which is compared to the separately determined fundamental laser pulses \(E_{\text{exc}}(t)\) such that the retarding response function \(R(t)\) can be extracted, fulfilling \(E_{\text{pl}}(t) = E_{\text{ret}}(t)\) with \(E_{\text{ret}} = E_{\text{exc}}(t) \ast R(t)\). Ideally, no assumptions about \(R(t)\) have to be made and the full response function is retrieved as in [And10]. As a first approach however, one can assume a single sided exponential decay for the retardation \(R(t \geq 0) = \exp(-t/T_2)\) and thus account for the damped harmonic oscillator model with Lorentzian lineshape, see Sec. 2.3. This yields the following scheme:

**IAC analysis**, details in Sec. 7.3:

The measured IFROG spectrograms acquired from the antenna THG are filtered as explained

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\(^2\)This is necessary to detect the broad PL completely with the spectroscopy setup tuned for the full visible range.
in Sec. 3.5.3 and the corresponding THG autocorrelation $IAC_{pl} = I_{THAC}^{TH}(t_d)$ is extracted$^3$. The fundamental laser excitation $E_{exc}(t)$ is measured via instantaneous SHG FROG, so that the THG IAC of the retarded excitation $E_{ret} = E_{exc}(t) \ast R(t)$ can be calculated ($IAC_{ret}$) and compared to the one from the antenna $IAC_{pl}$.

Since this requires some assumptions about $R(t)$ and furthermore reduces the information contained in the full spectrograms, it is better to reconstruct the retarded response directly from the complete trace. This is more complex but can be done with the DE algorithm described in Sec. 3.5.3, according to the following scheme:

**Full reconstruction**, details in Sec. 7.4:
The fringed IFROG traces are taken as acquired, except that they are corrected with the transmission spectrum. No filtering is applied, since the DE algorithm [Hyy17a, Hyy17b] is able to reconstruct the original electric field directly. In this case, the underlying pulse is the retarded one, so $E_{ret} = E_{exc}(t) \ast R(t)$ would be retrieved. However, a sophisticated adaption is made: $E_{exc}(t)$ is taken from the independently measured SHG FROG trace and entered via the convolution in the algorithm as well, so that $R(t)$ is retrieved by the algorithm. This strategy has the advantage, that no assumptions regarding the form of $R(t)$ are required and a general complex function $R(t) : \mathbb{R} \rightarrow \mathbb{C}$ is assumed. Thereby, details about the phase change during the retardation can be extracted directly.

7.2.1 Technical parameters

To resolve the dynamics of the plasmon excited in the nanostructure, the resolution needs to be on the sub-femtosecond scale. So for the phase retrieval from reconstructed IFROG spectrograms not only the full coverage of the spectral range is important, but also certain requirements according to the temporal resolution need to be fulfilled [AR04, Sti05]. An estimation of the Nyquist frequency and the corresponding limit determine which parameters guarantee that sufficient information is contained in the spectrograms.

For the presented experiments, the step size of the delay stage in the IFROG interferometer is set to 50 nm, which is added twice per round trip to the optical path through the length-adjustable interferometer arm. This corresponds to a temporal retardation of 0.67 fs per delay step. The total delay range is set to $\pm 10 \text{ \mu m}$, i.e. $\pm 67$ fs. So for a THG wavelength of $\lambda = 400$ nm, an optical cycle takes $T = c/\lambda = 1330$ as, which is sampled twice with the 670-as-step size. According to the sampling theorem by Nyquist and Shannon this is sufficient. The integration time for each spectrum is set to 300 ms. To minimize influences by drift of setup components or of the nanostructure in and out of the laser focus, the overall measurement time is optimized.

$^3$As mentioned previously, it is not possible to reconstruct the original electric field from the filtered trace since it can not be reduced to a common THG FROG: chirp in the pulses denies the reversal of the time axis [Pol10]. Details are explained in Sec. 3.5.3.
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Figure 7.4: SEM micrographs of three typical prototypes as used in the experiments: (a) a polycrystalline gold bowtie with broad base, as well as a slim one (b) and its monocrystalline equivalent (c).

with a new control and automation of the delay and sample stages, so that basically only the time to measure all 400 spectra of one full IFROG trace is needed, only marginally more than 400 · 0.3 s = 2 minutes.

Moreover, the setup is optimized to guarantee the same optical path length for the laser pulses when sent to either the pulse duration analysis unit (SHG FROG or 2DSI, Sec. X in Fig. 7.1) or the IFROG interferometer to excite the nanostructure. Thereby, it is assured that the retrieval results for $E_{exc}(t)$ can be taken for the electric field at the position of the sample and used for comparison with the retarded pulses.

7.2.2 Parameters of the plasmonic nanostructure

The geometry of the nanostructures to study the dynamical plasmonic behavior is selected according to the specific requirements in ultrafast and highly nonlinear light-matter interaction and also with respect to their further application. The bowtie geometry combines all relevant features: an extremely high field enhancement in the gap region due to its sharp tips and coupling behavior and a broad spectral support for the ultrafast pulses due to their wide resonance (see Sec. 2.3 and 2.4). Therefore, it is also employed as plasmonic transmitter in nanocircuits as for the tunneling experiments described in [Ryb16, Ryb18], see Sec. 2.4 and 4.1. Among others, this application mainly motivates the investigation of bowtie antennas. Two types of polycrystalline bowtie structures are used for the experiments: they differ in their aperture angle, and come with aspect ratios between triangle height $h$ and base $b$ of $b/h = 1.5$ (broad) and $b/h = 0.75$ (slim), see Fig. 7.4 (a) and (b). Furthermore, the slim type is compared to its monocrystalline equivalent as shown in Fig. 7.4 (c), to investigate the influence of grain boundaries on the damping of the collective electron oscillation.

The structure size is determined with BEM simulations to be resonant to the fundamental NIR pulses at a central wavelength $\lambda_{exc}$ of around 1200 nm, see Fig. 7.2. This yields typical triangle heights of $h = 240 - 280$ nm for the slim type and $h = 200 - 240$ nm for the broad base. The thickness of the gold layer is 30 nm for the polycrystalline and 60 nm for the monocrystalline antennas.
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Figure 7.5: THG IFROG spectrograms (color-coded intensity versus frequency $\omega$ and delay time $t_d$) as acquired for a polycrystalline (a) and a monocrystalline (b) gold bowtie antenna (both with aspect ratios of $b/h = 0.75$) and the remaining contributions after Fourier filtering (c)/(d), respectively. (e)/(f) Corresponding spectrally integrated THG IAC analog, depicted as intensity over delay time $t_d$.

Typical results of acquired IFROG spectrograms are presented in Fig. 7.5 (a) and (b) for a poly- and a monocrystalline nanostructure, respectively. In the following sections their underlying plasmonic retardation is extracted, either by investigating the corresponding IAC or reconstructing the full spectrogram, as mentioned above.

7.3 Plasmonic dephasing time extracted from the third-order intensity autocorrelation

As explained in Sec. 3.5.3 it is possible to extract the THG IAC from the IFROG traces with a few filtering steps. The fringe-free autocorrelation equivalent is in the following termed $IAC_{pl}(t_d)$ for the antenna response. Fig. 7.5 illustrates this for a poly- and monocrystalline dataset: panels (a) and (b) show the interferometric THG intensity traces as acquired in the experiment, panel (c) and (d) the respective fringe-filtered spectrograms and panel (e) and (f) their respective time marginal $IAC_{pl}$, i.e. the integration over the frequency axis of the filtered spectrograms. The THG IACs are shifted with their center of mass peak (evaluated for values above 50% of the maximal intensity) to $t_d = 0$ delay time.

As a comparison, Eq. 3.5.15 $IAC = I_{IAC}^{TH}(t_d) = \int[I(t) \otimes I^2(t)](t_d) + [I^2(t) \otimes I(t)](t_d)$ with the intensity $I(t) = |E(t)|^2$ of an electric field $E(t)$ allows calculating the expected result from the
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Figure 7.6: Analysis of the THG IAC (spectrally integrated intensity over delay time $t_d$) for a polycrystalline gold bowtie with broad base (a) as well as for a slim one (b) and its monocrystalline equivalent (c). The red graphs depict the autocorrelation $IAC_{pl}$ extracted from the THG IFROG spectrograms (see Fig. 7.5 and Sec. 3.5.3). They are compared to the most suitable calculated THG IAC from the retarded excitation $IAC_{ret}$ (dark blue). The undelayed and therefore narrower calculated THG IAC $IAC_{exc}$ response from the the plain excitation is also shown (blue - - -). The vertical green lines mark the boundaries within which the RMS error is minimized to determine the plasmonic dephasing time $T_2$.

Retarded fundamental laser excitation by inserting $E(t) = E_{ret}(t) = E_{exc}(t) \ast R(t, T_2)$:

$$IAC_{ret}(t_d, T_2) = |E_{exc} \ast R|^2 \otimes |E_{exc} \ast R|^4 + |E_{exc} \ast R|^4 \otimes |E_{exc} \ast R|^2.$$  

(7.3.1)

To account for the damped harmonic oscillator model, a single-sided exponential decay is assumed for the retardation function $R(t)$:

$$R(t, T_2) = \begin{cases} 0 & \text{if } t < 0 \\ e^{-\frac{t}{T_2}} & \text{if } t \geq 0 \end{cases}$$  

(7.3.2)

In order to find the most suitable time constant $T_2$, the root means square error (RMS) of the difference is minimized: $T_2 = \text{argmin}\{\text{RMS}(IAC_{pl} - IAC_{ret}(T_2))\}$. This is done on a delay time interval of $t_d = \pm 8$ fs. Outside, the THG signal is too low for reliable analysis.

Figure 7.6 presents the results for a typical prototype of each sample geometry: polycrystalline with broad (a) and slim (b) base, as well as a monocrystalline bowtie (c). Every panel contains the measured $IAC_{pl}$ from the respective antenna (red) and the retarded response $IAC_{ret}$ (blue) calculated from the fundamental pulse $E_{exc}(t)$ convoluted with $R(t, T_2)$ for the dephasing time $T_2$ that yielded the minimum RMS error. For comparison, the undelayed response $IAC_{exc}$ from the fundamental light is also shown (light blue - - -). The green dashed lines border the region where the RMS error is evaluated. As can be seen from the given data, outside of the RMS boundary the satellite structure is not reconstructed very well by the calculated IAC. This hints to a different from exponential behavior of $R(t)$ for larger delay times $t_d$. Details are revealed in the next section.
Figure 7.7: Dephasing time $T_2$ averaged over all measurements of each structure type (indicated at the right broad and slim polycrystalline bowtie, as well as monocrystalline bowtie). The bars indicate the standard deviation. The dephasing times of the three specific prototypes from Fig. 7.6 are marked red and the respective results determined with the full IFROG reconstruction green (details in the next section).

Measurements as shown for the three prototypes in Fig. 7.6 have been done several times for many antennas of each geometry. The average$^4$ dephasing times $T_2$ are given with the corresponding standard deviation in Fig. 7.7 (blue). The results of the specific datasets presented in Fig. 7.6 are marked red. All results range between $T_2 = 1$ and $T_2 = 6$ fs approximately, in accordance with former studies$^5$ or slightly shorter in the polycrystalline case [Lam99, Sön02, Han09, And10, Han11, Bos13, Kra16].

Determining the dephasing time $T_2$ by minimizing the RMS error of the fit is done with a resolution of 0.1 fs. However, as the standard deviation from the statistical analysis including all measurements indicates, the uncertainty in the dephasing time is at least about ±1 fs. In addition, the fitting depends on the entered excitation field $E_{exc}$, which is retrieved from the SHG FROG. Other possible reconstructions with the FROG algorithm yield slightly different pulse shapes, changing the pulse duration of $E_{exc}(t)$ by ±0.1 fs. Entering these in the fitting process may shift the results of the dephasing time by up to ±0.5 fs. Nonetheless, some trends are observable: monocrystalline structures exhibit in general a longer dephasing time than their polycrystalline counterparts, despite their larger volume.

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$^4$First, the $T_2$ results from repeated measurements at one specific structure (2-5) are reciprocally weighted with their RMS error and averaged. Then these results for all measurements of one structure type (15-20) are averaged. The number of single measurements at one antenna serves as weight.

$^5$Due to the dependence on size, shape, plasmonic resonance, excitation, material and technical influences, it is crucial to carefully check the used parameters of the study. Additionally one should make sure, whether the dephasing time $T_2$ (corresponding to the decay in terms of field) or the decay time $\tau = T_2/2$ in terms of energy is stated.
7.4 Retrieval of the full plasmonic response

Now the full retrieval of the retarded field $E_{pl}(t)$ is extracted with the DE algorithm as described before. Fig. 7.8 shows in panel (a) and (b) the measured THG IFROG trace for a polycrystalline and a monocrystalline nanoantenna, and in panel (c) and (d) exemplarily reconstructed traces. 10 runs of the algorithm are performed, yielding slightly different retarded pulse shapes, as demonstrated by the lines in panel (e) and (f). The retrieved phase is displayed only as the shaded area between the upper and lower boundaries of all runs combined. For further analysis, the mean of the 10 reconstructions is taken.

For these averaged retarded pulses, a deconvolution can be done in reverse, in the sense, that some assumed retardation function $R(t,p)$ with a parameter $p$ (e.g. an exponential decay with $p = T_2$) is convolved with the incoming field $E_{exc}(t)$ known from the instantaneous SHG FROG analysis. The result is compared to the retarded field $E_{pl}$ extracted from the IFROG reconstruction and the error is minimized in dependence of the fit parameter $p$. The procedure is in principle similar to the analysis in the preceding section, but thanks to the superior DE algorithm and especially our project partners who implemented it, the detour via the IAC can be circumvented. Thus, now it is legitimate to use a broader fit area ranging from $t_p = -10$ fs to
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Figure 7.9: Excitation pulse (blue - - - ) retarded with a single exponential decay (convolution: dark blue —) to fit the antenna response (red) for a polycrystalline bowtie with broad base (a) as well as for a slim one (b) and its monocrystalline equivalent (c). Depicted is intensity versus time. The vertical green lines mark the range relevant for the fit to determine the plasmonic dephasing time $T_2$. Data courtesy of Janne Hyyti.

$t_p = 15$ fs instead of only the area between $\pm 8$ fs. For the three prototype datasets highlighted in Fig. 7.6 the results based on the full reconstruction are depicted in Fig. 7.9.

The red line marks the averaged pulse intensity retrieved from 10 reconstructions from the raw THG IFROG trace, while the light blue line represents the incoming pulse as measured with SHG FROG. The convolution $E_{ret}(t) = E_{exc}(t) \ast R(t)$ with $R(t)$ a single-sided exponential decay (see Eq. 7.3.2) is depicted in dark blue by its envelope intensity.

The resulting dephasing times are shorter than from the less accurate IAC analysis in the previous section, where the same prototypes were analyzed. A reason for the lower values might stem from the SHG FROG evaluation: another retrieval for $E_{exc}$ than the one used for the IAC analysis was applied. Although various retrievals differ only marginally, the minor changes still have rather strong influence of up to $\pm 0.5$ fs change in $T_2$, as mentioned in the previous section. Taking this into account decreases the difference. Still, the values are lower with the full reconstruction approach. Yet the difference between the monocrystalline and polycrystalline antennas remains: the grain boundaries in the polycrystalline material seem to cause faster dephasing, since they hinder the collective oscillation.

In principle, an alternative to the comparison of the “by hand” retarded original pulse with the plasmonic response via a fitting process exists. It involves a transformation to the Fourier space, as demonstrated in [And10], in order to circumvent the mathematically not unambiguously defined deconvolution. With the Fourier transform of the convolution $E_{ret}(t) = E_{exc}(t) \ast R(t)$ and known $E_{exc}(t)$, the problem is transferred to resolving a product $E_{ret}(\omega) = E_{exc}(\omega)R(\omega)$ in the frequency domain followed by an inverse Fourier transform of the result. Unfortunately, this is a dangerous process, because $R(\omega)$ may become zero or at least extremely small, at least at the edges. This causes additional numerical problems, apart from the general difficulties with numerical artifacts in Fourier transformations. Thus, the procedure to retrieve an unknown convolution function $R(t)$, which is not necessarily well defined in the first place, by Fourier
transformation should be handled with care. Yet, tests with the Fourier analysis by Janne Hyyti lead to promising results: firstly, the spectral lineshape reproduces not only the Lorentzian in terms of intensity, but also the characteristic phase jump by $\pi$ at the resonance. Secondly, the spectral position of the resonance revealed in the Fourier space is in perfect accordance with the antenna resonance peak predicted by the BEM simulations. The difference is a shift of only about 20 nm [Hyy18]. Furthermore, also the timescales found with the Fourier analysis reflect very well the short dephasing times of only 2 - 3 fs for polycrystalline bowties and the ones a bit longer (3 - 4 fs) for monocrystalline antennas. A more detailed report on the Fourier analysis is in progress.

Furthermore, another approach to retrieve the full plasmonic retardation function $R(t)$ is to be finalized at the moment: as aforementioned, $R(t)$ can enter directly in the DE algorithm, included in the convolution $E_{\text{exc}}(t) \ast R(t)$ with the previously determined $E_{\text{exc}}(t)$. Thereby, $R(t)$ is retrieved immediately. However, for reliable results it is necessary to improve the parameter adjustment, as momentarily the algorithm is too easily confused by the satellite pulses. First results point to an exponentially decaying behavior at least for extremely short times of $\pm 2$ fs. Towards longer timescales, other components seem to influence the decay. Further details on the parameters and progress can be found in [Hyy18].

### 7.5 Discussion and outlook

As the data analysis of the full reconstruction is still in progress, only the “classical approach” is discussed for now. The statistical evaluation based on the harmonic oscillator model yields extremely short dephasing times for the investigated bowtie structures. With either method, $T_2$ is determined to be as short as 2 - 3 fs approximately for polycrystalline devices. A clear trend for monocrystalline bowties towards $T_2 = 3 - 4$ fs is observed. This confirms the expectation of longer dephasing times for single crystal structures [Kut08, Che10, Sch12], as there no grain boundaries hinder the collective charge carrier oscillation in addition to the strong radiation damping. So far, most studies ignore to test monocrystalline material experimentally. Nishiyama et al. actually find the contrary behavior with their comparison between nanorods of both types: the polycrystalline rods in their study exhibit longer dephasing times. However, the authors admit that the results for the single crystal structures might be influenced by a surfactant adhered to the particle surface.

The exact geometry of the nanostructures seems to influence the dephasing behavior, too, as the bowties with broader base yield slightly different results. One could speculate if multimode oscillations in the broader base cause the deviation. The present data is not very expressive, however.

Also for the full reconstruction, future experiments should target further datasets, especially with regard to noise reduction. The retrievals performed so far strongly hint that this improves the algorithm performance sufficiently to extract the complex retardation function $R(t)$ in a direct
approach. This gives insight in its exact shape, free of any model influence. Moreover, with access to the full phase information the response function can be examined towards the behavior of the phase jump due to delayed response between driving field and plasmon oscillation. To improve the comparison to the instantaneous behavior, future measurements will be redesigned to directly detect the incident electric field at the sample location and also in a third-order nonlinear process.
8 Summary and Outlook

The focus of this thesis lay on the investigation of light-matter interaction in plasmonic nanostructures: Upon excitation with ultrashort pulses in the near infrared regime (NIR), nonlinear optical effects such as third harmonic generation (THG) and multi-photon photoluminescence (MPPL) could be driven and detected in the visible range. All experiments were performed at single gold nanoantennas.

To accomplish the proposed investigations, several experimental challenges had to be mastered. Combining ultrafast optics with nanoscaled plasmonic transmitters demands a four-dimensional confinement of electromagnetic waves. Therefore, nanostructures of different geometry, such as rods and bowties, were custom-tailored to conform to the various requirements. High-resolution electron beam lithography was applied to produce polycrystalline gold nanoantennas, while a novel concept was developed to extent the scope to equivalent structures made from single crystals. The scheme is based on a combination of a wet-chemical process to grow extremely thin monocrystalline gold microplates and focused ion beam-milling (FIB) of the nanostructures with highly resolved edges. The growth of the single crystal plates was optimized, increasing their area significantly while conserving the smooth surface and a moderate thickness. The structuring procedure with the FIB could be refined until exceptionally sharp tips and feed gaps of only 8 nm were feasible. Both methods enable full control over the size parameters. Consequently, tuning of the plasmonic resonance is possible. To optimize the conformity with the adjustable excitation wavelength, computer simulations based on boundary element method (BEM) support the fabrication. The complete process was performed in-house, together with the plasmonic experiments in the optical setup and the subsequent data analysis.

The setup to investigate the plasmonic and nonlinear optical response is based on an Er:fiber-laser system with a spectral detection unit, which was optimized for the respective experiments. The broad laser spectrum, generated in a nonlinear fiber, was either compressed over its full spectral range to yield ultrashort pulses with a duration of only 7 fs. Alternatively, the broad spectrum was exploited to tune the central wavelength of the excitation from 900 nm to 2000 nm.

The technical challenges included the excitation of the gold nanostructures at extremely high peak intensities, without damaging the plasmonic transmitter. The high intensities then allowed to drive nonlinear optical effects. The signal strength was strong enough to be detected spectrally resolved, thanks to the efficient excitation and high field enhancement in the well defined structures. The nonlinear response could thus be separated in coherent THG and incoherent photoluminescence, revealing the spectral substructure of the latter and its differences for mono- and polycrystalline emitters. While the peaks in the MPPL spectrum have been reported before, they have been attributed erroneously to particular interband transitions and thus declared as an intrinsic feature of the gold band structure. However, the
polarization analysis of the response in combination with a comparison of polycrystalline and monocrystalline gold revealed clearly, that the external antenna geometry together with the internal crystal structure cause the spectral landscape of the photoluminescence [Kni15]. This finding is additionally supported by BEM simulations: the photoluminescence peaks correspond to different plasmonic resonances instead of effects inherent to the gold band structure.

The dependence on crystallinity affects only the spectral shape of the nonlinear response. The mechanism behind the MPPL, a cascaded absorption of several photons via intra- and interband transitions, is not influenced by the grain structure. Instead, it is fully governed by intrinsic material properties, as could be experimentally demonstrated. The key to this result was a detailed analysis of the overall nonlinear order, giving deeper insight into the involved processes in general. The efficient excitation of the plasmons and subsequent detection of the optical response generated strong photoluminescence over the full visible range, enabling a spectrally resolved investigation of the nonlinear order. In contrast to former studies targeting only the integrated emission, it could be shown that the number of absorbed photons increases significantly with the emission energy: up to 6 NIR photons are necessary to generate short-wavelength photoluminescence down to the very edge of the visible regime [Kni17]. This corresponds to a Stokes shift of up to 0.6 eV: energy lost in the cascade of overlapping photon absorptions.

Not only the nonlinear response was spectrally resolved for the experiments in this thesis. Moreover, the broad tunability of the laser system was exploited to investigate the spectral dependence on the excitation. The concurrent occurrence of THG and MPPL thereby enabled to directly link this spectral dependence to the dispersion of the fundamental origin of the two distinct effects: the nonlinear susceptibility of the gold. By separately investigating the coherent and incoherent contribution generated at the very same nanoemitter, it was possible to circumvent the undetermined influence of the field enhancement, which normally prevents direct access to the nonlinear susceptibility. The separation into THG and MPPL revealed a strong increase of THG towards excitation at higher energy. The opposite trend was observed for the photoluminescence, yet not so distinct. While the latter conforms to the expectation, simply because the volume of the plasmonic transmitter increases for devices resonant at longer wavelengths, the behavior of the THG requires a more sophisticated explanation: the interband contribution to the third order susceptibility becomes resonantly enhanced the closer the excitation approaches the “band gap” energy, so that free states are available to additionally support the THG. This utilization of MPPL and THG highlights once more the immense importance of a full understanding of both effects and their dependencies, not only for advanced applications but also in terms of fundamental physical aspects.

To complete this goal and derive a comprehensive representation of the plasmonic response, the investigation was expanded towards the subcycle temporal regime. With interferometric frequency resolved optical gating (IFROG), the ultrashort laser pulses could be employed to examine the plasmonic decay behavior. The setup was therefore equipped with an autocorrelator to excite the nanosstructures with delayed copies of the laser pulses at high
temporal resolution and the detection unit was optimized to record the complete third harmonic spectrum at every delay step. This is crucial since the aim of the investigation is to determine the full plasmonic response by direct reconstruction of the IFROG spectrograms. The therefore necessary algorithm is based on a differential evolution (DE) scheme and provided by Prof. Dr. Günther Steinmeyer and M.Sc. Janne Hyyti from the Max-Born-Institute. It requires all spectral components and a high temporal resolution. Both were achieved with the setup adaption. The plasmonic dephasing time was then determined in gold bowtie nanostructures to be on the order of 2 - 3 fs. This proves the bowtie antenna to be an exquisite transmitter to be embedded in nanocircuits for tunneling experiments [Ryb16]: the short plasmonic dephasing time preserves the necessary ultrashort optical pulse structure under excitation. Furthermore, it was demonstrated that monocrystalline structures tend to have longer dephasing times of 3 - 4 fs. This supports the thesis that the collective electron oscillation is indeed less restricted by structure-internal grain boundaries [Kni18].

At the moment, the analysis of the full reconstruction with the DE algorithm is still in progress as it requires a careful handling of all relevant parameters, especially for noise-afflicted measurements. The quality of the recorded spectrograms was sufficient for a full reconstruction, yet the determination of the temporal decay behavior was still based on the dephasing time in a damped harmonic oscillator model. In a next step, deconvolution of the plasmonic retardation function and the laser excitation directly during the IFROG reconstruction progress is targeted. This could explicitly validate the exponential decay of the plasmons in gold nanostructure or even reveal different behavior on extremely short timescales.

In summary, the combination of simulations and experiments in 4-dimensional confinement at guaranteed high temporal and spectral resolution led to the results presented in this thesis, which were able to give deeper insight into the interaction of ultrashort light pulses with custom-tailored plasmonic nanostructures. The involved nonlinear processes are now better understood and the new conclusions lead to full control of the optical response, thereby giving access to new possibilities in plasmonic applications and further progress in fundamental physics.
9 Zusammenfassung

Der Schwerpunkt dieser Arbeit lag auf der Erforschung der Wechselwirkung von Licht mit plasmonischen Nanostrukturen. Durch Anregung mit ultrakurzen Laserimpulsen im nahen Infrarotbereich (engl.: near infrared, NIR) konnten nichtlineare optische Effekte wie die Generation der dritten Harmonischen (engl.: third harmonic generation, THG) sowie Multi-Photonen-Photolumineszenz (MPPL) im sichtbaren Spektralbereich angeregt und detektiert werden.


Beide Methoden ermöglichten die volle Kontrolle über alle Größenparameter, wodurch die plasmonische Resonanz beliebig im nahinfraroten Spektralbereich einstellbar war. Für eine möglichst gute Anpassung an die durchstimmbare Anregungswellenlänge wurden die konkreten Parameter prozessbegleitend durch Computersimulationen auf Basis der Rändelementmethode (engl.: boundary element method, BEM) bestimmt. Der gesamte Herstellungsprozess wurde, ebenso wie die plasmonischen Experimente im optischen Aufbau, mit der vor Ort verfügbaren Laborausstattung durchgeführt.

Der experimentelle Aufbau zur Untersuchung der nichtlinearen optischen Antwort der Goldnanoantennen basiert auf einem Erbium-dotierten Femtosekunden-Faserlasersystem mit Impulskompressionseinheit und angeschlossener spektraler Detektion, jeweils optimiert für die verschiedenen Experimente. Das breite Laserspektrum wurde in einer hoch nichtlinearen Glasmatrix erzeugt und über die gesamte spektrale Bandbreite komprimiert. Damit standen ultrakurze Lichtimpulse von nur 7 fs Dauer zur Verfügung. Alternativ diente die enorme Breite
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des Spektrums dazu, die Zentralwellenlänge des anregenden Lichts von 900 nm bis 2000 nm durchzustimmen.

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Selected contributions to international conferences


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