Charge-Carrier Dynamics in Solids and Gases Observed by Time-Resolved Terahertz Spectroscopy

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Tobias Kampfrath

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Erstgutachter: Prof. Dr. Martin Wolf
Zweitgutachter: Prof. Dr. Rolf Diller
Drittgutachter: Prof. Dr. Thomas Elsässer

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Introduction

Why Charge-Carrier Dynamics Are so Interesting

Besides the fundamental significance, knowledge of the dynamics of charge carriers in matter is extremely important for technological applications. The manner in which electrons relax their energy and their average velocity by interaction with their surroundings crucially influences the performance of, for instance, electronic circuits [Int05], solar cells [Hen05], and insulating gases [Chr00].

Electronic devices, for example, have to become smaller, faster, and cheaper. Moore’s law roughly predicts that the number of transistors on an integrated circuit chip doubles every 18 months. At present, this development has led to silicon-based field-effect transistors with linear dimensions of about 50 nm [Int05]. Further miniaturization requires a higher conductivity to reduce the size of the conducting channels and a higher electron density to keep the screening length of the gate electric fields below the transistor dimensions [Rot04]. In addition, a smaller size implies a lower capacitance and thus permits higher clock frequencies. Possible alternatives to traditional semiconductors like Si and Ge include carbon nanotubes [Rot04] and thin graphite films [Nov04] as base materials for smaller and faster electronic devices.

In view of their technological potential in future electronics and due to their close relationship to each other, the charge-carrier dynamics in carbon nanotubes and graphite are investigated in this work by time-resolved THz spectroscopy: The sample is excited by an ultrashort visible laser pulse and, after some temporal delay, probed by a THz pulse which is particularly sensitive to the charge carriers as detailed below.

Charge-carrier dynamics not only play a major role in solids; they are also important in gases, for example in insulating gases inside high-voltage equipment. Here, highly mobile electrons have to be quenched very efficiently before they start to generate sparks and short-circuits by avalanche ionization of gas molecules. SF$_6$ is used as an insulating gas in such facilities because of its large cross section for electron capture [Chr00].

In this work, THz pulses are used to probe the decay and the velocity relaxation of quasifree electrons in optically ionized gases such as O$_2$, Ar, and SF$_6$.
Introduction

Why THz Radiation Is so Sensitive to Charge Carriers

The electronic conductivity of a material is dominated by the free and weakly bound electrons, that is, by charge carriers with low excitation energies. Therefore, THz radiation is particularly sensitive to these carriers because of its low photon energy $\hbar \omega$ of, for instance, 4.1 meV for a frequency of $\omega/2\pi = 1$ THz. In contrast, the response to visible light with photon energies of $\sim 1$ eV is dominated by electronic transitions of higher energy. Thus, visible light mainly probes carriers which do not contribute to the transport properties in the steady state.

The sensitivity of THz radiation to low-energy excitations is illustrated by the following examples:

- In a single-particle picture, the conductivity of a solid is due to the “free” electrons and holes near the Fermi energy. THz radiation with its low photon energy probes electronic transitions close to this range, whereas visible light also accesses electrons much further below the Fermi edge, which are usually “frozen” [Bea02].

- Bound electron-hole pairs (excitons) in semiconductors like GaAs have binding energies from about 10 to 100 meV [Mad78]. THz radiation can probe the internal excitations of excitons and thus quantify their population [Hub05a]. Due to the discrete nature of the lower-lying excitonic states THz radiation can distinguish between the response of excitons and free charge carriers.

Other interesting excitations also lie in the THz-range, including molecular vibrations, phonons, and magnons.

THz Spectroscopy

Despite its importance, THz radiation was not easily available as a spectroscopic probe until 15 years ago due to a lack of powerful THz sources and suitable detectors [Bea02]. As a consequence of the low THz power, the probing THz radiation arriving at the He-cooled bolometer is completely overwhelmed by the black-body radiation of the surrounding. Note that at a temperature of 300 K and according to Wien’s law, the black-body radiation has its intensity maximum at 17 THz.

Alternative radiation sources to bridge the so-called “THz gap” in the electromagnetic spectrum are CO$_2$ and other molecule-based lasers which, however, lack frequency tunability [Bea02]. The quantum-cascade laser is still under development and does not produce short THz pulses which are required for a good temporal resolution in pump-probe experiments [Lab05]. Free-electron lasers (FEL) like FELBE located near Dresden (Germany) produce THz pulses with picosecond duration, but such devices are large and expensive. Moreover, the synchronization with pump pulses from a femtosecond laser is complicated due to a temporal jitter between the FEL and the visible femtosecond pulses [Ros05].
Fortunately, the availability of femtosecond laser pulses has led to the development of so-called THz time-domain spectroscopy or, shorter, THz spectroscopy (TS) which offers the following key features:

- Femtosecond laser pulses are employed to generate short THz pulses which extend over only a few oscillation cycles of the electric field. As a consequence, these pulses have an extremely large bandwidth comparable to the pulse center frequency. For example, the THz pulses used in this work are generated by 10-fs laser pulses, extend from about 10 to 30 THz, and have a duration as short as 100 fs. More “traditional” THz spectroscopy operates at around 1 THz with pulses of about 1 ps in duration.

- Femtosecond laser pulses are used as an ultrashort temporal gate to detect the electric field of the THz pulses rather than spectral intensities without phase information.

These features lead to important applications:

- The detection of the electric field enables the measurement of the complex dielectric function of a sample. Conventional spectroscopy detects only the spectral intensity and has to make problematic use of the Kramers-Kronig relations in order to extract the dielectric function. The knowledge of the dielectric function is, for example, crucial for the identification of the optical gap in the THz response of superconducting MgB$_2$ [Kai02].

- Moreover, the THz field emitted by an optically excited sample can be measured. Such THz emission spectroscopy has given important information on the acceleration of electrons in high electric fields [Lei99b] and the charge transfer in optically excited molecules [Bea02].

- Short THz pulses are useful probes in pump-probe experiments where the sample is excited by a visible pump pulse and probed by a temporally delayed THz pulse. By means of this time-resolved THz spectroscopy (TRTS), the temporal evolution of the dielectric function of the excited sample can be monitored. TRTS has been successfully employed to obtain new and important information on the charge dynamics in semiconductors [Hub01], insulators [Sha03], and nonpolar liquids [Kno01].

**This Thesis**

In this work, THz spectroscopy is the experimental method of choice to investigate the charge-carrier dynamics in optically excited graphite and carbon nanotubes, and in several optically ionized gases. This thesis will deal with the following issues:

- Graphite is the prototype of a semimetal and exhibits a very small Fermi surface compared to metals like Al. As a consequence, electrons can only be scattered by
**Introduction**

Phonons from a quite restricted subset of wavevectors. Does this imply a slow energy transfer from the optically excited electrons to the graphite lattice? Or is this restriction compensated for by the high quantum energies of the optical phonons? How do these phonons influence the Drude collision rate of the electrons?

- Carbon nanotubes are hollow cylinders made of carbon atoms. Depending on their geometrical structure, carbon nanotubes are purely metallic, or exhibit an electronic energy gap around 1 eV or 20 meV. Does the optical excitation generate excitons or free charge carriers in the tubes with the large energy gaps? How do the excited electrons relax in the tubes with the small energy gaps? Can THz radiation detect the spatial localization of charge carriers in the nanotubes?

- Gases become conducting upon optical ionization due to the generation of quasifree electrons. How “hot” are these electrons? How are they captured in a monatomic gas like Ar and a molecular gas like O\(_2\)? Does the electron scavenger SF\(_6\) really accelerate the electron decay? Which mechanisms dominate the relaxation of an electronic current in these plasmas?

In order to obtain answers to these questions, certain experimental and analytical efforts were necessary. These include the construction of two THz spectrometers driven by either a femtosecond oscillator or by an amplified femtosecond laser system. The latter was imperative to optically ionize gases and probe the resulting plasma with THz pulses. Data analysis included a thorough description of the THz-wave propagation through the excited sample. Finally, in order to achieve a microscopic understanding of several experimental results, modeling based on linear-response theory and the 2-temperature model was required.
1. Theoretical Background

This chapter provides the background to interpret the dielectric function which is the quantity measured in THz spectroscopy. After an overview of the dynamics of charge carriers in optically excited metals, a model Hamiltonian describing a crystalline solid is introduced. This Hamiltonian is the basis for the rate equations governing the energy relaxation of excited electrons. Moreover, it is the starting point for a microscopic theory of the dielectric function. Finally, the case of a rapidly varying sample is discussed.

1.1. Ultrafast Processes in Optically Excited Metals

Since this work investigates the charge carrier dynamics in selected materials, it is useful to summarize the typical processes that electrons undergo after excitation by an ultrashort laser pulse. Here, the example of electrons in metals is chosen. Most of the following facts have been found by pump-probe techniques where an ultrashort laser pulse “pumps” charge carriers in the sample to excited states. The carriers are probed by a subsequent laser pulse, for instance by measuring the reflectivity of the sample or by photoemitting electrons whose kinetic energy is finally detected. The latter scheme is also called time-resolved photoelectron spectroscopy (TRPES).

The pump pulse with a duration of typically less than 100 fs and a photon energy of $\hbar \omega_{pump} \sim 1 \text{ eV}$ mainly interacts with the electrons of the system and couples their stationary quantum-mechanical states. As shown in the single-electron picture of Fig. 1.1(a), this leads to a polarization due to the superposition of single-electron eigenstates below and above the Fermi energy $\epsilon_F$.

However, due to the interaction with the other electrons and the phonons, the phases between the superimposed stationary states are randomized on a time scale of 1 to 100 fs, and the system is left in a mixed state which is completely characterized by the occupation numbers of the eigenstates. In other words, the induced polarization has decayed, and the incident pump pulse has created electrons above $\epsilon_F$ and holes below $\epsilon_F$, as illustrated in Fig. 1.1(b).

The above implies that the pump pulse energy is initially mainly deposited in the electronic system. Scattering processes exchange the energy among the excited and unexcited electrons and equilibrate to a Fermi-Dirac distribution which is characterized by an increased electronic temperature $T_e$. This electron thermalization takes place on a time scale of 10 to 1000 fs and is depicted in Fig. 1.1(c) [Hoh98].
1. Theoretical Background

![Figure 1.1: Processes induced by a fs-laser pulse arriving at a metal surface. The metal is in thermal equilibrium before excitation. (a,b,c) After generation of a coherent polarization by the laser pulse and its decay, the excited electrons exchange energy with other electrons by electron-electron scattering. This thermalization finally leads to a Fermi-Dirac distribution of temperature $T_e$. (d) Directly after excitation, the electrons start to transfer energy to the cold lattice via electron-phonon coupling. The 2-temperature model becomes valid as soon as the electrons and phonons can be described by temperatures $T_e$ and $T_{ph}$, respectively. (e) Finally, electrons and phonons arrive at the same temperature. Transport processes lead to energy dissipation in the considered volume, too.

The interaction between the lattice and the excited electrons leads to the emission of phonons and the cooling of the electrons on a time scale of 0.1 to 10 ps as seen in Fig. 1.1(d). In many cases, the resulting phonon population can be described by a Bose-Einstein distribution with phonon temperature $T_{ph}$, as for example in the 2-temperature model [Ani74]. However, this is not true in general, as shown for semiconductors [Els89] or the semimetal graphite in this work, where a non-equilibrium population of “hot phonons” is generated. The heat transfer from the electrons to the lattice fades as soon as electrons and phonons have arrived at the same temperature, $T_e = T_{ph}$, see Fig. 1.1(e).

It should be emphasized that all processes mentioned can temporally overlap. For example, the generation of phonons takes place already before the electrons have thermalized. Moreover, spatial transport processes set in from the very beginning. However, they can be neglected on these short time scales, if the pump pulse creates a homogeneously excited sample. On much longer time scales, heat diffusion leads to a cooling of the sample to the ambient temperature.

These mechanisms have important consequences in areas such as surface femtochemistry [Bon99]. For example, the hot electrons of laser-excited Ru were shown to trigger chemical reactions of adsorbed molecules that do not occur under equilibrium conditions [Bon99].

The dynamics of optically excited charge carriers in semiconductors and gases proceeds similarly to that in metals [Sha99]. Major differences concern the time scales involved and the recombination of electrons and holes which proceeds by phonon emission in metals. This is not possible in semiconductors where the phonon energies are much smaller than the band gap of $\sim 1$ eV. Instead, photon emission, Auger and other processes lead to electron-hole recombination on a time scale of typically 1 ns. Long before, electrons and
holes thermalize to individual Fermi-Dirac distributions and equilibrate with the lattice by phonon emission.

The goal of this thesis is to study the dynamics of optically excited charge carriers in solids and gases by measuring the temporal evolution of its dielectric function in the far-infrared. The following sections give the theoretical background used in this work.

### 1.2. Model Hamiltonian of a Crystalline Solid

In the single-electron approach, the electrons in a solid are thought to move within a mean potential produced by the static lattice and the other electrons [Mad78]. The translational symmetry of a perfectly crystalline solid implies the Bloch theorem which states that the eigenstates of the single-electron Hamiltonian are Bloch states

$$|K⟩ = |kB⟩.$$  

In real space, these states are plane waves modulated by the lattice-periodic Bloch factor $u_K$,

$$⟨x|K⟩ = \exp(ikx)u_K(x).$$

The quantum numbers involved are the wavevector $k$, which is restricted to the 1st Brillouin zone (BZ), and the band index $B$, which also contains the spin degree of freedom. The corresponding single-electron eigenenergies $\epsilon_K$ constitute the band structure. When we neglect spin effects like ferromagnetism and spin-orbit coupling, $\epsilon_K$ will not depend on the spin, and the Bloch states factorize into an orbital and a spin part, $|K⟩ = |kB⟩ = |kb⟩ \otimes |±⟩$ where $|±⟩$ is the electronic spin-up and spin-down state, respectively. In the following, we mainly consider the orbital part $|k⟩ := |kb⟩$.

Phonons (ph) are the energy quanta $\hbar \Omega_Q$ of the fundamental lattice vibrations $Q = (q, r)$ which are fully characterized by the phonon wavevector $q$ and the phonon branch $r$; $q$ is also restricted to the BZ.

The interaction between the lattice and the electrons can be understood as scattering an electron from state $|K⟩$ into another state $|K'⟩$,

$$|K⟩ \xrightarrow{\text{e-ph}} |K'⟩,$$

accompanied by the annihilation (+) and generation (−) of phonons $Q^± = (q^±, r)$, respectively. The matrix element $M_{K'K}^r$ of this process implies conservation of the total wavevector,

$$k' = k \pm q^± + G,$$

where a reciprocal lattice vector $G$ has to be added such that all wavevectors involved lie in the Brillouin zones. This can be abbreviated as

$$q^± = [±(k' - k)] \mod \text{BZ}.$$
So-called umklapp processes occur when $G \neq 0$.

Electrons can also be scattered by impurities (imp) described by an impurity potential $V^{\text{imp}}$. Its matrix element $V^{\text{imp}}_{K'K} = \langle K'|V^{\text{imp}}|K \rangle$ quantifies the amplitude of this scattering process $|K\rangle \xrightarrow{\text{e-imp}} |K'\rangle$.

With these definitions, the resulting model Hamiltonian of a crystalline solid can be written as \cite{Nol01, Gri81, Mad78}

$$
\hat{H} = \sum_K \epsilon_K \hat{a}_K^\dagger \hat{a}_K + \sum_Q \hbar \Omega_Q \hat{b}_Q^\dagger \hat{b}_Q + \sum_{KK'} M_{KK'}^{r} \hat{a}_{K'}^\dagger \hat{a}_K \left(\hat{b}_q^{+} + \hat{b}_q^{-}\right) + \sum_{KK'} V^{\text{imp}}_{KK'} \hat{a}_{K'}^\dagger \hat{a}_K .
$$

(1.1)

Here, $\hat{a}_K^\dagger$ and $\hat{a}_K$ are operators creating and annihilating an electron in a state $|K\rangle$, respectively, whereas the operators $\hat{b}_Q^\dagger$ and $\hat{b}_Q$ do the same in the phonon subsystem. For example, e-ph coupling can be interpreted as the annihilation of an electron in state $|K\rangle$ and its creation in a new state $|K'\rangle$. This scattering process is induced by the generation or annihilation of a phonon $(q^+, r)$ or $(q^-, r)$, respectively. The e-ph interaction is screened by the surrounding mobile electrons and lattice ions.

Electron-electron interaction is neglected here, since it is already mainly contained in the Bloch states and the band structure.

### 1.3. Population Dynamics and 2-Temperature Model

#### 1.3.1. Rate Equations

The dynamics of a solid are rigorously described by the evolution of its total density matrix which is extremely complicated to calculate for a many-body system. Therefore, the dynamics is often modeled by rate equations which only take the population of the stationary states, that is the diagonal elements of the density matrix, into account. The population then changes due to transitions between stationary states, and the transition probabilities are calculated by Fermi’s Golden Rule which implies strict conservation of energy. This is, however, not true any more on short time scales where time-energy uncertainty starts to play a role. Such effects have been observed in the energy relaxation of electrons by phonon emission in GaAs \cite{Fur96}.

Within a single-particle picture, the population is given by the occupation numbers $f_k$ and $b_Q$ of electronic Bloch states $|k\rangle$ and lattice vibrational modes $Q$, respectively. The resulting rate equation for the electronic population is \cite{Mad78, All87, Gri81}

$$
\frac{\partial f_k}{\partial t} = \sum_{k'} \left[ w_{kk'} \cdot f_{k'} \cdot (1 - f_k) - w_{kk'} \cdot f_k \cdot (1 - f_{k'}) \right]
$$

(1.2)
where the two terms describe the scattering into $|k\rangle$ and out of $|k\rangle$, respectively. The transition rates $w_{kk'}^{e\text{-}ph}$ for e-ph scattering involve both phonon generation ($-$) and annihilation ($+$),

$$w_{kk'}^{e\text{-}ph} = \frac{2\pi}{\hbar} \sum_{r,\pm} |M^r_{kk'}|^2 \left(b_{Q\pm} + \frac{1}{2} \pm \frac{1}{2}\right) \delta (\epsilon_{k'} - \epsilon_k \pm \hbar \Omega_{Q\pm}).$$  (1.3)

The annihilation rate of phonons $Q^+ = (q^+, r)$ grows linearly with their occupation number $b_{Q^+}$ whereas the generation rate is proportional to $b_{Q^-} + 1$ since also “spontaneous emission” of phonons $Q^- = (q^-, r)$ can occur for $b_{Q^-} = 0$. The $\delta$-functions enforce energy conservation in an e-ph scattering process.

Electron-impurity and e-e scattering give corresponding contributions to this rate equation [Mad78]. Especially, in case of a real (not complex) impurity potential, e-imp scattering is elastic and does not change the energy of the involved electron. In addition, the optical excitation of the metal can also be described by a term analogous to (1.3).

The rate equation for the phonon distribution $b_Q$ is very similar but with a contribution from ph-ph scattering instead of e-e scattering which originates from the anharmonic coupling between the normal lattice vibrations $Q$. It is responsible for the energy redistribution within the phonon system.

It should be noted that the rate equation (1.2) does not take transport effects into account.

### 1.3.2. 2-Temperature Model for Metals

In order to simplify the rate equations, the 2-temperature model (2TM) describes the electrons and phonons by merely 2 temperatures:

- The electrons are assumed to be thermalized at any time and thus to follow a Fermi-Dirac distribution

$$(f(\epsilon) = \frac{1}{\exp(\beta_e \epsilon - \beta_e \mu) + 1}$$  (1.4)

with temperature $T_e = 1/k_B \beta_e$ and chemical potential $\mu$. The electron occupation numbers are then $f_K = f(\epsilon_K)$. The reason for this assumption is that the e-e interaction is usually stronger than the e-ph interaction. Therefore, the electron subsystem thermalizes before the thermal equilibrium between electrons and phonons is established. As a consequence, e-e and e-imp scattering can be neglected in the rate equations.

- Similarly, the phonons are assumed to follow a Bose-Einstein distribution

$$b(\Omega) = \frac{1}{\exp(\beta_{ph} \hbar \Omega) - 1}$$  (1.5)

with temperature $T_{ph} = 1/k_B \beta_{ph}$. The phonon occupation numbers are then $b_Q = b(\Omega_Q)$. This assumption can be easily violated in semiconductors [Els89] or semimetals as shown in Chapter 4 for graphite.
1. Theoretical Background

The total energy of the electron subsystem is

\[ E_e = 2 \sum_k f_k \epsilon_k \]

where the factor of 2 is due to the spin degeneracy. Its temporal change can be calculated with the aid of Eqs. (1.2) and (1.3). Since the occupation numbers only depend on energy, \( f_k = f(\epsilon_k) \) and \( b_Q = b(\Omega_Q) \), one obtains an integral over the initial electron energy \( \epsilon \), final electron energy \( \epsilon' \), and phonon frequency \( \Omega \) [All87],

\[
\frac{\partial E_e}{\partial t} = 4\pi \int \int \int d\epsilon \, d\epsilon' \, d\Omega \, S(\epsilon, \epsilon', \Omega) \, \Omega \delta(\epsilon' - \epsilon - \hbar \Omega) \, H(\epsilon, \epsilon', \Omega) \tag{1.6}
\]

Here,

\[ S(\epsilon, \epsilon', \Omega) = [f(\epsilon) - f(\epsilon')]b(\Omega) - [1 - f(\epsilon)]f(\epsilon') \]

embraces all occupation numbers. The auxiliary function

\[ H(\epsilon, \epsilon', \Omega) = \sum_{kk'} |M_{kk'}^r|^2 \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}) \delta(\Omega - \Omega_Q) \]

is proportional to the Eliashberg function \( \alpha^2 F(\epsilon, \epsilon', \Omega) \) which contains all necessary information on e-ph interaction [Gri81, All87].

Sources of the electronic energy such as the exciting laser pulse have to be added on the right-hand side of Eq. (1.6). As mentioned before, transport effects are neglected.

Most electronic transitions of interest occur around the Fermi edge. In metals, the electronic density of states (eDOS)

\[ D(\epsilon) = 2 \sum_k \delta(\epsilon - \epsilon_k) \tag{1.7} \]

shows only small relative variations there such that \( \alpha^2 F \) is usually evaluated at \( \epsilon = \epsilon' = \epsilon_F \). However, this is not possible for the semimetal graphite where we have to take the strongly varying eDOS into account.

1.4. What Is Measured in an Optical Experiment?

The dielectric function of a sample is the central quantity that is measured in THz spectroscopy. The following sections give a definition of the dielectric function and its relation to the microscopic properties of the sample.
1.4. What Is Measured in an Optical Experiment?

1.4.1. Induced Electric Polarization

In a typical optical experiment, a light wave is incident on a sample, partially transmitted, and finally detected. Inside the sample, the electric field $E$ of the light wave modifies the charge distribution and thus induces an electric polarization $P$ or, equivalently, an electric current density

$$j_{\text{ind}} = \frac{\partial P}{\partial t}. \quad (1.8)$$

This in turn alters the total electric field $E$ and makes wave propagation in matter different from that in vacuum. Detecting the transmitted light wave therefore means measuring how easily the light field can polarize the sample or, equivalently, how easily it can induce an electric current. This ease is quantified by the so-called dielectric function and can be determined by THz spectroscopy.

Before turning to the formal relation between electric field, induced polarization, and dielectric function, it is worth mentioning the following points:

- The material response to the magnetic component of the electromagnetic field is largely negligible at THz and higher frequencies since the magnetic dipoles within the material cannot follow the fast magnetic field oscillations [Mil98]. An exception are so-called optical metamaterials. In these arrays of small LC oscillators, magnetic effects can become important at THz frequencies [Lin04].

- Most theories consider only macroscopic fields $E$ and $P$ which are the true microscopic fields averaged over a length $l_{\text{avg}}$. In this way, one gets rid of all variations on length scales much smaller than the characteristic length $l_{\text{opt}}$ of the electromagnetic wave where $l_{\text{opt}}$ can be its wavelength $\lambda$ or attenuation length. Therefore, $l_{\text{avg}}$ should be well below $l_{\text{opt}}$ but large compared to the length scale $l_{\text{mat}}$ on which the microscopic electric field varies in the unperturbed matter. In a solid one typically has $l_{\text{mat}} \sim 1$ Å and $l_{\text{opt}} \sim \lambda \sim 100$ nm at optical frequencies. In this case, the choice $l_{\text{avg}} \sim 10$ nm surely fulfills the condition $l_{\text{mat}} \ll l_{\text{avg}} \ll l_{\text{opt}}$.

1.4.2. Dielectric Function $\varepsilon$

How is $P$ related to the intrinsic properties of the sample? In general, it will depend on the electric field $E$ in a complicated manner. Fortunately, the strength $\sim e/(1\,\text{Å})^2 \sim 10^9\,\text{V cm}^{-1}$ of the microscopic fields in unperturbed matter is often much larger than $E$. In this case, $P$ can be expanded in a power series with respect to $E$,

$$P(E) = P^{(1)} + P^{(2)} + \ldots, \quad (1.9)$$

where $P^{(j)}$ is of exactly $j$th order in $E$. This series is sometimes called a Volterra series since the expansion argument is not a number but a complete function $E(x, t)$ [Gra78]. The
1. Theoretical Background

The leading term $P^{(0)}$ is zero since a vanishing macroscopic field does not induce a polarization at THz and higher frequencies. In the following we assume that $E$ induces only a spatially localized polarization $P$. In other words, $E(x, t)$ induces a coherent polarization within a radius around $x$ that is much smaller than $l_{\text{opt}}$ [Mil98]. In contrast, the polarization response is temporally nonlocal in general, that is the complete past of the electric field affects the polarization at time $t$.

In case the sample is in a steady state, one can switch from the time domain to frequency space by a Fourier transformation where the linear response becomes simply

$$P^{(1)}(x, \omega) = \chi(x, \omega)E(x, \omega). \quad (1.10)$$

The 2nd-rank tensor $\chi(x, \omega)$ is called the linear susceptibility at angular frequency $\omega$ which reduces to a scalar in a locally isotropic medium. The dielectric function $\varepsilon$, the conductivity $\sigma$, and the refractive index $n$ are often used instead of $\chi$. They contain the same amount of information and are defined in $\omega$ space by

$$\varepsilon = 1 + 4\pi\chi, \quad \sigma = -i\omega\chi = \frac{\omega}{4\pi i} (\varepsilon - 1), \quad \text{and} \quad n = \sqrt{\varepsilon},$$

respectively. $\varepsilon$ and $\chi$ will be used equally in this work. By using Eq. (1.8), the term “conductivity” becomes clear from its relation to the induced current,

$$j^{(1)}_{\text{ind}}(x, \omega) = \sigma(x, \omega)E(x, \omega).$$

The relation between the dielectric function and the microscopic structure of the sample will be discussed in the following section.

A simple macroscopic interpretation can be at least given for the imaginary part of the dielectric function: It describes how efficiently the medium can absorb light. According to Poynting’s theorem, the temporally averaged power $dP_{\text{abs}}$ absorbed from a monochromatic light wave $E(x, t) = \text{Re}[A(x) \exp(i\omega t)]$ in a volume $dV$ around point $x$ is [Röm94]

$$\frac{dP_{\text{abs}}}{dV} = \left\langle E \frac{\partial P}{\partial t} \right\rangle = \frac{1}{2} \omega |A|^2 \text{Im} \varepsilon(x, \omega),$$

where the medium is assumed to be optically isotropic. The real part of the dielectric function is connected to its imaginary part by the Kramers-Kronig relations which are a direct consequence of causality [Röm94].

Due to the knowledge of the electric field of the probing pulse, THz spectroscopy allows to measure the dielectric function of a sample, which is the ultimate goal of linear optical spectroscopy. In TRTS, the sample is excited by a pump pulse, and one can even monitor the evolution of the dielectric function as a function of the delay between pump and THz probe pulse. It is, therefore, desirable to know the relation between the dielectric function and the microscopic properties of the sample. This issue is discussed in the next sections using classical models and a more rigorous quantum-theoretical description.
1.5. Microscopic Models for $\varepsilon$

1.5.1. Classical Models

Bound Electrons: Lorentz Oscillator

In the Lorentz model, a bound particle $j$ with charge $q$ and mass $m$ is located in the minimum position of some potential. The light field $E$ acts on the charge as a small perturbation and, within the dipole approximation, leads to a harmonic oscillation $x_j(t)$ with resonance frequency $\omega_0$ and damping rate $\gamma$ around the potential minimum at $x_{0j}$. The dipole moment induced by the oscillating charge is $p_j = q \cdot (x_j - x_{0j})$, and the macroscopic polarization is the sum of all $N$ dipoles per averaging volume $V_{\text{avg}} = l_{\text{avg}}^3$ around position $x$. In $\omega$ space, this yields

$$P(x, \omega) = \frac{1}{V_{\text{avg}}} \sum_{j=1}^{N} p_j = \frac{\varepsilon_{\text{Lorentz}}}{4\pi} - \frac{1}{4\pi} E(x, \omega)$$

with the dielectric function

$$\varepsilon_{\text{Lorentz}}(\omega) = 1 + \frac{4\pi N q^2}{V_{\text{avg}} m} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}. \quad (1.11)$$

Equation (1.11) exhibits a resonance denominator such that $\text{Im} \varepsilon_{\text{Lorentz}}(\omega)$ and the absorption of light peak at $\omega = \omega_0$ in case of small damping, $\gamma \ll \omega$. Although based on classical mechanics, the Lorentz model describes the optical response of molecular vibrations and phonons quite well [Ash76].

Free Electrons: Drude Model

The Lorentz model contains also the limiting case $\omega_0 = 0$ of free or unbound electrons which yields the Drude formula

$$\varepsilon_{\text{Drude}}(\omega) = 1 - \frac{\Omega_{\text{pl}}^2}{\omega^2 + i\Gamma \omega} \quad (1.12)$$

with squared plasma frequency

$$\Omega_{\text{pl}}^2 = \frac{4\pi n_e e^2}{m_e} \quad (1.13)$$

and free-electron density $n_e$. The damping rate $\Gamma$ can be interpreted more explicitly when the damping of the electron oscillation is caused by collisions of the electron with obstacles. If each collision completely randomizes the electron velocity, $1/\Gamma$ is just the time between 2 subsequent collisions. In other words, $1/\Gamma$ is the characteristic time it takes to relax an electronic current when the driving electric field is switched off [Ash76].
1. Theoretical Background

Although the Drude formula is based on an extremely simplified model, it often provides a good phenomenological description of the optical properties of metals and doped semiconductors. As will be discussed below, it can be derived under certain assumptions from more sophisticated models.

1.5.2. Semiclassical Theory: Boltzmann Equation

In a semiclassical approach and in a spatially homogeneous system, the electrons can be described by a distribution function \( f(\mathbf{v}, t) \) where \( f(\mathbf{v}, t) \, d^3\mathbf{v} \) is the density of electrons having their velocity in the interval \([\mathbf{v}, \mathbf{v} + d\mathbf{v}]\). The dynamics of \( f \) in a homogeneous external electric field \( \mathbf{E} \) is described by the Boltzmann equation [Hol65]

\[
\frac{\partial f}{\partial t} - \frac{e}{m_e} \frac{\partial f}{\partial \mathbf{v}} \mathbf{E} = \frac{\partial f}{\partial t} \bigg|_{\text{scatt}}.
\]

The term on the right-hand side describes scattering events between the electrons and other obstacles which can change the velocity \( \mathbf{v} \) of an electron and therefore lead to a redistribution of \( f(\mathbf{v}, t) \). In case of a vanishing electric field, thermalization by electron-electron scattering results in the familiar Maxwell-Boltzmann distribution

\[
f(\mathbf{v}, t) = n_e \left( \frac{m_e}{2\pi k_B T_e} \right)^{3/2} \exp \left( -\frac{m_e \mathbf{v}^2}{2k_B T_e} \right), \tag{1.14}
\]

with electronic temperature \( T_e \).

An external electric field \( \mathbf{E} \) modifies this distribution and induces an electric current. By treating \( \mathbf{E} \) as a weak perturbation and assuming that the electrons undergo only binary collisions with much heavier obstacles such as ions or neutral particles, one can derive the dielectric function of such a system [Hol65],

\[
\varepsilon_{\text{Boltzmann}}(\omega) = 1 + \frac{(4\pi e)^2}{3m_e \omega^2} \int_0^\infty dv \frac{\partial f}{\partial \mathbf{v}} v^3 \frac{1}{\omega + i\gamma(v)}. \tag{1.15}
\]

Here,

\[
\gamma(v) = \sum_j v n_j \sigma_{ej} \tag{1.16}
\]

is the collision rate of an electron having velocity \( v = |\mathbf{v}| \) caused by scattering off all sorts \( j \) of obstacles. Each obstacle species \( j \) is characterized by a density \( n_j \) and a momentum-transfer cross section \( \sigma_{ej} \) for scattering with electrons.

Note that electrons with a velocity around a fixed value \( v \) make a Drude-like contribution to the integration in Eq. (1.15). Moreover, if the collision rate \( \gamma(v) \) does not depend on the electron velocity \( v \), one can show, that Eq. (1.15) reduces exactly to the Drude formula (1.12) with electron density \( n_e = \int d^3\mathbf{v} f \) [Hol65].
1.5. Microscopic Models for $\varepsilon$

It should be mentioned that the relation (1.15) does not account for e-e scattering. Quantum effects can be included in Eq. (1.15) by calculating the cross sections $\sigma_{ej}$ according to quantum mechanics and by using the Fermi-Dirac distribution (1.4) instead of the Maxwell-Boltzmann distribution [Mad78].

1.5.3. Quantum-Mechanical Theory: Kubo Formula

Assume that only the electrons of some system interact with a classical light wave given by the vector potential $A(x, t)$. Then, to 1st order in the light field and in Coulomb gauge, this interaction is described by the Hamiltonian [Czy04]

$$\hat{H}_{\text{e-light}} = -\frac{1}{c} \int d^3x \hat{j}(x) A(\hat{x}, t).$$

where the operator of the electronic current density

$$\hat{j}(x) = -\frac{e}{2m_e} \sum_j [\hat{\pi}_j(\hat{x} - \hat{x}_j) + \delta(\hat{x} - \hat{x}_j)\hat{\pi}_j]$$

contains position $\hat{x}_j$ and canonical momentum $\hat{\pi}_j$ of all electrons labeled $j$. Application of 1st-order perturbation theory in $\hat{H}_{\text{e-light}}$ yields the Kubo formula for the tensor of the dielectric function [Czy04],

$$\varepsilon_{Kubo}^{\alpha\beta}(\omega) = -\frac{4\pi n_e e^2}{m_e \omega^2} + \frac{4\pi}{V \omega^2} \sum_{mm'} \frac{\langle m'|\hat{j}_\alpha|m \rangle \langle m|\hat{j}_\beta|m' \rangle}{E_{m'} - E_m - \hbar\omega - i0^+ (\rho_{mm} - \rho_{m'm'})}. \tag{1.17}$$

In this expression, one has to sum over all initial and final eigenstates $|m\rangle$ and $|m'\rangle$ of the unperturbed system, respectively. Light with frequency $\omega$ is absorbed if the photon energy $\hbar\omega$ matches the difference between 2 eigenenergies $E_{m'}$ and $E_m$ and if the population $\rho_{mm}$ of the initial state exceeds the population $\rho_{m'm'}$ of the final state. The infinitesimally small positive number $0^+$ ensures that the perturbing electric field $E$ is off in the far past.

The derivation of this formula involves the dipole approximation and therefore leads to a spatially local response. It moreover neglects the off-diagonal elements $\rho_{mm'}$ of the density matrix, that is any coherences in the unperturbed system. Finally, the derivation assumes the unperturbed system to change slowly within 1 cycle $2\pi/\omega$ of the probing light field. This point will be discussed in Section 1.8.

It should be mentioned that the Kubo formula can be rewritten in terms of fluctuations of the current density which leads to a version of the fluctuation-dissipation theorem: Photon absorption is related to fluctuations of the current density in the unperturbed system [McQ76].
1. Theoretical Background

![Figure 1.2:](image)

**Figure 1.2.:** Photon absorption by *resonant* direct and indirect optical transitions of Bloch electrons. Direct transitions conserve the electron wavevector and appear as vertical arrows in the band structure. Indirect optical transitions, in contrast, involve an additional wavevector source and appear as nonvertical arrows.

1.5.4. Local Electric Field

All models for the dielectric function presented up to here tacitly assume that the total macroscopic field $\mathbf{E}$ perturbs the motion of the electrons. Strictly speaking, one has to consider the local electric field $\mathbf{E}_{\text{loc}}(\mathbf{x}, t)$ which is the total electric field acting on a charge at position $\mathbf{x}$ [Adl62].

Although the local field does generally not equal the macroscopic field one usually neglects local-field effects by setting $\mathbf{E}_{\text{loc}} = \mathbf{E}$. This can lead to significant discrepancies between modeled and calculated dielectric function [Yu99].

1.6. Optical Transitions in Crystalline Solids

In the following, the Kubo formula is considered for the Bloch electrons of a crystalline solid. As seen above, the absorption of a photon is possible by a transition $|m\rangle \rightarrow |m'\rangle$ between eigenstates of the unperturbed system. Application of the Kubo formula to the model Hamiltonian (1.1) shows, that 2 distinct classes of optical transitions $|k\rangle \rightarrow |k'\rangle$ between electronic Bloch states contribute to the linear optical response of a crystalline solid [Bas75]:

1. A *direct* optical transition (DOT) only involves the interaction between Bloch electrons and the light field; the influence of lattice imperfections is neglected. In a DOT, the electron wavevector remains nearly unchanged, $\Delta k = 0$, since the wavevector of the light field is much smaller than the linear dimensions of the BZ. Therefore, photon absorption by a DOT corresponds to a resonant *vertical* transition in the band structure as illustrated in Fig. 1.2.

2. An *indirect* optical transition (IOT) is a higher-order process since it involves the interaction between Bloch electrons, the light field, and lattice imperfections like
impurities and phonons. It generally implies changes in the electronic wavevector, $\Delta \mathbf{k} \neq 0$. Photon absorption by an IOT corresponds to a resonant nonvertical transition in the band structure as shown in Fig. 1.2.

In the following, DOTs and IOTs are explained in more detail and compared to the classical Drude model. For this purpose, the Drude formula (1.12) is linearized in $\Gamma$ resulting in

$$\varepsilon^{\text{Drude}} = 1 - \frac{\Omega_{\text{pl}}^2}{\omega^2} + i \frac{\Omega_{\text{pl}}^2}{\omega^3} \Gamma.$$  (1.18)

It will turn out that $\text{Re} \varepsilon^{\text{Drude}}$ can be assigned to direct intraband transitions (intraDOTs), whereas the dissipative part $\text{Im} \varepsilon^{\text{Drude}}$ of the Drude formula can be associated with IOTs, that is

$$\varepsilon^{\text{Drude}} = \varepsilon^{\text{intraDOT}} + i \text{Im} \varepsilon^{\text{IOT}}.$$

### 1.6.1. Direct Optical Transitions

As described above, direct optical transitions conserve the electron wavevector, and the transition is therefore

$$|b\rangle \xrightarrow{\text{photon}} |b'\rangle.$$

It is useful to separate the DOTs in interband ($b \neq b'$) and intraband ($b = b'$) transitions,

$$\varepsilon^{\text{DOT}} = \varepsilon^{\text{interDOT}} + \varepsilon^{\text{intraDOT}}.$$

The diagonal elements of the interband part are [Ped03]

$$\varepsilon^{\text{interDOT}}_{\alpha\alpha} = \frac{2 \cdot 4\pi e^2 \hbar^2}{m_e^2 V} \sum_{b'b/k \neq b/k} \frac{|\langle b'k | \hat{\mathbf{e}}_\alpha |bk \rangle|^2 (f_{b'k} - f_{bk})}{(\epsilon_{b'k} - \epsilon_{bk})^2 (\epsilon_{b'k} - \epsilon_{bk} - \hbar \omega - i0^+)}.$$  (1.19)

where $V$ is the volume of the system. The factor of 2 accounts for the electron spin which is conserved in the transitions considered due to $\langle + | - \rangle = 0$. Similar to the Kubo formula, the resonance denominator enables light absorption if the photon energy $\hbar \omega$ matches an energy difference $\epsilon_{b'b} - \epsilon_{bk}$.

If the occupation numbers depend only on the electron energy, $f_k = f(\epsilon_k)$, the intraband part of $\varepsilon^{\text{DOT}}$ is [Ped03]

$$\varepsilon^{\text{intraDOT}} = 1 + \frac{1}{\omega^2} \frac{2 \cdot 4\pi e^2}{V} \sum_k \left| \frac{\partial f}{\partial \epsilon} \right|_k \mathbf{v}_k \mathbf{v}_k$$

with $v_k$ being the band velocity

$$\mathbf{v}_k = \frac{1}{\hbar} \frac{\partial \epsilon_k}{\partial \mathbf{k}}.$$  (1.20)
1. Theoretical Background

Since an intraDOT has vanishing transition energy its contribution to the optical response is often called *free-carrier response*. It becomes appreciable for a large eDOS and large band velocities around the Fermi edge where $\partial f/\partial \epsilon \neq 0$. The intraDOTs are a nonresonant contribution, affect only the real part of the dielectric function, and result in a negative $\text{Re} \, \varepsilon_{\text{intraDOT}}$ with a typical $1/\omega^2$ dependence.

Due to these properties, intraDOTs resemble the situation of the collisionless Drude model. This becomes even more apparent for the case of quasifree electrons with effective mass $m_{\text{eff}}$ and density $n_e$. They are described by 1 parabolic band

$$\epsilon_k = \frac{\hbar^2}{2m_{\text{eff}}} k^2$$

which implies a band velocity proportional to their wavevector,

$$v_k = \frac{\hbar}{m_{\text{eff}}} k.$$  \hspace{1cm} (1.21)

Such situation occurs, for example, in several metals like Na [Ash76] or in doped semiconductors like n-GaAs or n-InAs [Els89]. Provided the band is not completely filled or empty, one obtains a scalar dielectric function $\varepsilon_{\text{intraDOT}} = 1 - 4\pi e^2 n_e / |m_{\text{eff}}| \omega^2$, just like in the collisionless Drude model.

This striking analogy and Eq. (1.18) lead to a generalized definition of the *free-carrier plasma frequency*

$$\Omega_{\text{pl}}^2 = -\frac{8\pi e^2}{V} \sum_k \partial f / \partial \epsilon_k v_k^2 = -\frac{8\pi e^2}{V} \int \text{d} \epsilon \, \frac{\partial f}{\partial \epsilon} v^2 D(\epsilon).$$  \hspace{1cm} (1.22)

Here, the velocity-weighted eDOS

$$v^2 D(\epsilon) = \sum_k v_k^2 \delta(\epsilon - \epsilon_k)$$  \hspace{1cm} (1.23)

has roughly the same spectral structure like the ordinary eDOS $D(\epsilon)$ of Eq. (1.7) [All71]. Note that $\Omega_{\text{pl}}^2$ is a 2nd-rank tensor which is diagonal in an appropriately chosen coordinate system.

Metals usually exhibit a large and nearly constant eDOS around the Fermi edge. Then one can set $\epsilon = \epsilon_F$ in Eq. (1.22), which makes the plasma frequency independent of the electron distribution $f(\epsilon)$. Assuming moreover a constant band velocity $v_{k\alpha}^2 = v_F^2 / 3$ provides the estimate

$$\Omega_{\text{pl} \alpha}^2 \sim \frac{4}{3} \pi e^2 v_F^2 D(\epsilon_F) / V,$$

where $D$ is the eDOS, and $v_F$ can be interpreted as the electron band velocity averaged over the Fermi surface.
1.6. Optical Transitions in Crystalline Solids

1.6.2. Indirect Optical Transitions

The effect of lattice imperfections like impurities or phonons on the optical response is now taken into account to lowest nonvanishing order. The resulting summation over the IOTs

\[ |k\rangle = |kb\rangle^{\text{photon}} |k''\rangle = |kb''\rangle^{\text{ph, imp}} |k'\rangle = |kb'\rangle^{\text{ph, imp}} \]

makes an additional contribution only to the imaginary part of the dielectric function as is exactly the case in the linearized Drude formula (1.18). One obtains \[\text{(1.24)}\]

\[ \text{Im} \varepsilon_{\alpha\alpha}^{\text{IOT}} = \frac{2(2\pi \hbar e)^2}{(\hbar \omega)^4 V} \sum_{kk'} w_{kk'\alpha} (v_{k\alpha} - v_{k'\alpha})^2 f_k \cdot (1 - f_{k'}) \]

where the electron transition rate due to electron-impurity-photon and electron-phonon-photon coupling is

\[ w_{kk'\omega}^{\text{e-imp}} = |V_{imp}^{kk'}|^2 \cdot \left[ \delta(\epsilon_{k'} - \epsilon_k - \hbar \omega) - \delta(\epsilon_{k'} - \epsilon_k + \hbar \omega) \right] \]

and

\[ w_{kk'\omega}^{\text{e-ph}} = \sum_{r\pm} |M_{k'k}^r|^2 \left( b_Q\pm + \frac{1}{2} \pm \frac{1}{2} \right) \left[ \delta(\epsilon_{k'} - \epsilon_k \pm \hbar \Omega_{Q\pm} - \hbar \omega) - \delta(\epsilon_{k'} - \epsilon_k \pm \hbar \Omega_{Q\pm} + \hbar \omega) \right], \]

respectively. In this formalism, the lattice imperfections scatter the more electrons from \(|k\rangle\) to \(|k'\rangle\) the more electrons are in the initial state and the less electrons are in the final state. However, as suggested by Eq. (1.24), absorption of light being polarized along the \(\alpha\) direction only occurs if the electron changes its band velocity \(v_{k\alpha}\) along the same direction \(\alpha \in \{x, y, z\}\).

This situation again is quite similar to that of the Drude model and together with Eq. (1.18) motivates the definition of a generalized Drude scattering rate \[\text{(1.26)}\]

\[ \Gamma(\omega) = \frac{\omega^3}{\Omega_{\text{pl}}^2} \text{Im} \varepsilon_{\alpha\alpha}^{\text{IOT}}. \]

Assuming a constant band velocity \(v_{k\alpha}^2 = v_F^2/3\), constant matrix elements \(|V_{imp}^{kk'}|^2 = |V_{imp}^F|^2\) for impurity scattering, and a constant eDOS \(D\) around the Fermi edge yields an estimate

\[ \Gamma^{\text{imp}} \sim \frac{\pi}{\hbar} |V_{imp}^F|^2 D(\epsilon_F) \]

for the Drude scattering rate where \(v_F\) and \(|V_{imp}^F|^2\) can be understood as averages over the Fermi surface. A large eDOS \(D(\epsilon_F)\) implies many initial and final states for scattering electrons and thus leads to a large velocity-relaxation rate.

In general, \(\Gamma\) has to be calculated according to Eqs. (1.24) and (1.26) and thus depends on temperature and light frequency which is especially relevant for a strongly varying eDOS around the Fermi energy and for e-ph scattering.

---

1 This formula is also derived in [All71] for low temperatures. Note that a factor of \(1/V\) is missing there.
1. Theoretical Background

1.7. Remarks

- Equation (1.24) describing the contribution of the IOTs to $\varepsilon$ is valid for slow relaxation only, that is $\Gamma \ll \omega$ [All71]. In case of fast relaxation or strong e-ph coupling, multiphonon processes have to be taken into account. The Holstein theory does so but is complicated and designed for metals with parabolic bands only [All71].

- Moreover, Eq. (1.24) considers only processes

\[ |k b\rangle \xrightarrow{\text{photon}} |k b\rangle \xrightarrow{\text{ph, imp}} |k' b'\rangle \]

where the photon-related step leaves the electron in the same Bloch state. This is only correct when other bands are energetically separated by significantly more than the photon energy $\hbar \omega$ [Dum61].

- The case of an e-e collision is shown in Fig. 1.3. In free-electron metals with only 1 parabolic band, e-e scattering is not expected to make a significant contribution to the photon absorption in an IOT [Kav84]. First, the Coulomb interaction is effectively screened in metals. Second, wavevector conservation

\[ k_1 + k_2 = k'_1 + k'_2 + G \] (1.28)

and the band velocity (1.21) imply that the average velocity of the electron system does not change in an e-e collision for $G = 0$. Only umklapp processes involving a vector $G \neq 0$ of the reciprocal lattice can relax an electronic current.

This situation can change in semimetals like graphite where the screening of charges is less effective due to a smaller number of electrons at the Fermi edge. Moreover, the occurrence of bands with strongly differing curvature can lead to a change in the average velocity also for collisions with $G = 0$.

In all cases, the relaxation rate grows with electronic temperature [Kav84],

\[ \Gamma^{\text{e-e}} = A T_e^2, \]

because higher temperatures imply a larger number of initial and final electron states.
1.8. Rapidly Changing Sample

Up to now, the sample was assumed to change its optical properties only little within the duration of 1 cycle $2\pi/\omega$ of the probing radiation. In TRTS, one can get quite easily beyond this quasistatic regime, for example, when a 1-THz wave with an oscillation period of 1 ps transmits a sample where free electrons decay on a 300-fs time scale. Such behavior has mainly 2 consequences:

- The quasistatic relationship (1.10) between polarization and driving field is possibly not valid any more. Therefore, the standard relations describing the wave propagation [Yeh88] are modified which is important for the extraction of the dielectric function. This problem is in principle solved; the relation between incident and transmitted THz field is, for example, given in Section 2.6.2 or in Ref. [Ném02].

- A probably more serious consequence of a quickly changing sample is that the microscopic interpretation of the dielectric function by means of the Kubo formula (1.17) is not possible any more, since this relation was derived under the assumption of a quasistatic sample [Czy04]. Therefore, knowledge of the dielectric function beyond the quasistatic regime is of somewhat limited use at present unless one can compare it to the results of explicit theoretical calculations as for example done in Ref. [Hub05b].

In the following, the general case of a linear response is considered which leads to a definition of the instantaneous spectral response and its determination in a pump-probe experiment.

1.8.1. General Linear Response

Consider a physical system which is perturbed by some “input” signal $x(t)$ and, as a consequence, changes an “output” observable $y(t)$. Examples for $x$ and $y$ are listed in Table 1.1. Here, the most interesting situation is, of course, a pump-probe experiment where the pump pulse triggers a rapidly evolving change in the susceptibility and transmittivity of the sample.

The relation between input and output can be formally written $y(t) = F_t[x(t')]$ where $F_t$ is a functional since it has the complete function $x(t')$ as an argument. In many cases

<table>
<thead>
<tr>
<th>input $x$</th>
<th>output $y$</th>
<th>linear response function $R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>applied voltage $V$</td>
<td>induced current $I$</td>
<td>resistance</td>
</tr>
<tr>
<td>electric field $E$</td>
<td>induced polarization $P$</td>
<td>susceptibility $\chi^{(1)}$</td>
</tr>
<tr>
<td>magnetic field $B$</td>
<td>induced magnetization $M$</td>
<td>permeability $\mu$</td>
</tr>
<tr>
<td>incident light field $E_{\text{inc}}$</td>
<td>transmitted field $E_{\text{trans}}$</td>
<td>sample transmittivity</td>
</tr>
</tbody>
</table>

Table 1.1: Examples for perturbations $x$ of a system and observables $y$ which are influenced by the perturbation. The corresponding linear response functions are also shown.
1. Theoretical Background

the input perturbs the system considered only weakly such that one can linearize $F_t$ with respect to $x(t')$ and obtains [Gra78]

$$y(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dt' R(t,t') x(t')$$

(1.29)

where $F_t(0) = 0$ was assumed without loss of generality. The response function $R(t,t') = (2\pi)^{-1/2} F_t / \delta x$ is the functional derivative of $F_t$, and the prefactor of $1/\sqrt{2\pi}$ was introduced for consistence with the symmetric definition (B.1) of the Fourier transformation used in this work. Note that in Eq. (1.29) the complete history $t' < t$ of the input $x(t')$ contributes to the output $y(t)$ at time $t$. The causality principle implies that a future input does not contribute to the present output; thus one has

$$R(t,t') = 0 \quad \text{if} \quad t < t'.$$

The ultimate goal is the measurement of the response function $R$ since it contains important information about the system investigated.

1.8.2. Instantaneous Spectral Response

Is there a quantity that describes the response properties of the sample at a certain instant of time? The answer to this question is not immediately obvious since $R(t,t')$ depends on 2 time variables. Therefore, we eliminate the time $t'$ by a Fourier transformation (B.1) and obtain

$$y(t) = \frac{1}{\sqrt{2\pi}} \int d\omega' R(t, -\omega') x(\omega')$$

where $R(t, \omega')$ is the Fourier transformed $R(t,t')$ with respect to $t'$. The last equation can be rewritten as

$$y(t) = \frac{1}{\sqrt{2\pi}} \int d\omega' R_t(\omega') \cdot x(\omega') \exp(-i\omega't)$$

(1.30)

where

$$R_t(\omega') := R(t, -\omega') \exp(i\omega't)$$

(1.31)

can be interpreted as the instantaneous spectral response to the component $x(\omega') \exp(-i\omega't)$ of the input.

This interpretation makes sense: As will be shown below, $R_t(\omega')$ does not change with time $t$ for a sample in a steady state; such system is often called a linear time-invariant (LTI) system [Mey97]. Time-invariant means that, if an input $x(t)$ induces an output $y(t)$, the temporally shifted input $x(t + t_0)$ will just induce the same but temporally shifted output $y(t + t_0)$. Equation (1.29) then leads to $R(t - t_0, t' - t_0) = R(t,t')$ and especially

$$R(t, t') = R(0, t' - t),$$

(1.32)
1.8. Rapidly Changing Sample

such that the instantaneous spectral response (1.31) becomes

\[ R_t(\omega') = R(t = 0, -\omega') =: R(\omega'), \]

which does not depend on time \( t \). Therefore,

\[ \Xi = \left| \frac{1}{\omega' R_t(\omega')} \frac{\partial R_t(\omega')}{\partial t} \right| \]

is a measure how quickly the sample changes its linear response within 1 cycle of an input of frequency \( \omega' \).

For example, if \( R_t \) is the pump-induced change \( \Delta \chi_t = (\Delta \varepsilon_t - 1)/4\pi \) in the linear susceptibility and fulfills \( \Xi \ll 1 \), the Kubo formula (1.17) can be used for the interpretation of \( \chi \) or the dielectric function \( \varepsilon \). In the opposite case, the Kubo formula is probably not valid any more: Its derivation assumes that the occupation numbers \( \rho_{mm} \) undergo only small relative changes within 1 optical cycle \( 2\pi/\omega \) \[Czy04\].

Before turning to an instructive example, some remarks are added:

- In frequency space, the response (1.30) reads

\[ y(\omega) = \int d\omega' R_{\omega-\omega'}(\omega')x(\omega'). \tag{1.33} \]

and reduces to the familiar relation

\[ y(\omega) = R(\omega)x(\omega) \tag{1.34} \]

in the steady-state case because Eq. (1.32) then implies \( R_{\omega-\omega'}(\omega') = R(t = 0, -\omega')\delta(\omega-\omega') \).

- The definition (1.31) of the instantaneous response agrees with that proposed in Ref. \[Say94\]. In this publication, the argumentation relies on the special example of a rapidly changing plasma. Here, a definition based on more general considerations is given.

- The above motivation of the instantaneous spectral response \( R_t(\omega') \) started with the elimination of the time \( t' \) in \( R(t, t') \) which is actually possible by any transformation \( x(t') \mapsto x(\sigma') \) with respect to an orthonormal basis set \( b_{\sigma'}(t') \). It can be shown, however, that the Fourier basis \( b_{\omega'}(t') \propto \exp(-i\omega' t') \) is the only basis set that results in a \( t \)-independent expression for the transformed \( R_t(\sigma') \) if the sample is in equilibrium. The proof mainly shows that \( \partial_t R_t(\sigma') = 0 \) only and only if the Fourier basis is used.

In the following we will mainly use \( R_t(\omega') \) instead of \( R(t, t') \) due to its easier interpretation and since it reduces to the familiar expressions in the equilibrium case.
1. Theoretical Background

**Example: Spectrally Flat Response**

For the sake of simplicity, we assume that the instantaneous response $R_t(\omega')$ does not change over the spectrum of the input $x(t')$ which is centered at $\omega'_0$ such that one can set $R_t(\omega') \approx R_t(\omega'_0)$. Then the response is simply a multiplication

$$y(t) = \text{Re} \left[ R_t(\omega'_0) \cdot x_C(t) \right]$$

(1.35)

with the analytic signal $x_C(t)$ [Die96]. The true signal $x(t)$ is just the real part of the analytic signal, $x = \text{Re} x_C$. Equation (1.35) implies the following points:

- Due to the modulation of the input $x(t)$ by $R_t$, new frequencies are created in the output $y(t)$. This effect is strong when $R_t$ changes substantially within 1 period $2\pi/\omega'$ of the input signal, that is when $\Xi \sim 1$.

- $R_t$ can be measured by using input pulses peaking at different times $\tau$. For example, a delta-like input pulse $x(t) \propto \delta(t - \tau)$ yields $y(t) \propto R_\tau(\omega'_0)$. This is the principle of a pump-probe experiment.
2. Nonlinear Wave Propagation

Strong laser pulses can induce a nonlinear polarization in matter. One example is a polarization that oscillates much slower than the incident light. This phenomenon can be employed in the generation of THz pulses. Similarly, a strong laser pulse temporally modifies the optical properties of a medium which are detected by a subsequent weak probe pulse. This effect can be used to scan the THz pulses or to study the dynamics of the optically excited medium in real time.

In this chapter, 2 classes of nonlinear polarization are discussed which are relevant for this work. By using a perturbational approach, we pay particular attention to the propagation of light when such nonlinear effects are present. These considerations are especially important to extract the dielectric function from the data of pump-probe experiments.

2.1. Wave Equation

Maxwell’s equations yield a wave equation for the propagation of the total macroscopic electric field \( E(\mathbf{x}, t) \) in matter [Mil98],

\[
\left( \nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{E} \right) = -\frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{P},
\]

where \( c \) is the vacuum speed of light, \( \mathbf{x} \) and \( t \) points in space and time, respectively. The electric polarization \( \mathbf{P} \) induced by \( \mathbf{E} \) acts as a source term on the right-hand side of this equation and makes light propagation in matter different from that in vacuum where \( \mathbf{P} = 0 \).

In the following, we first restrict ourselves to a polarization linear in \( \mathbf{E} \) which describes the domain of linear optics. Later, nonlinear contributions to \( \mathbf{P} \) are taken into account and considered as small perturbations to calculate how they modify the propagation of the electric field.

2.2. Linear Optics

When we assume a medium in a steady state and consider only linear effects of \( \mathbf{E} \) on \( \mathbf{P} \), the induced polarization is given by Eq. (1.10). Switching from the time domain to frequency
2. Nonlinear Wave Propagation

space via a Fourier transformation results in the wave equation of linear optics
\[
\left( \nabla \times \nabla \times + \frac{\omega^2}{c^2} \epsilon \right) E = 0, \tag{2.1}
\]
which is a linear and homogeneous differential equation.

If the medium is locally homogeneous and isotropic around \( \mathbf{x} \), plane harmonic waves
\[
E(\mathbf{x}, t) = A \exp(\mathbf{i} \mathbf{k} \cdot \mathbf{x} - i \omega t)
\]
with frequency \( \omega/2\pi \), complex wavevector \( \mathbf{k} \), and complex amplitude \( A \) are the eigenmodes of the electric field. Wavevector, frequency, and refractive index \( n = \sqrt{\epsilon} \) are connected by the so-called dispersion relation
\[
c^2 k^2 = \omega^2 n^2.
\]
The wavelength is given by \( \lambda = 2\pi/|\text{Re} \mathbf{k}| \), whereas \( 1/|\text{Im} \mathbf{k}| \) is the attenuation length.

2.3. Nonlinear Polarization: 2 Examples

We now take the nonlinear part of the induced polarization into account, that is all deviations
\[
P_{\text{NL}} := P - P^{(1)}
\]
of \( P \) from the linear part \( P^{(1)} \). It appears as a source term on the right-hand side of the wave equation
\[
\left( \nabla \times \nabla \times + \frac{\omega^2}{c^2} \epsilon \right) E = 4\pi \frac{\omega^2}{c^2} P_{\text{NL}} \tag{2.2}
\]
and thus perturbs the linear wave propagation.

\( P_{\text{NL}} \) can, for instance, describe sum- and difference-frequency generation or the effect of the pump pulse on the propagation of the probe pulse in a pump-probe experiment. Before solving the wave equation, these examples of a nonlinear polarization are considered in more detail.

2.3.1. Sum- and Difference-Frequency Mixing: THz Generation and Detection

We consider only nonlinear effects to lowest order that is effects quadratic in \( E \). For a medium in a steady state one obtains [Gra78, Boy92]
\[
P_i^{(2)}(\omega) = \sum_{jk} \int \limits_{-\infty}^{\infty} d\omega_1 \int \limits_{-\infty}^{\infty} d\omega_2 \chi_{ijk}^{(2)}(\omega, \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)
\]
2.3. Nonlinear Polarization: 2 Examples

Figure 2.1.: Principle of THz generation. Each frequency pair \((\omega_1, \omega_2)\) within the spectrum of a visible laser pulse generate a polarization at the difference frequency \(\Omega = \omega_1 - \omega_2\).

with the abbreviation

\[
\chi^{(2)}(\omega, \omega_1, \omega_2) = \chi^{(2)}(\omega_1, \omega_2) \delta(\omega - \omega_1 - \omega_2).
\]

Here, \(\chi^{(2)}(\omega_1, \omega_2)\) is the third-rank susceptibility tensor which vanishes in media with inversion symmetry. The \(\delta\)-function shows that only the sum or difference of 2 light frequencies \(\omega_1\) and \(\omega_2\) can be generated by this 2nd-order process.

It is convenient to restrict oneself to positive frequencies \(\omega, \omega_1, \omega_2 > 0\). By exploiting general symmetry properties of \(\chi^{(2)}\), the 2nd-order polarization can be written as [Boy92]

\[
P_i^{(2)}(\omega) = 2 \sum_{jk} \int \int d\omega_1 d\omega_2 \left[ \chi^{(2)}_{ijk}(\omega, \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2) + \chi^{(2)}_{ijk}(\omega, \omega_1, -\omega_2)E_j(\omega_1)E_k^*(\omega_2) \right]
\]  

The 1st term in the integrand contributes for \(\omega = \omega_1 + \omega_2\) and thus describes sum-frequency generation (SFG), whereas the 2nd term becomes operative for \(\omega = \omega_1 - \omega_2\) and describes difference-frequency generation (DFG).

**THz Generation**

As visualized by Fig. 2.1, DFG can be employed to generate THz radiation of frequency \(\Omega = \omega_1 - \omega_2\) from spectrally broad visible light of high intensity. For example, one of the lasers used in this work delivers pulses with a 100-nm bandwidth centered at 780 nm. Applying DFG to these pulses should result in THz pulses covering the spectrum from 0 to about 50 THz. In reality, however, propagation effects restrict the DFG process to those frequencies which fulfill the so-called “phase matching” condition. This point is discussed in Section 2.6.1.

It must be emphasized that the polarization induced by DFG does *not* depend on the absolute phase of all spectral components \(E_j(\omega)\) since only the phase differences enter in Eq. (2.3).
2. Nonlinear Wave Propagation

Figure 2.2.: Electrooptic detection of a THz waveform. The visible sampling pulse and the THz pulse propagate collinearly through the $\chi^{(2)}$ crystal. Due to the linear electrooptic effect, the visible pulse sees a birefringent medium where the birefringence is proportional to the THz electric field at the position of the sampling pulse. The resulting ellipticity of the sampling pulse is largest if both pulses propagate with the same velocity but vanishes if the sampling pulse sweeps over a complete THz cycle. To avoid this effect, ZnTe crystals of only 10 $\mu$m thickness are used [Lei99a].

THz Detection: Electrooptic Effect

DFG and SFG can be also employed to detect the THz radiation: When a visible laser pulse with field $E_{VIS}$ and a THz wave $E_{THz}$ travel collinearly through a crystal with $\chi^{(2)}_{ijk} \neq 0$, the THz wave effectively changes the refractive index for the visible pulse via the 2nd-order polarization (2.3). Due to this so-called electrooptic or Pockels effect the visible laser pulse “feels” the THz field which can be detected by this interaction.

More formally, the electrooptic effect can be reasoned as follows: The total field propagating through the crystal is $E = E_{THz} + E_{VIS}$ and induces the nonlinear polarization (2.3). By retaining only cross terms, it has the formal structure $P_i^{(2)} \propto \sum_{jk} \chi^{(2)}_{ijk} E_{THz,j} E_{VIS,k}$ which just corresponds to an electric polarization linear in $E_{VIS}$. In other words, the contribution $\sum_{j} \chi^{(2)}_{ijk} E_{THz,j}$ represents a change in the linear optical properties of the medium due to the presence of the THz electric field.

The change in the linear susceptibility makes the crystal temporarily birefringent. In practice and as detailed in Fig. 2.2, this birefringence is measured by detecting the ellipticity the visible sampling pulse has accumulated due to its collinear propagation together with the THz pulse. As in many nonlinear processes, propagation effects limit the efficiency of the detection process.

2.3.2. Pump-Probe Experiments

The pump-probe technique is a method of choice to observe the dynamics of an optically excited sample with the best temporal resolution available. In such an experiment, a short pump pulse with a duration of typically 10 to 100 fs excites the sample, and the ensuing various relaxation processes can be studied by a temporally delayed probe pulse. After reflection from or transmission through the sample, the probe pulse pulse contains information about the current sample state, for instance, the temperature, magnetization, and so on.
2.3. Nonlinear Polarization: 2 Examples

From a formal point of view, the electric field \( \mathbf{E} = \mathbf{E}_{\text{pump}} + \mathbf{E}_{\text{probe}} \) is incident on the sample in a pump-probe experiment and induces a nonlinear polarization \( \mathbf{P}_{\text{NL}} \). Since often the probe field is weak, \( |\mathbf{E}_{\text{probe}}| \ll |\mathbf{E}_{\text{pump}}| \), an expansion of \( \mathbf{P}_{\text{NL}}[\mathbf{E}] \) with respect to \( \mathbf{E}_{\text{probe}} \) is reasonable and similar to Eq. (1.29) yields

\[
\mathbf{P}_{\text{NL}}(x, t) = \mathbf{P}_{\text{NL}}[\mathbf{E}_{\text{pump}}] + \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt' \; \Delta \chi(x, t, t') \mathbf{E}_{\text{probe}}(x, t') + \mathcal{O}(\mathbf{E}_{\text{probe}}^2). \tag{2.4}
\]

This approach takes also those nonlinear-polarization effects into account that cannot be described by a perturbation series like (1.9) any more, for example the field ionization of molecules.

The 1st term on the right-hand side of Eq. (2.4) describes a pump-induced polarization that would also occur without the probe pulse, for instance sum- and difference-frequency generation. The 2nd term contains all effects of the pump pulse and the sample on the weak probe pulse. Due to \( \mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}_{\text{NL}}, \chi := \chi^{(1)} + \Delta \chi \) can be understood as the total linear polarization response of the system "sample and pump pulse", and

\[
\Delta \varepsilon = 4\pi \Delta \chi
\]

is the pump-induced change in the dielectric function of the sample.

THz detection can also be considered as a pump-probe experiment: As seen above, the THz pulse acts as the pump pulse and modifies the linear optical properties of a nonlinear medium which are seen by a copropagating visible probe pulse.

One conceptual problem remains: The separation \( \mathbf{E} = \mathbf{E}_{\text{pump}} + \mathbf{E}_{\text{probe}} \) is well defined before the sample, but within the sample pump and probe beam interact with each other. Thus, the role of pump and probe beam is not clear any more after the sample. The most natural solution is to define the probe field as the field that is experimentally detected. It should disappear when the probe beam is blocked before the sample. Indeed, most experimental
2. Nonlinear Wave Propagation

setups apply spatial, spectral, or polarization filters to the total field $E$ such that no light reaches the detector when the probe beam is blocked. When we formally represent this filter by a linear operator $\hat{F}$, the probe field is simply

$$E_{\text{probe}} = \hat{F}E.$$ 

It has a much smaller intensity than the “rest” $E_{\text{pump}} = E - E_{\text{probe}}$. The considerations made above should be understood with these definitions of pump and probe beam.

The pump-probe configurations used in this work employ spectral filtering: In the THz detection, the pump and probe pulse are in the THz and visible spectral range, respectively. In TRTS, it is the other way around. We apply spectral filtering $\hat{F}_{\text{spec}}$ to Eq. (2.2) and obtain

$$\left(\nabla \times \nabla \times + \frac{\omega^2}{c^2} \varepsilon\right) E_{\text{probe}} = 4\pi \frac{\omega^2}{c^2} \hat{F}_{\text{spec}} P_{NL},$$

since $\hat{F}_{\text{spec}}$ commutates with $\nabla$ and $\varepsilon$. This equation together with (2.4) describes the probe field detected in a TRTS experiment. It is of the same structure as the general wave equation (2.2).

2.4. Solution of Wave Equation: Perturbational Approach

In this section, a method for the solution of the wave equation (2.2) is developed which is analog to the Born series in quantum scattering theory [Sch93]. As a perturbational method, it is only applicable when the nonlinear polarization does not affect the wave propagation too strongly. On the other hand, it gives an intuitive picture of the underlying mechanism and is easier to implement than numerical methods like the finite-difference time-domain scheme [Bea02]. In this work, it is applied to more complicated systems like carbon nanotubes embedded in a dielectric host where the pump beam induces additional anisotropies and inhomogeneities.

In order to find the solution of Eq. (2.2) we rewrite it as

$$\hat{D}E = -\xi \cdot 4\pi \frac{\omega^2}{c^2} P_{NL},$$

with the abbreviation

$$\hat{D} = \nabla^2 - \nabla(\nabla \cdot) - \frac{\omega^2}{c^2} \varepsilon$$

and consider its right-hand side as a perturbation. The perturbation parameter $\xi$ will be set to $\xi = 1$ finally. The perturbation expansion of $E$ with respect to $\xi$ is

$$E = \xi^0 E^{(0)} + \xi^1 E^{(1)} + \xi^2 E^{(2)} + \ldots .$$ (2.5)
2.4. Solution of Wave Equation: Perturbational Approach

Figure 2.4.: The fundamental wave $E^{(0)}$ travels through the medium according to linear optics. However, it induces a nonlinear polarization $P^{(0)}_\text{NL}$ at each position $x'$ which in turn creates an outgoing wave $\propto P^{(0)}_\text{NL}(x', \omega) G_{x'}(x, \omega)$. All these waves add up to the 1st-order correction $E^{(1)}$.

Its substitution in $P^{(0)}_\text{NL}(E)$, for example given by Eq. (2.3) or (2.4), yields an expansion of the nonlinear polarizability

$$P_{\text{NL}} = \xi^0 P^{(0)}_{\text{NL}} + \xi^1 P^{(1)}_{\text{NL}} + \xi^2 P^{(2)}_{\text{NL}} + \ldots,$$

where each coefficient $P^{(j)}_{\text{NL}}$ is a function of $E^{(0)}, \ldots, E^{(j)}$. Substitution in Eq. (2.2) leads to the following hierarchy of coupled differential equations:

\begin{align*}
\hat{D}E^{(0)} &= 0 \quad (2.6) \\
\hat{D}E^{(1)} &= -4\pi \frac{\omega^2}{c^2} P^{(0)}_{\text{NL}} \quad (2.7) \\
& \vdots \\
\hat{D}E^{(j+1)} &= -4\pi \frac{\omega^2}{c^2} P^{(j)}_{\text{NL}} \quad (2.8) \\
& \vdots
\end{align*}

The 1st equation describes the wave propagation when all nonlinearities are switched off which is the domain of linear optics. The resulting “fundamental wave” $E^{(0)}$ induces the lowest-order nonlinear polarization $P^{(0)}_{\text{NL}}$ which acts as a source for the 1st-order correction $E^{(1)}$. Here, the term “source” becomes clear when the Green function $G_{x'}(x, \omega)$ is employed to solve Eq. (2.8) for

$$E^{(j+1)}(x, \omega) = -4\pi \frac{\omega^2}{c^2} \int d^3 x' G_{x'}(x, \omega) P^{(j)}_{\text{NL}}(x', \omega).$$

(2.9)

The Green function is defined by the relation $\hat{D}G_{x'} = \delta_{x'} 1$ and can be understood as the wave that is scattered by a point-like spatial perturbation at $x'$. It has to be an outgoing wave in order to fulfill the causality principle. For example, in case the unperturbed medium is spatially homogeneous and isotropic, $G_{x'}$ is an outgoing spherical harmonic wave starting at $x'$ [Jac83].

This result permits a simple interpretation of the perturbational solution: The wave $E^{(0)} + \cdots + E^{(j)}$ induces a polarization $P^{(j)}_{\text{NL}}$ which in turn at each point $x'$ creates an outgoing wave.
2. Nonlinear Wave Propagation

proportional to $P_{NL}(x', \omega)$. All these outgoing waves add up to the next-order correction $E^{(j+1)}$. Figure 2.4 illustrates the case $j = 0$ which in many cases already gives a good approximation.

2.5. 1-Dimensional Case

The solution (2.9) of the wave equation is still complicated since one has to integrate over 3-dimensional space with the Green-function being a $3 \times 3$ tensor. Fortunately, many cases of interest are effectively 1-dimensional: In all situations in this thesis, the light beams can be considered as plane waves which see a homogeneous medium across their beam cross section. Therefore, the problem can be reduced to the propagation along one axis $z$ and a suitable component $E$ of the electric field $E$. Equation (2.8) becomes

$$\hat{D}E^{(j+1)}(z, \omega) = -4\pi \frac{\omega^2}{c^2} P_{NL}^{(j)}(z, \omega)$$ (2.10)

with

$$\hat{D} = \partial^2_z + k^2(z).$$

Here, $k(z)$ is the local wavevector of the fundamental wave given by

$$k^2 = \frac{\omega^2}{c^2} \varepsilon(z, \omega).$$

The derivation of Eq. (2.10) assumes $\nabla E = 0$ and $P_{NL}[E] = P_{NL}[E]$ which is fulfilled in all situations relevant for this work. The solution of Eq. (2.10) is analog to that of Eq. (2.9), but the 3-dimensional integration is reduced to an integration over $z$,

$$E^{(j+1)}(z, \omega) = -4\pi \frac{\omega^2}{c^2} \int dz' G(z, \omega) P_{NL}^{(j)}(z', \omega).$$ (2.11)

2.5.1. Film between 2 Half-Spaces

A very frequent experimental configuration is shown in Fig. 2.5: A plane wave in the left-hand half-space (medium 1) is incident onto a film (medium 2) of thickness $d$, partially transmitted through the film into the right-hand half-space (medium 3), and partially reflected back. Multiple reflections at the 2 boundaries of the film lead to additional “echoes” propagating forward and backward.

Fundamental Wave

The fundamental wave $E^{(0)}$ in the 3 media 1, 2, and 3 is, respectively [Yeh88],

$$\frac{E^{(0)}}{E_{\text{inc}}} = \begin{cases} \exp(-ik_1z) + A_1^+ \exp(-ik_1z) & \text{(incident + reflected)} \\ A_2^+ \exp(ik_2z) + A_2^- \exp(-ik_2z) & \text{(forward + backward)} \\ A_3^+ \exp(ik_3z - ik_3d) & \text{(transmitted)} \end{cases}$$ (2.12)
2.5. 1-Dimensional Case

Figure 2.5: Film of thickness \(d\) between 2 half-spaces. The fundamental wave is incident on the film from the left, partially reflected back and partially transmitted. The Green function has its source at \(z = z'\) inside the film and creates an outgoing wave which also undergoes reflections at the 2 boundary planes of the film at \(z = 0\) and \(z = d\).

where \(E_{\text{inc}}\) is the incident electric field at \(z = 0^-\) just before the left boundary. All coefficients are defined in Table 2.1. The quantities

\[
t_{ij} = \frac{2n_i}{n_i + n_j} \quad \text{and} \quad r_{ij} = \frac{n_i - n_j}{n_i + n_j}
\]

are the Fresnel transmission and reflection coefficients, respectively, for the case of normal incidence onto the boundary plane between medium \(i\) and \(j\). The factor

\[
M = \frac{1}{1 - r_{21} r_{23} \exp(2ik_2d)}
\]

accounts for infinitely many reflections between the 2 boundary planes of the film which produce echoes in the reflected and transmitted beam. More generally, \(M\) can be expanded in a geometrical series

\[
M = \sum_{j=0}^{\infty} [\exp(ik_2d) r_{23} \exp(ik_2d) r_{21}]^j
\]

in which the \(j\)th term represents the \(j\)th reflection echo. The last expression nicely shows that the wave has to travel back and forth through the film between consecutive echoes. One can set \(M = 1\) if multiple reflections are not important, for example in a thick film where the reflection echoes \(j \geq 1\) are outside the temporal detection window.

Green Function

If the nonlinear response \(P_{\text{NL}}(z', \omega)\) is restricted to medium \(2\) with \(z' \in [0, d]\), the Green function in medium 1, 2, and 3 becomes

\[
2ik_2G_{z'}(z, \omega) = \begin{cases} 
B_1^- \exp(-ik_1z) & \text{(backward only)} \\
\exp(ik_2|z-z'|) + B_2^+ \exp(ik_2z) + B_2^- \exp(-ik_2z) & \text{(sph + fw + bw)} \\
B_3^+ \exp(ik_3z - ik_3d) & \text{(forward only)} 
\end{cases}
\]

(2.13)
2. Nonlinear Wave Propagation

<table>
<thead>
<tr>
<th>med</th>
<th>fundamental wave</th>
<th>Green function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$A_1^+ = [r_{12} + r_{23} \exp(2ik_2d)] M$</td>
<td>$B_1^+ = [\exp(ik_1z') + r_{23} \exp(2ik_2d - ik_2z')] t_{21}M$</td>
</tr>
<tr>
<td>2</td>
<td>$A_2^+ = t_{12}r_{23} \exp(2ik_2d) M$</td>
<td>$B_2^+ = B_3^+ \exp(ik_2d) r_{23}/t_{23}$</td>
</tr>
<tr>
<td>3</td>
<td>$A_3^+ = t_{12}t_{23} \exp(ik_2d) M$</td>
<td>$B_3^+ = [\exp(-ik_2z') + r_{21} \exp(ik_2z')] \exp(ik_2d) t_{23}M$</td>
</tr>
</tbody>
</table>

Table 2.1.: Coefficients of the forward and backward propagating components of the fundamental wave $E^{(0)}$ and Green function $G_{z'}$ of a film between 2 half-spaces as described by Eqs. (2.12) and (2.13).

respectively. This function fulfills $DG_{z'} = \delta_{z'}$, is an outgoing wave, and, like its associated magnetic field, continuous at the film boundaries. The coefficients $B_j^\pm (z')$ depend on the center position $z'$ of the Green function and are listed in Table 2.1.

2.6. Applications

2.6.1. THz Generation in GaSe

In this work, the optically uniaxial crystal GaSe is used to generate THz radiation from about 10 to 30 THz. The generation process is discussed in detail in Ref. [Sch05] based on the above formalism. Briefly, as shown in Fig. 2.6, the visible generation beam transmits a GaSe crystal where it propagates as an ordinary (o) and an extraordinary (e) wave with wavevectors $k_o(\omega + \Omega)$ and $k_e(\omega)$ and frequencies $\omega + \Omega$ and $\omega$, respectively. Via difference-frequency mixing, both waves together create a polarization with frequency $\Omega$ along the ordinary direction if the azimuthal angle $\phi$ of the crystal is 60° [Sch05]. Application of the above formalism leads to a THz wave with wavevector $k_o(\Omega)$ which is proportional to the so-called phase-matching factor

$$\frac{\exp(i\Delta kd_{GaSe}) - 1}{\Delta k} \quad \text{with} \quad \Delta k = k_o(\omega + \Omega) - k_e(\omega) - k_o(\Omega)$$
at the output plane of the GaSe crystal [Kai99]. Therefore, an efficient THz generation of frequency $\Omega$ requires $|\Delta k d_{\text{GaSe}}| \ll 1$. In order to fulfill this condition over a wide range of THz frequencies, GaSe crystals of a thickness $d_{\text{GaSe}}$ of less than 100$\mu$m are used [Hub00].

2.6.2. Probe-Pulse Propagation

Exciting the film in Fig. 2.5 by a pump pulse at time $t = -\tau$ leads to a change $\Delta\varepsilon_{t=\tau}(\omega)$ in the dielectric function of the film which is seen by the THz probe pulse $E$ arriving at time $t = 0$ at the sample. Here, $\Delta\varepsilon_t$ means the instantaneous dielectric function as defined in Section 1.8.2. Since all experiments in this work are transmission experiments, we calculate the probe pulse $E(z = d + 0^+, \omega)$ directly after the film.

According to Eqs. (2.4) and (1.33), the relevant nonlinear polarization in $\omega$ space is

$$P_{NL\tau}(z, \omega) = \int d\omega' \Delta\varepsilon_{\omega-\omega'}(z, \omega') E(z, \omega') e^{-i(\omega-\omega')\tau}.$$ 

It induces a pump-induced change $\Delta E_{\tau}(d + 0^+, \omega)$ in the electric field directly after the film which can be calculated by the aid of Eq. (2.11). To 1st order in $\Delta\varepsilon$, one obtains

$$\Delta E_{\tau}(d + 0^+, \omega) = -\frac{\omega^2}{c^2} \int dz \Delta\varepsilon_{\omega}(z, \omega) E(0)(z, \omega) G_z(z + d, \omega).$$

In a pump-probe experiment, $\Delta E_{\tau}$ is detected for a complete sequence of pump-probe delays $\tau$. In order to get access to the dielectric function, we apply a Fourier transformation $\tau \rightarrow \Omega$ to the last equation and find

$$\Delta E_{\Omega}(d + 0^+, \omega) = -\frac{\omega^2}{c^2} \int dz \Delta\varepsilon_{\omega-\Omega}(z, \omega) E(0)(z, \omega-\Omega) G_z(z + d, \omega).$$

Inserting the expressions (2.12) and (2.13) for the fundamental wave $E(0)$ and the Green function $G_z(d + 0^+, \omega)$, respectively, leads to a quite lengthy relation between the incident field $E_{\text{inc}}$ and the pump-induced change $\Delta E_{\Omega}(d + 0^+, \omega)$ in the transmitted field.

However, the films used in this work are much thinner than the wavelength of the THz probe radiation such that one can set $\exp(i k_2 d) = 1$. As a consequence, the fundamental wave is $E(0)(d + 0^+, \omega) = E_{\text{inc}} t_{12} t_{23} M \; R_{\infty} E_{\text{inc}}$ where

$$R_{\infty} = \frac{E(0)(d + 0^+, \omega)}{E_{\text{inc}}} = \frac{t_{12} t_{23}}{1 + r_{12} r_{23}}$$

is the response of the unexcited sample. The Green function (2.13) can be written as $G_z(d + 0^+, \omega) = B_3^+ / 2i k_2 = R_{\infty} / 2i k_1$ which leads to the compact relation

$$\Delta E_{\Omega}(d + 0^+, \omega) = \Delta R_{\Omega}(\omega-\Omega) E_{\text{inc}}(\omega-\Omega).$$

(2.15)
2. Nonlinear Wave Propagation

Here, the pump-induced change

\[ \Delta R_\Omega(\omega - \Omega) = \frac{i\omega}{2cn_1(\omega)} R_\infty(\omega - \Omega) R_\infty(\omega) \int dz \Delta \varepsilon_\Omega(z, \omega - \Omega) \]  

(2.16)

in the sample response function is the experimentally accessible quantity and can be easily solved for the spatially averaged change in the dielectric function. In the course of this work, this formula will be applied to thin films of graphite and carbon nanotubes.

If all terms with the argument \( \omega - \Omega \) in Eq. (2.15) are sufficiently flat, this argument can be approximated by \( \omega - \Omega \approx \omega \). An inverse Fourier transformation with respect to \( \Omega \) yields

\[ \Delta R_\tau(\omega) = \frac{\Delta E_\tau(d + 0^+, \omega)}{E_{\text{inc}}(\omega)} = \frac{i\omega}{2cn_1(\omega)^2} \int dz \Delta \varepsilon_\tau(z, \omega), \]  

(2.17)

which can be interpreted as the quasistatic limit of Eq. (2.15): The wave propagates as if the sample changes its optical properties only very slowly.

**WKB Approximation**

We assume a quasistatically changing sample such that the wave equation (2.10) can be rewritten as

\[ \left[ \partial_z^2 + k_\tau^2(z) \right] E_\tau(z, \omega) = 0 \]  

(2.18)

with

\[ k_\tau^2 = \frac{\omega^2}{c^2} \left[ \varepsilon_\infty(z, \omega) + \Delta \varepsilon_\tau(z, \omega) \right]. \]

When a wave is incident from \( z = -\infty \) and equals \( E_{\text{inc}} \) at \( z = z_0 \), the field at a position \( z > z_0 \) is, according to the so-called WKB approximation, given by [Sch93]

\[ E_\tau(z, \omega) = E_{\text{inc}} \exp \left[ i \int_{z_0}^z dz' k_\tau(z') \right]. \]  

(2.19)

The WKB approximation is valid if the local wavevector \( k_\tau \) varies only slightly over 1 wavelength of the radiation, that is, if \( |\partial k_\tau/\partial z| \ll |k_\tau^2| \) [Sch93].

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3. Experimental Details

In the course of this work, 2 different THz-transmission spectrometers were built. The “MHz-setup” is driven by 10-fs, 10-nJ pulses at a 75-MHz repetition rate and allows for high-quality measurements of the steady-state THz response of a given sample as well as the instantaneous THz response of a sample that was optically excited by relatively weak pump pulses. In contrast, the “kHz-setup” is driven by optimized 1-mJ pulses at a 1-kHz repetition rate and permits measurements of the instantaneous THz response of strongly excited samples such as laser-generated gas plasmas. In the following, the laser systems and the THz spectrometers together with the work sequence of THz spectroscopy are described.

3.1. Laser Systems

3.1.1. MHz-Laser Oscillator

A laser is a light oscillator consisting of an optical resonator and an amplification unit. The latter coherently amplifies the transmitted light and thus compensates for losses such as light that is coupled out for the user. The amplification mechanism is called “light amplification by stimulated emission of radiation” which also coined the term LASER for such an oscillator.\(^1\)

Ti-doped sapphire, Ti:Al\(_2\)O\(_3\), is the perfect amplification material to generate ultrashort laser pulses. Pumping Ti:sapphire with 532-nm light results in an extremely broad emission band ranging from 650 to 850 nm [Hir98]. A linear optical resonator of length \(l\) restricts the radiation to longitudinal modes \(j \in \mathbb{N}\) with frequency \(f_j = j\Delta f\) where \(\Delta f = c/2l\).

Continuous-wave lasing generally starts at 1 frequency \(f_{j_0}\) since the amplification profile of Ti:sapphire is homogeneously broadened.

How can one couple many longitudinal modes coherently to generate pulsed radiation? One way is to modulate some suitable parameter of the laser with frequency \(\Delta f\) which results in spectral sidebands at \(f_{j_0} \pm \Delta f\). These sidebands are also amplified and in turn generate sidebands and so on, eventually leading to a large number of phase-locked laser modes.

\(^{1}\)A. Schawlow, one of the inventors of the laser, once joked that no one wanted to call a laser an oscillator since this would turn the laser into a LOSER [Yen87].
3. Experimental Details

Figure 3.1: Schematic of the MHz-laser oscillator (Femtosource M1, Femtolasers GmbH). The light-amplifying Ti:sapphire crystal is pumped by a continuous-wave Nd:YVO₄ laser via a focusing lens L. The linear optical resonator is formed by the end mirror EM and the slightly transmitting output coupler OC. The focusing mirrors FM1 and FM2 are responsible for a high power density in the crystal thus enhancing the Kerr effect. Chirped mirrors CM1 and CM2 compensate for the group-velocity dispersion accumulated by 1 pulse roundtrip in the resonator. All beams are incident on the Ti:sapphire crystal under the Brewster angle to minimize losses, and the orientation of FM1 and FM2 is chosen to compensate for the astigmatism introduced by the Ti:sapphire crystal. The OC has the shape of a double-wedge to avoid multiple reflections into and out of the resonator. The external cavity dispersion control ECDC consists of 2 chirped mirrors where each double reflection compensates for the dispersion introduced by a 1-mm thick plate of BK7 glass.

Ti:sapphire permits passive mode locking, that is, self-modulation of the resonator via the optical Kerr-effect. This $\chi^{(3)}$ effect causes a change in the refractive index of the Ti:sapphire crystal which is proportional to the instantaneous light intensity. As a result, the Gaussian intensity profile of the laser beam induces an index profile which acts as a transient lens and so modulates the resonator with the desired frequency $\Delta f$ provided pulsed operation is on. So-called “chirped mirrors” in the resonator compensate for the group-velocity dispersion of the Ti:sapphire crystal which would increase the duration of the laser pulse and finally switch the Kerr lens off. The use of broadband reflecting and chirped mirrors enables the generation of pulses with a duration of 10 fs and less. Details of the femtosecond laser-oscillator used are shown and described in Fig. 3.1.

3.1.2. kHz-Amplified Laser System

Many optical experiments, for example pump-probe experiments with highly excited samples, require laser-pulse energies much higher than those generated by the MHz oscillator described in the previous section. Larger pulse energies are obtained by amplifying the MHz oscillator pulses in another Ti:sapphire crystal. Since the latter produces a limited output power of $\sim 1$ W the pulse repetition rate has to be reduced to the kHz range by pulse pickers like a Pockels cell. The so-called seed-laser pulses are temporally stretched before entering the amplification stage in order to avoid too high peak intensities which could induce undesired nonlinear effects in the optical components or even damage them. After several amplification passes, the resulting laser pulses are temporally compressed.

Figure 3.2 shows the kHz amplifier used in this work. In this system, an acousto-optic
3.2. THz Spectrometer

The two THz spectrometers constructed during the work of this thesis are driven by the laser oscillator and the amplified laser system with a 75-MHz and a 1-kHz repetition rate, respectively. The “MHz setup” and the “kHz setup” are based on the same schematic which is shown in Fig. 3.3. However, they differ in some details which will be explained in the following for the various stages of the THz spectrometer.
3. Experimental Details

Figure 3.3.: Schematic of the THz spectrometer. A near-infrared generation pulse from a Ti:sapphire laser is focused onto a GaSe or ZnTe crystal to generate THz radiation by difference-frequency mixing. After collimation by a 90° off-axis parabolic mirror PM1, the remaining generation light is blocked by a high-resistivity Si wafer whereas the THz radiation is transmitted and focused by PM2 onto the sample. After recollimating by PM3 and refocussing by PM4, the THz beam finally transmits the ZnTe crystal for detection. A 2nd Si wafer is employed to combine the THz beam with a beam of near-infrared sampling pulses such that the 2 beams propagate collinearly through ZnTe. The THz-induced ellipticity of the sampling beam is detected by using a λ/4-wave plate and a Wollaston prism. The MHz setup employs spherical mirrors instead of lenses to avoid unnecessary longitudinal and transverse chirp of the 10-fs laser pulses.

3.2.1. THz Generation

The THz radiation covering a spectrum from 1 to 3 THz is produced by difference frequency mixing in ZnTe, whereas GaSe is employed to obtain pulses covering a spectrum from about 10 to 30 THz. The λ/2-wave plate before the generation crystal adjusts the polarization of the generation beam, which is 45° with respect to the p direction in case of GaSe and 0° in case of ZnTe. The resulting THz radiation is p polarized. The GaSe crystal can be rotated about an axis parallel to the laser table to change the phase matching angle ϑ_{inc} as shown in Fig. 2.6.

Although the electric field of each laser pulse has the same envelope, the phase between the envelope and the carrier wave generally differs from shot to shot [Bra00]. Fortunately, the THz generation process does not depend on the absolute phase of the input pulse as emphasized in Section 2.3.1 and thus delivers the same THz waveform for each laser shot.

In the MHz setup, the generation beam is focused tightly to a diameter of ≈ 15 μm onto the generation crystal in order to generate as much THz radiation as possible. In the kHz setup, such tight focusing might damage the generation crystal which is thus placed before the focus.
3.2. THz Spectrometer

3.2.2. THz Detection

As described in Section 2.3.1, the THz-pulse induces a birefringence in the ZnTe detection crystal via the electrooptic effect and thus makes the copropagating sampling pulse elliptically polarized. The ellipticity $\eta$ is detected as follows: First, the $\lambda/4$-wave plate transforms the elliptically polarized light into linearly polarized light whose polarization plane is now rotated by a corresponding angle $\eta$. Second, a Wollaston prism spatially separates 2 beams of perpendicular linear polarization and is oriented such that the power of the 2 beams is equal when no THz field is present. Third, the light power is measured by a pair of photodiodes whose current difference is proportional to $\eta$. The THz signal

$$S(t) \propto \eta(t)$$

is scanned step-by-step by moving the $t$-delay stage in Fig. 3.3.

The MHz setup employs standard Si photodiodes which are fast enough to resolve the chopper modulation frequency of 9 kHz (see below).

In the kHz setup, the sampling pulse is derived from the seed laser instead from the amplified laser beam for the following reasons: First, this allows to shape the amplified pulses without changing the sampling pulse. Second, the seed pulses have a 12-fs duration and small shot-to-shot energy fluctuations of $\approx 10^{-3}$. Thus they are significantly shorter and more stable than the amplified pulses resulting in a better signal-to-noise ratio. Due to the much larger repetition rate of the seed laser, only 1 of $\approx 75000$ sampling pulses coincides with a THz pulse. The temporal gating of precisely this sampling pulse requires fast photodiodes to resolve the 75-MHz sampling pulse train and an electronic gate which is provided by a boxcar integrator (Stanford SR250) [Rei03].

3.2.3. Computer-Controlled Data Acquisition

In both the MHz and the kHz setup, the 2 photodiodes deliver a current or voltage signal $S_0 + \Delta S + O$. Here, $S_0$ is due to the THz electric field when the pump-beam is off, and $\Delta S$ is caused by the pump-induced changes of the THz field. The slowly varying offset $O$ is due to drifts in the setup which can also lead to a photodiode signal although the THz beam is blocked. The goal is to measure both THz signals $S_0$ and $\Delta S$ which is achieved by “marking” these signals with different modulation frequencies.

In the MHz setup, a chopper wheel chops the THz generation beam leading to a multiplication of the total THz signal with a modulation function $M_1$ of fundamental frequency $f_1 \approx 9$ kHz. Another chopper in the pump beam modulates the pump-induced signal with a function $M_2$ centered at a frequency $f_2 \approx 70$ Hz. The total electric signal $O + S_0 \cdot M_1 + \Delta S \cdot M_1 M_2$ after the photodiodes is fed into a lock-in amplifier (Stanford Research SR830) which is phase-locked to $M_1$. The lock-in amplifier acts as a spectral filter and rejects possible noise like a dc offset $O$ outside its filter band which is much
3. Experimental Details

Figure 3.4: (a) Typical THz waveform taken with the MHz setup. This waveform implies a pulse duration of about 100 fs. (b) Spectral amplitude and phase of the waveform in (a). The amplitude spectrum implies a bandwidth of about 15 THz. The spectral phase is essentially flat apart from the phase distortion below 10 THz where the refractive index of GaSe shows strong variations due to the presence of phonon resonances [Sch05].

broader than $f_2$; thus its output is $S_0 + \Delta S \cdot M_2$ and oscillates at a frequency $f_2$. Feeding the output of the 1st lock-in amplifier into a 2nd lock-in amplifier phase locked to $M_2$ eventually gives $\Delta S$. The 2 lock-in amplifiers are read out by a personal computer via an IEEE-488 interface at a rate of 512 Hz. Numerical averaging yields the signals $S_0 + \Delta S/2$ and $\Delta S/2$, respectively.

In the kHz setup, a possible signal background $O$ is greatly reduced by a circuit which consists of a delay line and a current inverter. They perform a subtraction of each current pulse from its preceding pulse. Thus, the boxcar integrator delivers the signal $S_0$ or $S_0 + \Delta S$ depending on whether the pump beam is blocked or not. $S_0$ and $S_0 + \Delta S$ are obtained separately by blocking every 2nd pump pulse with a mechanical chopper. The boxcar integrator is read out shot-by-shot by a personal computer via a fast analog-to-digital conversion card (National Instruments PCI-MIO 16E4).

All data-acquisition software is written in LabVIEW (National Instruments). It also controls the electronic delay stages and features special tools to optimize the THz signal.

3.2.4. Technical Data

Figure 3.4 shows an exemplary THz waveform together with its spectral amplitude and phase. Note that the pulse has a duration of about 100 fs. The oscillations found for $t > 0.1$ ps are due to the distortion of the spectral phase at about 10 THz which originates from strong variations of the refractive index of GaSe.

Table 3.1 shows typical parameters of the two THz spectrometers. In the MHz setup, the signal-to-noise ratio is limited by the shot noise of the sampling beam. An average time of 1 s implies a filter bandwidth of 1 Hz and thus a signal-to-noise ratio of up to $10^4$. With this sensitivity one can still detect pump-induced phase shifts of a 20-THz wave which
3.3. Work Sequence of THz Spectroscopy

<table>
<thead>
<tr>
<th>parameter</th>
<th>MHz setup</th>
<th>kHz setup</th>
</tr>
</thead>
<tbody>
<tr>
<td>pulse repetition rate</td>
<td>75 MHz</td>
<td>1 kHz</td>
</tr>
<tr>
<td>THz peak electric field in focus</td>
<td>$\sim 100 \text{ V cm}^{-1}$</td>
<td>$\sim 100 \text{ kV cm}^{-1}$</td>
</tr>
<tr>
<td>THz pulse duration</td>
<td>$\approx 100 \text{ fs}$</td>
<td>$\approx 100 \text{ fs}$</td>
</tr>
<tr>
<td>THz spectrum</td>
<td>10 to 30 THz</td>
<td>10 to 25 THz</td>
</tr>
<tr>
<td>THz-focus diameter on sample</td>
<td>50 $\mu$m (intensity FWHM)</td>
<td>50 $\mu$m (intensity FWHM)</td>
</tr>
<tr>
<td>signal-to-noise ratio</td>
<td>up to $10^4 \text{ Hz}^{-1/2}$</td>
<td>up to $10^3 \text{ Hz}^{-1/2}$</td>
</tr>
</tbody>
</table>

Table 3.1.: Typical parameters of the two THz spectrometers.

correspond to a length of less than 1 nm. Since the path difference between the THz and sampling pulse drifts by roughly 20 nm per minute measurements of the THz waveforms have to be performed fast.

3.2.5. Sample Requirements

As the THz spectrometer probes the sample in transmission geometry, the sample has to be transparent for the THz radiation. Moreover, the pump-probe experiments require a substrate to minimize the thermal load of the sample induced by the pump pulse. Diamond is the ideal substrate material since it is transparent in the THz and visible spectral range and exhibits a good thermal conductivity. Moreover, it introduces negligible dispersion and only very small thermally induced phase shift changes in the far- and mid-infrared [Ruf00].

3.3. Work Sequence of THz Spectroscopy

The ultimate goal of every THz transmission experiment is to obtain the dielectric function $\varepsilon$ of the sample. For this purpose, the sample response to the THz radiation has to be compared to that of a sample with known response. The typical work steps in THz spectroscopy are the following:

1. Measure the THz signal $S$ for the sample of interest.
2. Measure the THz signal $S_{\text{ref}}$ for a reference sample which is a sample with well-known THz response.
3. Fourier-transform $S(t)$ and $S_{\text{ref}}(t)$ with respect to $t$ and use the ratio

   $$Q(\omega) = \frac{S(\omega)}{S_{\text{ref}}(\omega)}$$

   to determine the dielectric function $\varepsilon(\omega)$.

We discuss 2 typical examples:
3. Experimental Details

Figure 3.5.: Examples of the THz signal $S$ taken with the sample of interest and the reference signal $S_{\text{ref}}(t)$ from a sample of known response. (a) THz signal $S(t)$ after transmission of a 58 $\mu$m-thick tape (tesa kristallklar), and the reference signal $S_{\text{ref}}(t)$ without the sample. The tape delays the THz arrival at the detector by about 100 fs. Apart from this delay and an overall amplitude decrease, the tape does not severely distort the shape of the THz signal. (b) THz signal $S(t) = S_{0.5 \text{ps}}(t)$ after transmission through a 20 $\mu$m-thick film of optically ionized oxygen O$_2$ 0.5 ps after excitation. The reference signal $S_{\text{ref}}(t) = S_{\infty}(t)$ is taken for unexcited O$_2$. Parts of $S$ arrive earlier at the detector than these of $S_{\infty}$ since the real part of the refractive index of the laser-induced plasma is smaller than 1.

- Figure 3.5(a) shows data of a steady-state measurement where $S$ is obtained after transmission through “tesa” tape. The reference signal $S_{\text{ref}}$ is measured without tape.

- Figure 3.5(b) shows data of a pump-probe experiment where $S = S_{\tau}$ is taken for gaseous oxygen O$_2$ at a fixed delay $\tau$ after ionization of the gas by an intense pump pulse. $S_{\text{ref}} = S_{\tau=\infty} = S_{\infty}$ is obtained for the sample without, that is a long time after or before the excitation. Instead of $Q_{\tau} = S_{\tau}/S_{\infty}$ one often considers the pump-induced change

$$\Delta Q_{\tau}(\omega) = Q_{\tau}(\omega) - 1 = \frac{\Delta S_{\tau}(\omega)}{S_{\infty}(\omega)}.$$

As shown below, knowledge of the experimental quantity $Q$ allows to extract the dielectric function of the sample. The division connected with the calculation of $Q$ has important advantages:

- All spectrometer-related response functions cancel out at least for a slowly varying sample. This is especially the case for the detector response which was observed to drift slowly in the course of time due to degradation of the ZnTe crystal. Slow intensity variations of the generation and sampling pulse cancel in the same way.

- A slow temporal drift between the THz and the sampling pulse is removed since a temporal shift affects both $S$ and $S_{\text{ref}}$. The resulting phase factor in $\omega$ space cancels in the division $S/S_{\text{ref}}$. 

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## 3.4. Extraction of the Dielectric Function

Strictly speaking, the THz signal $S$ measured is not the electric THz field $E$ directly after the sample; it is rather the ellipticity $\eta$ of the sampling pulse that is induced by the copropagating THz field within the detection crystal. Therefore, $S$ and $E$ are related by

$$S(\omega) = E(\omega) R_{pd}(\omega)$$

where the function $R_{pd} = R_p R_d$ describes the THz propagation $R_p$ from the sample to the detector and the detection process $R_d$ itself. The detector response $R_d$ is detailed in Fig. 3.6.

### 3.4.1. Steady-State Measurements

In this case and according to Eq. (1.34), the signal measured is

$$S(\omega) = E(\omega) R_{pd}(\omega) = E_{inc}(\omega) R(\omega) R_{pd}(\omega)$$

where $E_{inc}$ is the field incident on the sample and $R$ the sample response. An analog expression is obtained for the reference sample with response $R_{ref}$. Note that all spectrometer-related response functions cancel such that one is left with the desired sample response

$$R(\omega) = Q(\omega) R_{ref}(\omega).$$

$R$ and $R_{ref}$ are related to the dielectric function $\varepsilon$ of the sample by standard formulas such as Eq. (2.12). Inverting these relations finally yields $\varepsilon$ which will be shown in detail for graphite in Section 4.6.3.

### 3.4.2. Pump-Probe Measurements

In this kind of experiment, the signal measured is a 2-dimensional mesh $\Delta S(\tau) = S(\tau) - S_{\infty}(\tau)$ where $\tau$ is the delay between pump and probe pulse. In the following we consider...
the pump-induced changes \( \Delta S_{\tau} = S_{\tau} - S_{\infty} \). In general, it is necessary to Fourier-transform the raw data with respect to both times \( t \) and \( \tau \) which implies the variable changes \( t \rightarrow \omega \) and \( \tau \rightarrow \Omega \). According to Eq. (2.15), the resulting \( \Delta S_{\Omega}(\omega) \) is related to the changed electric field \( \Delta E_{\Omega}(\omega) \) after the sample by

\[
\Delta S_{\Omega}(\omega) = \Delta E_{\Omega}(\omega) R_{pd}(\omega) = E_{\text{inc}}(\omega - \Omega) \Delta R_{\Omega}(\omega - \Omega) R_{pd}(\omega),
\]

where \( \Delta R_{\Omega} \) is the pump-induced change in the sample response.

The reference signal for the unexcited sample is \( S_{\infty} = E_{\text{inc}} R_{\infty} R_{pd} \). Thus, one finally obtains

\[
\Delta R_{\Omega}(\omega - \Omega) = R_{\infty}(\omega) \Delta Q_{\Omega}(\omega) \frac{E_{\text{inc}}(\omega)}{E_{\text{inc}}(\omega - \Omega)}.
\]  

(3.1)

Since the sample modulates the incident electric field by frequencies \( \Omega \), \( E_{\text{inc}} \) does not cancel any more in the last equation. It is in principle possible to reconstruct the incident electric field from the THz signal \( S \) by taking the propagation from the sample to the detector and the detector response into account [Ném02]. It turned out for all relevant data in this work, that this is not necessary: Due to the large bandwidth of the THz pulses of about 10 to 15 THz, \( E_{\text{inc}} \) has a quite flat spectrum such that the last factor in Eq. (3.1) is close to unity.

The dielectric function is obtained from \( \Delta R_{\Omega} \), for example with the aid of Eq. (2.16), and an inverse Fourier transformation with respect to \( \Omega \) yields its instantaneous spectral shape \( \Delta \varepsilon_{\tau} \) at time \( \tau \) after sample excitation. This procedure will be shown in Section 4.6.3 for graphite in detail.
4. Graphite: Strongly Coupled Optical Phonons in Action

In this chapter, TRTS is applied to the semimetal graphite. The raw data, the extraction of the dielectric function, and the fit to models based on the extremely well-developed theory of the electronic structure of graphite around the Fermi level are described in detail. This yields the temporal evolution of the electronic temperature, the plasma frequency, and the Drude scattering rate. Simple physical arguments and model calculations show that more than 90% of the initially deposited excitation energy is transferred to only few strongly coupled lattice vibrations within less 500 fs. These hot optical phonons also substantially contribute to the striking increase of the Drude relaxation rate observed during the first ps after photoexcitation. The subsequent cooling of the hot phonons yields a lifetime estimate of 5.4 ps for these modes.

Parts of this chapter have been published in Physical Review Letters 95, 187403 (2005).

4.1. Motivation

The textbook-like semimetal graphite has been studied for more than 6 decades due to its relatively simple quasi-2-dimensional structure [Dre88]. For example, it was among the first materials for which the electronic band structure was calculated [Wal47]. Despite this long history, graphite still attracts continuous attention in research as illustrated by the following examples:

- As shown in Fig. 4.1, thin graphite films exhibit a strong electric-field effect which demonstrates their potential for nanoelectronics: Due to the higher charge carrier density, they permit much higher current densities and shorter screening lengths than doped semiconductors and may lead to the construction of smaller and faster devices [Nov04].

- Graphite serves as a model system for metallic carbon nanotubes, particularly in terms of electrons around the Fermi edge and optical phonons which strongly couple to the electrons [Pis04, Mau04]. These phonons have quantum energies of up to 0.2 eV and are believed to decrease the dc conductivity of carbon nanotubes when high electric fields are applied [Jav04].
In view of possible applications in electronics, further investigations are required on how the strongly coupled optical phonons (SCOPs) influence the transport and energy relaxation of electrons. Time-resolved THz spectroscopy (TRTS) is a promising experimental approach to this question. A visible pump pulse excites charge carriers in the sample and thus enables them to emit optical phonons. A subsequent THz pulse probes the electrons around the Fermi edge.

In addition, TRTS has never been applied to a semimetal. Before presenting the experimental results, some basics of graphite are summarized.

### 4.2. General Properties

Graphite is, like diamond, one of the modifications of carbon (C). The 4 valence electrons of a C atom can produce a great variety of chemical bonds which strongly influence the properties of the resulting material [Hak03]. In graphite, each C atom is sp² hybridized and the center of 3 covalent σ and π bonds to other C atoms. These atoms are arranged on a honeycomb lattice and form a sheet of so-called graphene. Van der Waals forces lead to weaker and longer bonds between adjacent graphene sheets and to the typical layered structure which is illustrated in Fig. 4.2(a). Figures 4.2(b,c) show that the ABAB... stacking sequence results in a hexagonal close packed (hcp) lattice structure with 4 carbon atoms in the unit cell.

The distance \(c_0/2 = 3.35\,\text{Å}\) of 2 adjacent graphene layers is significantly longer than the \(\sigma\)-bond length of 1.42 Å [Hol92]. The layered structure of graphite implies a corresponding pronounced anisotropy in macroscopic properties such as electric conductivity, optical response and elasticity.
4.3. Electronic Structure

Figure 4.2.: (a) Schematic of the graphite lattice which is a stack of honeycomb meshes of C atoms. A single mesh is also called a graphene sheet. (b) Magnified section of the graphite lattice together with lattice constants $a_0 = 2.46 \text{ Å}$ and $c_0 = 6.71 \text{ Å}$. The graphene layers are stacked in an ABAB… sequence. (c) Possible hexagonal elementary cell containing the 4 atoms 1, 2, 3, and 4. Lattice basis vectors $b_1$, $b_2$, and $b_3$ are also shown where $b_3$ is parallel to the $c$ axis. One has $|b_1| = |b_2| = a_0$ and $|b_3| = c_0$. Parts of this figure were taken from [Hag05a].

4.2.1. Highly Oriented Pyrolytic Graphite

Synthetic graphite is produced by pyrolysis where gaseous hydrocarbons are thermally cracked. The resulting carbon gas covers a substrate in layer-by-layer growth while a substrate temperature of more than 2500$^\circ$C induces the $sp^2$ hybridization of the C atoms. The subsequent application of high pressures and temperatures results in so-called highly oriented pyrolytic graphite (HOPG) which is the material investigated in this chapter.

HOPG consists of graphite crystallites with linear dimensions of a few 10 $\mu$m perpendicular and a few 10 nm parallel to the $c$ axis [Ohl97]. All crystallites have their $c$ axes in the same direction but are rotated around their individual $c$ axis randomly.

4.3. Electronic Structure

In order to analyze the data presented in this chapter, knowledge on the electronic structure of graphite around the Fermi edge is required. The graphene model of the graphite band structure is sufficient for a qualitative argumentation whereas the more sophisticated model of Slonczewski, Weiss, and McClure (SWM) is used for the numerical simulations.
4. Graphite: Strongly Coupled Optical Phonons in Action

4.3.1. Graphene: Tight-Binding Model

In a first approach, the interaction between the graphite layers is neglected. It is then sufficient to consider only 1 graphene sheet. The sp² hybridization of the 2s and the 2pₓ, 2pᵧ and 2pᶻ orbitals leads to three sp² orbitals and one pᶻ orbital for the 4 valence electrons of a C atom where the z axis is perpendicular to the graphene sheet.

A σ bond between 2 adjacent C atoms is due to their well overlapping sp² orbitals and lowers the energy of the 2 participating electrons. The π bond is much weaker due to the smaller overlap of the pᶻ orbitals and, therefore, contains the electrons with the lowest excitation energies. For this reason, the bonding π and antibonding π* states mainly determine the electronic structure of graphite within a few eV around the Fermi energy.

In addition, the small overlap of the wavefunctions in a π bond does not significantly alter the pᶻ wavefunctions of the isolated atoms. Therefore, a tight-binding approach for the calculation of the band structure is promising in which the Bloch states are approximated by linear combinations of the pᶻ orbitals. Since the graphene unit cell contains two C atoms and since only 1 basis orbital is involved, solving the stationary Schrödinger equation yields 2 electronic bands [Dre88]

\[
\begin{align*}
\epsilon_{k\pi^*} & = \pm \frac{\gamma_0 w(k)}{1 \mp sw(k)} \\
\epsilon_{k\pi} & \approx \pm \frac{\sqrt{3}}{2} a_0 \gamma_0 |k_\perp - \Gamma X| \quad \text{with} \quad X \in \{K, K'\}.
\end{align*}
\]

with

\[w(k) = \sqrt{1 + 4 \cos^2(k_y a_0/2) + 4 \cos(\sqrt{3}k_x a_0/2) \cos(k_y a_0/2)}\]

which originate from the bonding π and antibonding π* states. As expected, the band structure depends only on the wavevectors \(k_\perp = (k_x, k_y, 0)\) perpendicular to the c axis. The interaction integral \(\gamma_0 = 3.03\) eV and overlap integral \(s = 0.13\) have been obtained by fitting Eq. (4.1) to ab-initio calculations [Sai98].

The resulting graphene band structure is plotted in Fig. 4.3 where valence and conduction band exhibit the typical conical shape near the only contact points K and K', that is

\[
\begin{align*}
\epsilon_{k\pi^*} & \approx \pm \frac{\sqrt{3}}{2} a_0 \gamma_0 |k_\perp - \Gamma X| \quad \text{with} \quad X \in \{K, K'\}.
\end{align*}
\]

As a consequence, the π band is completely filled in the ground state whereas the π* band is empty. Thus, the Fermi energy is \(\epsilon_F = 0\), and the Fermi surface merely consists of the HKH and H'K'H' edges of the graphite Brillouin zone in Fig. 4.3(a). The vanishing eDOS at \(\epsilon_F\) makes graphene a zero-gap semiconductor.

The graphene model provides a qualitative understanding of various properties of graphite, for example the rough location of the Fermi surface and the optical properties in the visible [Ped03]. It can also qualitatively explain the experimental data of this chapter. Moreover, a graphene sheet is a good starting point for modeling the electronic structure of carbon nanotubes (see Section 5.3). However, quantitative statements, especially about the electromagnetic response in the THz range, require a more detailed knowledge of the
4.3. Electronic Structure

Figure 4.3.: (a) Conventional hexagonal BZ of graphite. (b) Band structure of graphene. Due to the neglected coupling between the graphene sheets, the bands depend only on $k_x$ and $k_y$. The $\pi$ band is completely filled in the ground state and touches the empty $\pi^*$ band at the K and K' points where both bands have conical shape. The Fermi surface consists of the HKH and H'K'H' edges in panel (a). Parts of this figure were taken from [Hag05a].

low-energy electronic states which is provided by the model of Slonczewski, Weiss, and McClure (SWM).

4.3.2. Slonczewski-Weiss-McClure Model

In the graphene model of graphite, the $\pi$ bands are degenerate with respect to $k_z$, whereas for fixed $k_z$, a 2-fold degeneracy (without counting spin) remains which stems from the equivalence of non-interacting A and B graphene layers. Taking into account the layer-layer interaction lifts these degeneracies and splits the energy bands by up to 1 eV.

The SWM model is a semi-phenomenological band model of graphite and results in a $4 \times 4$ Hamiltonian that is compatible with the symmetries of the graphite lattice [Dre88]. It involves 7 free parameters which can be determined by fits to results of appropriate experiments or ab-initio calculations. The SWM model exploits that the Fermi surface of graphite lies in the proximity of the HKH and H'K'H' line in the BZ as suggested by the graphene model in Fig. 4.3. Here, we choose the alternative BZ shown in Fig. 4.6(a) which puts the Fermi surface in the zone center. Thus, the electron wavevectors of interest are

$$k = k_c + k_\perp = k_c + \Gamma X + \kappa \quad \text{with} \quad X \in \{K, K'\},$$

where $k_c = (0, 0, k_c)$ and $k_\perp$ are the $k$ components parallel and perpendicular to the $c$ axis, respectively. The small translation $\kappa$ is expressed in cylindrical coordinates as

$$\kappa = \kappa \begin{pmatrix} \cos \alpha \\ \sin \alpha \\ 0 \end{pmatrix}$$
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where $\alpha$ is the angle between $\kappa$ and $\overrightarrow{\Gamma K}$.

In the 1st step, the Bloch states $|k\rangle = |kb\rangle$ for all points $k_c + \Gamma X$ on the high-symmetry lines HKH and H'H' are determined by a tight-binding approach since the $p_z$ overlap of adjacent layers is small; this yields 4 states for each point. In the 2nd step, the $k \cdot \hat{\pi}$ method is applied to wavevectors slightly off the high-symmetry lines by rewriting the stationary Schrödinger equation $\hat{H}|k\rangle = \epsilon_k|k\rangle$ for the Bloch factors $u_k$ as [Pri91]

$$\hat{H}_k u_k = \epsilon_k u_k \quad \text{with} \quad \hat{H}_k = \frac{(\hat{\pi} + \hbar \kappa)^2}{2m_e} + \text{single-electron potential}.\quad (4.3)$$

By neglecting quadratic effects in $\kappa$, the Hamiltonian becomes

$$\hat{H}_k = \hat{H}_{k_c+\Gamma X} + \frac{\hbar}{m_e} \kappa \hat{\pi}.\quad (4.3)$$

In the basis of the tight-binding states $|k_c + \Gamma X, 1\rangle, \ldots, |k_c + \Gamma X, 4\rangle$, this finally gives the SWMeC Hamiltonian

$$H_k = \begin{pmatrix} E_1 & 0 & h_{13} & h_{13}^* \\ 0 & E_2 & h_{23} & -h_{23}^* \\ h_{13}^* & h_{23}^* & E_3 \\ h_{13} & h_{23} & 0 & E_3 \end{pmatrix} + \sigma \begin{pmatrix} 0 & h_{13} & h_{13}^* & 0 \\ 0 & 0 & h_{23} & -h_{23}^* \\ h_{13}^* & h_{23}^* & 0 & h_{33} \\ h_{13} & h_{23} & h_{33}^* & 0 \end{pmatrix}.\quad (4.4)$$

Its diagonalization leads to 4 states and 4 eigenenergies for each $k$ in the vicinity of the HKH or H'H' line; the eigenenergies for points lying exactly on this line ($\sigma = 0$) are

$$\begin{pmatrix} E_1 \\ E_2 \end{pmatrix} = \Delta \pm \gamma_1 \Gamma \quad \text{and} \quad E_3 = \frac{1}{2} \gamma_2 t^2$$

where the dimensionless parameters

$$\xi = \frac{k_z c_0}{2\pi}, \quad \Gamma = 2 \cos(\pi \xi), \quad \text{and} \quad \sigma = \frac{\sqrt{3}}{2} a_0 \kappa$$

have been introduced. The off-diagonal elements of the Hamiltonian are given by

$$h_{13} = (\mp \gamma_0 + \gamma_4 \Gamma) \frac{\exp(i\alpha)}{\sqrt{2}} \quad \text{and} \quad h_{33} = \gamma_3 \Gamma \exp(i\alpha)$$

where the 7 phenomenological parameters $\gamma_0, \ldots, \gamma_5$, and $\Delta$ can be estimated by tight-binding calculations which also elucidate their physical meaning. However, they have been determined by fits to various experimental results.

Like in graphene, $\gamma_0 = 3.16$ eV is the interaction integral of adjacent C atoms from the same layer; the interaction integral $\gamma_1 = 0.39$ eV of 2 adjacent C atoms from different layers is mainly responsible for the splitting of the originally multi-degenerate bands. These and all other values of the phenomenological parameters together with their interpretation can be
found in Ref. [Dre88]. They also fix the Fermi energy at $\epsilon_F = -0.024$ eV. Importantly, the momentum matrix elements projected on the $\kappa$ direction can be obtained by comparing Eqs. (4.3) and (4.4). They are essential for the calculation of the optical properties. As an illustration of the SWM model, Fig. 4.4 shows the band structure of graphite close to the HKH line and the resulting eDOS whose smallness at the Fermi energy makes graphite a semimetal. Computational details are described in Appendix C.1.

In summary, the semiphenomenological Hamiltonian (4.4) was developed by SWM to obtain the band structure and momentum matrix elements in the vicinity of the Fermi energy $\epsilon_F$ with 7 free parameters which have been determined by experimental data [Dre88]. It will be used extensively in the following to model the measured dielectric function of graphite between 1 and 30 THz.

### 4.4. Phonons and Their Coupling to Electrons

The strong sp$^2$-bonds and the low mass of the C atom lead to lattice vibrations of very high frequency as can be seen in Fig. 4.5 where phonon energies $\hbar \Omega_Q$ of up to 0.2 eV are found.

In general, electrons can partially screen the bare ion-ion interaction and thus soften the lattice vibrations in a solid. Such screening of a vibrational mode $Q = (r, q)$ requires virtual electronic transitions which have to conserve the electronic wavevector $k$ [Pis04, Ash76]. In graphite, the Fermi surface restricts the component $\Delta k_{\perp}$ of the change $\Delta k = \Delta k_e + \Delta k_{\perp}$ in the electronic wavevector to the vicinity of the $\Gamma$ and $K$ points, that is

$$\Delta k_{\perp} \approx KK = 0 \quad \text{or} \quad \Delta k_{\perp} \approx KK' = \Gamma K .$$

Figure 4.6 illustrates these intrapocket and interpocket transitions of the electrons. Therefore, only phonons with $q_{\perp}$ around $\Gamma$ or $K$ and strong coupling to the electrons can suffer...
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Figure 4.5: Dispersion curves \( \hbar \Omega_Q \) of the high-energy phonons in graphite taken from Ref. [Mau04]. Symbols (\( \bigcirc \) and \( \bullet \)) represent data taken by inelastic X-ray scattering whereas solid lines are fits to a force-constant calculation. The shaded areas at the \( \Gamma \) and \( K \) point are Kohn anomalies caused by the strong e-ph coupling of these phonon modes.

This is nicely seen in Fig. 4.5 where the \( \Gamma \) and \( K \) phonons of the highest energy exhibit kinks in their dispersion curves. These so-called Kohn anomalies are absent for all other modes with lower phonon energy since their e-ph matrix elements vanish as shown by density-functional theory calculations for graphene [Pis04]. In graphite, however, there should be some coupling to these modes due to dispersion along \( k_c \) [Ash76].

4.5. Optical Properties

No infrared-active phonon modes have been observed in graphite in the far- and mid-infrared [Pal91]. The main reason for this behavior is a very small static dipole moment of the nonpolar graphite lattice in contrast to ionic crystals like NaCl [Kim05]. This situation corresponds to a Lorentz oscillator where the particle interacting with the light has a very small charge, see Section 1.5.1.

The optical properties in the infrared and visible spectrum are dominated by electronic transitions. As explained in Section 1.6 and shown in Fig. 4.7, a Bloch electron can either absorb a photon by a direct optical transition (DOT) or by an indirect optical transition (IOT). As will be shown below, IOTs dominate the optical absorption in the far-infrared; both IOTs and DOTs are important in the mid-infrared, and DOTs dominate in the near-infrared and visible.
4.6. Experimental and Technical Details

4.6.1. Sample Preparation

The sample base material is a high-purity crystal of HOPG (quality ZYB, GE Advanced Ceramics) with a thickness of 2 mm along the c axis and a $12 \times 12$-mm$^2$ front surface area. The crystal is cleaved perpendicular to the c axis by means of sticky tape (tesa kristallklar, Beiersdorf AG) which is fixed to the crystal front surface. After careful removal from the crystal, graphite flakes are attached to the tape and used for the measurements. The area probed in the experiment is selected by transmission measurements at a wavelength of 780 nm in which the sample is put in the focus of the THz beam but with the Si filter removed. By using the formalism of Section 2.5.1, the local thickness of the graphite
film with a transverse spatial resolution better than 30 μm is determined. We exclusively choose graphite areas which show transmission changes less than 10% on an area larger than 0.2 × 0.2 mm².

For the pump-probe measurements, the sample is contacted to a diamond substrate, as sketched in Fig. 4.8(a). Otherwise, the thermal load of the sticky tape and the graphite would destroy the sample.

### 4.6.2. Sample Pumping and Probing

In all measurements, the THz beam is normally incident on the sample and thus probes the optical properties parallel to the graphite layers. In general, the graphite film should be as thick as possible to obtain phase shifts much larger than the phase drift of the spectrometer as discussed in Section 3.2.4. On the other hand, the sample thickness is limited since graphite absorbs light strongly. The 53-nm thick sample taken for the steady-state measurements is a good compromise. They were done without the diamond substrate which would introduce significant phase shifts between sample and reference signal owing to its thickness variations. We checked that the thickness variations of the sticky tape are negligible making this material a good reference sample.

In the pump-probe measurements, the pump beam is aligned such that pump and probe spot overlap on the sample. The angle between the pump and probe direction of propagation is smaller than 10° to excite all points of the probed sample spot within less than 40 fs. Using a graphite film thicker than the 33-nm penetration depth of the pump beam generates an inhomogeneous excitation profile

\[ P_\tau(z) = \frac{\Delta \varepsilon_\tau(z)}{\Delta \varepsilon_\tau(0)} \]  

which will rapidly change its shape due to transport processes, until a homogeneous profile \( P_\tau = 1 \) is established. This effect may complicate the extraction of the dielectric function from the data but can be circumvented by ensuring a homogeneous excitation profile immediately after sample excitation. For this purpose, we use a graphite film of only 17 nm thickness which results in \( P_{\tau=0^+} \approx 1 \) directly after excitation as shown in Fig. 4.8(b). The profile was calculated using the relation

\[ \Delta \varepsilon_{\tau=0^+}(z) \propto |E(\omega_{\text{pump}}, z)|^2 \]

which is valid for a 1-photon excitation process and small pump-induced changes \( \Delta \varepsilon_\tau(z) \) [Jas02]. The electric field \( E(\omega_{\text{pump}}, z) \) of the pump beam is given by Eq. (2.12) with \( \hbar \omega_{\text{pump}} = 1.6 \text{ eV} \).
4.6. Experimental and Technical Details

Figure 4.8: (a) Schematic of the graphite sample. The graphite film (2) is fixed to a diamond substrate (3) by sticky tape (1). The THz wave is normally incident on the sample and propagates along the $z$ axis which is parallel to the graphite $c$ axis. In the steady-state measurements, the diamond substrate is not used. (b) Calculated excitation profile for the sample in (a) with a 17-nm thick graphite film.

4.6.3. Data Analysis

As described in general in Section 3.4, the dielectric function of the unexcited and excited sample can be determined from the respective experimental data

$$Q(\omega) = \frac{S(\omega)}{S_{\text{ref}}(\omega)} \quad \text{and} \quad \Delta Q_\tau(\omega) = \frac{\Delta S_\tau(\omega)}{S_\infty(\omega)}.$$  

Here, $S$ is the THz signal of the sample in the steady state and $S_{\text{ref}}$ the reference signal without graphite; $\Delta S_\tau$ is the pump-induced signal at a delay $\tau$ after excitation, and $S_\infty$ the signal of the sample long after or before the arrival of the pump pulse.

Unexcited Sample

Figure 4.8(a) shows the structure of the sample. Although the beam propagates through the 3 layers 1, 2, and 3, “echoes” due to multiple reflections in the tape (1) and the diamond substrate (3) are outside the temporal window covered in the THz detection. Therefore, the sample can be seen as a film between 2 homogeneous half spaces, and Eq. (2.12) yields the response

$$R = \frac{E(d + d_3 + 0^+, \omega)}{E_{\text{inc}}(\omega)} = t_{01} \exp(ik_1d_1) \cdot A_3^+ \cdot \exp(ik_3d_3)t_{30}$$

of the 3-layer system in Fig. 4.8(a) where the 1st and the last factor account for a single transmission through layer 1 and 3, respectively. All quantities in this equation are defined in Section 2.5.1.

The response of the reference sample fulfills the same relation but with the transmission through graphite replaced by a single transmission through air (0), that is

$$R_{\text{ref}} = \frac{E_{\text{ref}}(d + d_3 + 0^+, \omega)}{E_{\text{inc}}(\omega)} = t_{01} \exp(ik_1d_1) \cdot \exp(ik_3d_3)t_{30} \cdot \exp(ik_0d).$$
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Division of the last 2 equations finally yields

\[
Q \exp(ik_0d) = A_3^+ = \frac{t_{12}t_{23}}{\exp(-i\delta) - r_{21}r_{23}\exp(i\delta)}
\]  

(4.6)

with \( \delta = kd \) being the phase shift of the graphite film. Note that a perfect cancelation of the phase factors only occurs when the thickness of tape and substrate is the same for both the sample and the reference measurement. For this reason, the steady-state measurements are done without diamond substrate, \( n_3 = n_0 = 1 \).

Equation (4.6) contains the desired \( \varepsilon = n_2 \) in the \( t_{ij} \) and \( r_{ij} \) terms and can in general be solved only numerically. However, in case of a thin layer 2, that is \( \delta = kd = \omega nd/c \ll 2\pi \), one can expand \( \exp(i\delta) \approx 1 + i\delta - \delta^2/2 \) up to 2nd order to obtain [Sch05]

\[
A_3^+ = Q \exp(ik_0d) = \frac{2n_1}{(1 - \delta^2/2)(n_1 + n_3) - i(n^2 + n_1n_3)\delta/n}
\]

which now allows to analytically solve for

\[
\varepsilon = \frac{-c}{\omega d} \frac{2n_1 \exp(-ik_0d)/Q + in_1n_3\omega d/c - n_1 - n_3}{i + (n_1 + n_3)\omega d/2c}.
\]

(4.7)

This “thin-film formula” is correct to the 2nd order in \( \delta \) and is an improvement of the 1st-order formula used in the literature [Ave02].

We use \( n_1 = 1.46 \) for the sticky tape as obtained by THz transmission measurements covering the spectral range from 1 to 3 THz and 10 to 30 THz whereas \( n_3 = 2.38 \) for diamond is taken from literature [Pal91].

Excited Sample

We do not observe a pump-induced optical anisotropy perpendicular to the graphite c axis since the signal does not change for different pump-beam polarizations (data not shown). Therefore, the response in this plane is determined by only 1 scalar dielectric function. Since the graphite film is much thinner than the probing wavelength we can apply Eq. (2.16), and the pump-induced change in the sample response is

\[
\Delta R_\Omega(\omega - \Omega) = \frac{\Delta E_r(d + 0^+,\omega)}{E_{inc}(\omega - \Omega)} = \frac{i\omega}{2cn_1(\omega)} R_\infty(\omega) R_\infty(\omega - \Omega) d\Delta \varepsilon_\Omega(\omega - \Omega).
\]

Here we have exploited that the graphite sample is homogeneously excited, and the response \( R_\infty \) of the unexcited sample is approximated by Eq. (2.14). According to Eq. (3.1), \( \Delta R_\Omega(\omega - \Omega) \approx R_\infty(\omega) \Delta Q_\Omega(\omega) \) which finally yields the pump-induced change

\[
\Delta \varepsilon_\Omega(\omega) = \frac{2cn_1(\omega + \Omega)}{i \cdot (\omega + \Omega) dR_\infty(\omega)} \Delta Q_\Omega(\omega + \Omega).
\]

(4.8)
4.7. Results: Unexcited Sample

By applying an inverse Fourier transformation with respect to $\Omega$, one obtains the the pump-induced change $\Delta \varepsilon_r(\omega)$ in the dielectric function at time $\tau$ after sample excitation. If the sample does not change too fast, one can set $\omega + \Omega \approx \omega$ leading to the quasistatic result

$$
\Delta \varepsilon_r(\omega) = \frac{2cn_1(\omega)}{i\omega dR_{\infty}(\omega)} \Delta Q_r(\omega).
$$

We found this relation to give results in good agreement with the more general Eq. (4.8) for $\tau > 0.1$ ps.

### 4.7. Results: Unexcited Sample

The following measurements of the sample in the steady state provide the parameters necessary to analyze the pump-probe measurements. The raw data of a steady-state measurement is shown in Fig. 4.9. Note that the graphite film introduces a very small phase shift but a significant amplitude decrease of the THz signal. The dielectric function is calculated according to Eq. (4.7); we start with a discussion of the 1-to-3-THz range.

#### 4.7.1. Dielectric Function Between 1 and 3 THz

The dielectric function $\varepsilon$ of graphite between 1 and 3 THz is shown in Fig. 4.10. Note that $\text{Re} \Delta \varepsilon$ is negative and increases with decreasing frequency. According to Section 1.6.1, this is a clear signature of free charge carriers. Indeed, intraDOTs and IOTs are expected to dominate the response in this frequency window since the SWM model together with Eq. (1.19) predicts negligible contributions of interDOTs as can be seen in Fig. 4.10. Technical details concerning this calculation are found in Appendix C.1.
4. Graphite: Strongly Coupled Optical Phonons in Action

![Graphite: Dielectric Function between 1 and 3 THz](image)

**Figure 4.10.** Measured dielectric function of graphite (O) between 1 and 3 THz together with a fit to the Drude model (thick solid line). The Drude contribution is expected to dominate the response since the theoretical contribution of interDOTs (thin solid line) is much smaller than the measured \( \varepsilon \). The dielectric function is the average of measurements on 3 different sample positions, and the error bars represent the resulting standard deviation.

We fit the dielectric function to the Drude formula (1.12) where the fit parameters are the plasma frequency \( \Omega_{pl} \) and the Drude scattering rate \( \Gamma \). The best fit is shown in Fig. 4.10 and obtained for the values

\[
\hbar \Omega_{pl} = 0.92 \text{ eV} \quad \text{and} \quad \Gamma = 10 \text{ THz}.
\]

The agreement with the values \( \hbar \Omega_{pl} = 0.44 \text{ eV} \) and \( \Gamma = 5 \text{ THz} \) found in Ref. [Phi77] is reasonable if one takes into account that they have been obtained by Fourier-transform infrared spectroscopy on naturally grown graphite and by subsequent application of the Kramers-Kronig relations.

Moreover, the measured plasma frequency of graphite agrees excellently with the theoretical value of 1.0 eV calculated here using Eq. (1.22), the SWM model, and an electronic temperature of 300 K. The plasma frequency is small compared to that of normal metals like Al with \( \hbar \Omega_{pl} = 9.2 \text{ eV} \) [Ash76] which is just a result of the small eDOS around the Fermi edge of the semimetal graphite.

The measured \( \Gamma \) and the band velocity (1.20) of \( \approx 1 \text{ nm fs}^{-1} \) at the Fermi edge [Dre88] imply a mean free path of \( \approx 100 \text{ nm} \) for the electrons moving parallel to the graphite layers. In other words, they pass more than 300 unit cells before collisions with obstacles have completely randomized their initial velocity. In contrast, the Fermi velocity of 2 nm fs\(^{-1}\) and the scattering rate of 125 THz in Al lead to a mean free path of only 20 nm [Ash76]. The reason for this behavior is again mainly the small density of states at the Fermi energy which restricts the number of possible electronic scattering events, see also Eq. (1.27).

### 4.7.2. Dielectric Function Between 8 and 27 THz

The dielectric function of graphite between 8 and 27 THz is shown in Fig. 4.11(a). It cannot be explained by the extrapolated Drude behavior found for the dielectric function between 1 and 3 THz since the imaginary part of the Drude tail remains way below that measured.
4.7. Results: Unexcited Sample

Figure 4.11: (a) Measured dielectric function of graphite (○) between 8 and 27 THz together with the fit (thick solid line) to Eq. (4.10). The dielectric function is the average of 5 measurements at different sample positions, and the error bars represent the resulting standard deviation. (b) Contributions of DOTs and IOTs to the fit to Im ε.

Therefore, now DOTs have to make a strong contribution to the light absorption, and we fit the dielectric function to

\[ \varepsilon^{\text{fit}} = \varepsilon^{\text{Drude}} + C \varepsilon^{\text{interDOT}} + \text{real offset.} \]  

(4.10)

\( \varepsilon^{\text{interDOT}} \) is calculated using Eq. (1.19), the SWM band model, and an electronic temperature of \( T_e = 300 \) K, for details see Appendix C.1. \( \varepsilon^{\text{Drude}} \) is given by the Drude formula (1.12) and Eq. (4.9). The only fit parameters are a real factor \( C \), which scales the contribution of the DOTs, and a real offset which accounts for optical transitions with resonances outside the frequency window considered.

The best fit result is shown in Fig. 4.11(a) and obtained for \( C = 0.65 \) and a real offset of 38. Figure 4.11(b) shows the respective contributions of IOTs and DOTs to Im ε. For \( C = 1 \) and above 20 THz, the imaginary part of the fit function would be significantly larger than the experimental result. This behavior is most likely due to local-field effects which are neglected in the theory of the dielectric function as mentioned in Section 1.5.4. They are roughly accounted for by the overall scaling factor \( C < 1 \).

In summary, DOTs and IOTs make comparable contributions to the absorption of electromagnetic radiation between 8 and 27 THz in graphite. This behavior is exploited for the time-resolved measurements where the DOTs serve as a “thermometer” of the electrons and the IOTs as a probe for the velocity relaxation of the electrons. In contrast, the absorption of visible probe pulses in graphite is mediated mainly by DOTs. They have been exploited to determine the distribution function of the electrons at very high fluences by time-resolved transmission and reflection measurements [Sei90].
4. Graphite: Strongly Coupled Optical Phonons in Action

Figure 4.12.: Raw data of the TRTS measurements of graphite for an absorbed fluence of 5 µJ cm\(^{-2}\).
(a) Gray-scale plot of the 2-dimensional pump-induced THz signal \(\Delta S_\tau(t)\). There is no signal for larger negative pump-probe delays \(\tau\) where the pump pulse arrives at the sample long after the probe pulse. At \(\tau = 0\), the center of pump and probe pulse arrive simultaneously at the sample, and the trailing part of the probe pulse \((t > 0)\) already sees an excited sample whereas the leading part \((t < 0)\) still does not. This behavior is marked by the white dashed diagonal line. (b) Line scan along line 1 where the local THz time is fixed at \(t = -12\) fs. (c) Line scan along line 2 for a constant pump-probe delay \(\tau = 0.5\) ps. The signal \(S_\infty(t)\) of the unperturbed sample is also shown and exhibits a phase shift of \(\approx 90^\circ\) with respect to \(\Delta S_\tau(t)\). (d) Relative change \(H_\tau/H_\infty - 1\) in the power of the transmitted THz pulse according to Eq. (4.11). There is a crossover from decreased to increased transmission at \(\tau \approx 1\) ps.

4.8. Results: Excited sample

4.8.1. Raw Data

Figure 4.12 shows the raw data \(\Delta S_\tau(t)\) of a TRTS experiment where the graphite film absorbs a pump fluence of 5 µJ cm\(^{-2}\) corresponding to a molar energy density of \(W_{\text{pump}} = 18\) J mol\(^{-1}\). The dashed diagonal line \(t + \tau = 0\) in the 2-dimensional gray-scale plot of \(\Delta S_\tau(t)\) in Fig. 4.12(a) defines the times when the pump pulse and the overlapping portion of the probe pulse arrive simultaneously at the sample.

A line scan along the vertical line \(t = -12\) fs is plotted in Fig. 4.12(b) and exhibits a fast signal rise and a decay on a ps time scale. The line scan along the horizontal line \(\tau = 0.5\) ps
is plotted in Fig. 4.12(c). The phase shift between $\Delta S_\tau$ and $S_\infty$ is $\approx 90^\circ$ indicating that the pump-induced sample response is dominated by dispersion, that is by $\text{Re } \Delta \varepsilon_\tau$. In this case, the excited sample induces phase shifts of the THz wave rather than amplitude decreases which are due mainly to $\text{Im } \Delta \varepsilon_\tau$.

Since the THz signal is roughly proportional to the electric field at the detector, the energy per THz pulse transmitted through the sample is roughly proportional to

$$H_\tau = \int dt \ S_\tau(t)^2.$$  

Therefore, $H_\tau/H_\infty - 1$ is approximately the pump-induced change in the THz power transmitted through the sample. It is plotted in Fig. 4.12(d) and reveals that the sample transmission decreases directly after excitation and later turns into an increased transmission. A spectral analysis is absolutely necessary to disentangle the processes causing this response.

### 4.8.2. Dynamics of the Dielectric Function and Model Fits

#### Dynamics of the Dielectric Function

The pump-induced changes $\Delta \varepsilon_\tau(\omega)$ in the dielectric function are calculated according to Eq. (4.8), and the results are plotted for 3 exemplary delays and for frequencies $\omega/2\pi$ between 10 and 26 THz in Fig. 4.13.

As already expected from the raw data, the real part dominates the optical response. Moreover, it is negative and decreasing towards higher frequencies which is the typical signature of a free-carrier response as detailed in Section 1.6.

The imaginary part of all spectra shows 2 remarkable features: For the lower frequencies, we find $\text{Im } \Delta \varepsilon_\tau > 0$ and thus increased absorption, whereas for the higher probe frequencies one has $\text{Im } \Delta \varepsilon_\tau < 0$ and thus decreased absorption. This behavior can be explained by the different response of DOTs and IOTs to a change in the electronic occupation numbers as depicted in the graphene band structure of Fig. 4.7: Exciting the sample with a visible pump pulse via a DOT transfers electrons from the valence band to the conduction band. After $\approx 0.5$ ps these hot electrons have thermalized and can be described by a Fermi-Dirac distribution with electronic temperature $T_e$ as has been revealed by time-resolved photoemission spectroscopy (TRPES) [Moo01]. The newly created electron-hole pairs block some of the originally possible DOTs in a range of $k_B T_e$ around the Fermi energy $\epsilon_F$ and decrease the absorption of photons $h\omega \sim k_B T_e$. However, the elevated electronic temperature enables additional IOTs thus leading to an increased THz absorption predominantly at the lower frequencies as suggested by Eq. (1.24). Therefore, the frequency dependence of $\text{Im } \Delta \varepsilon_\tau$ displayed in Fig. 4.13 reflects the interplay between DOTs and IOTs in graphite.
Figure 4.13: (a,b,c) Pump-induced change $\Delta \varepsilon_\tau$ in the dielectric function of graphite (○) between 10 and 26 THz for at various times $\tau$ after excitation. Thick solid lines are fits according to Eq. (4.10). The real part exhibits a typical free-carrier response which also dominates the imaginary part at the lower frequencies. At the higher frequencies, however, the negative $\text{Im} \Delta \varepsilon_\tau$ displays a decreased absorption induced by the blocking of DOTs. (d) Contributions of DOTs and IOTs to the fit to $\text{Im} \Delta \varepsilon_\tau$.

**Modeling of $\Delta \varepsilon_\tau$**

The band structure and Bloch states of the excited graphite sample are expected to remain unchanged upon excitation by the pump pulse since the molar excitation energy of $W_{\text{pump}} = 18 \text{ J mol}^{-1}$ is quite small. For example, this corresponds to only $10^{-4}$ pump photons per carbon atom and an increase of the total graphite temperature $T$ by

$$\Delta T = \frac{W_{\text{pump}}}{C}.$$  \hfill (4.12)

This corresponds to less than 3 K according to the total heat capacity of $C \approx 9 \text{ J mol}^{-1} \text{ K}^{-1}$ around $T = 300 \text{ K}$ [Nih03]. Moreover, we assume a thermalized electron system such that the electronic occupation numbers are given by a Fermi-Dirac distribution. The model dielectric function is the difference

$$\Delta \varepsilon_{\text{fit}} = \varepsilon_{\text{fit}}(T_e, \Omega_{\text{pl}}, \Gamma) - \varepsilon_{\text{fit}}(T_{\infty}, \Omega_{\infty}\text{pl}, \Gamma_{\infty})$$

where $\varepsilon_{\text{fit}}$ is the fit function (4.10) of the steady-state case. The fit parameters are now $T_e$, $\Omega_{\text{pl}}$, and $\Gamma$. For the unexcited sample, they are fixed to $T_{\infty} = 300 \text{ K}$, $\hbar \Omega_{\infty}\text{pl} = 0.92 \text{ eV}$,
4.8. Results: Excited sample

Figure 4.14: (a) Measured transient plasma frequency $\hbar \Omega_{pl}$ vs. electronic temperature $T_e$ together with a theoretical calculation based on Eq. (1.22) and the SWM model. (b) Velocity-weighted density of states $v^2D(\epsilon)$ and derivative $-\partial f/\partial \epsilon$ of the Fermi-Dirac function at an electronic temperature of $T_e = 300$ K. The width of $-\partial f/\partial \epsilon$ grows with $T_e$, and $v^2D(\epsilon)$ becomes larger beyond the Fermi energy $\epsilon_F$. Therefore the squared plasma frequency $\Omega_{pl}^2$, which is the area under the product curve $-v^2D(\epsilon) \cdot \partial f/\partial \epsilon$, increases as well.

and $\Gamma_\infty = 10$ THz. In this model, the electronic temperature completely determines the contribution of the interDOTs, whereas $\Omega_{pl}$ and $\Gamma$ parametrize the contributions of the remaining, Drude-like transitions.

As shown in Fig. 4.13, the fits excellently reproduce the experimental data. The temporal dynamics of the 3 fit parameters $T_e$, $\Omega_{pl}$, and $\Gamma$ are the main outcome of the preceding analysis and basis of the following discussions. For example, the decay of the electronic temperature is shown Fig. 4.15(a).

4.8.3. Plasma-Frequency Decay: Consistency Check

We start with considering the plasma frequency which is displayed versus the electronic temperature $T_e$ in Fig. 4.14(a). For delays $\tau > 0.5$ ps, it increases roughly linearly with electronic temperature. A similar rise was also observed for the plasma frequency along the c axis by electron energy loss spectroscopy [Jen91]. This behavior is typical for semimetals due to their strongly varying electronic density of states near the Fermi edge and is detailed in Fig. 4.14(b). In contrast, it does not occur in metals with their rather constant cDOS as already mentioned in Section 1.6.1.

Figure 4.14(a) moreover shows that the slope of the measured $\Omega_{pl}$ vs. $T_e$ agrees well with a theoretical prediction based on Eq. (1.22) and the SWM band structure. The absolute values deviate from those measured by less than 10%. This agreement demonstrates the consistency of our fit results. For delays $\tau < 0.5$ ps, $\Omega_{pl}$ vs. $T_e$ clearly leaves the linear trend. This finding indicates that the electrons have not sufficiently thermalized at this early stage after excitation as also seen in experiments employing TRPES [Moo01].
4. Graphite: Strongly Coupled Optical Phonons in Action

![Graphite: Strongly Coupled Optical Phonons in Action](image)

Figure 4.15.: (a) Temporal evolution of the electronic temperature $T_e$. The dashed line indicates the hypothetical $T_e$ decay if only cold SCOPs were involved; the solid line marks an exponential decay with a time constant of 5.4 ps. (b) Temporal evolution of the pump-induced excess energy $\Delta E_e$ of the electrons. Note that the initially deposited energy is much higher than that measured for delays $\tau > 0.5$ ps.

4.8.4. Temperature Decay: Ultrafast Generation of Few Optical Phonon Modes

The dynamics of the electronic temperature $T_e$ is shown in Fig. 4.15(a) for $\tau > 0.5$ ps since, according to the preceding section, the temperature concept does not make sense for earlier delays. $T_e$ vs. $\tau$ follows an exponential decay with a 5.4-ps time constant.

Ultrafast Phonon Heating

$T_e$ can be converted into the pump-induced excess energy of the electrons by

$$\Delta E_e = \int_{T_{\infty}}^{T_e} dT \, C_e(T)$$

where the electronic heat capacity $C_e$ used has been determined via the theoretical eDOS of graphite [Nih03]. Fig. 4.15(b) shows the temporal decay of the electronic excess energy $\Delta E_e$ featuring a remarkable result: Although the entire absorbed pump-pulse energy is initially deposited in the electron system, more than 90% (!) of this energy has left the electron system already 0.5 ps after sample excitation.

Only heat transfer to the graphite lattice can explain this finding, since, in contrast to other time-resolved experiments [Moo01], ultrafast transport does not occur in our thin and homogeneously excited sample. As mentioned in Section 4.4, electrons in graphite are solely scattered by phonons which have their wavevector component $q_\perp$ close to the \Gamma or K point of the Brillouin zone. Therefore, only a quite restricted phonon subset can directly dissipate the electronic energy and heats up. These hot phonons cool down by heat transfer to cold lattice modes via ph-ph coupling on a much longer time scale of $\sim 10$ ps.
4.8. Results: Excited sample

The latter time scale is suggested by the decay time of coherent lattice vibrations which can be generated by a short laser pulse [Mis00]. In this way, the hot phonons dictate the observed slow decay of $T_e$ with a time constant of 5.4 ps in Fig. 4.15(a).

The maximum temperature increase of the hot phonons can be estimated from the absorbed laser fluence as follows: Figure 4.6(b) shows that electrons of higher energy $\epsilon - \epsilon_F$ will emit or absorb phonons with a larger wavevector

$$|\Delta k_\perp| \approx \frac{|\epsilon - \epsilon_F|}{\gamma_0}$$

where $\gamma_0 \approx 3$ eV is the slope of the graphene bands. When we set the electron energy to half the pump photon energy, $|\epsilon - \epsilon_F| = \hbar\omega_{\text{pump}}/2 \approx 0.8$ eV, we obtain an upper limit of $|\Delta k_\perp|$ that corresponds to $\sim 10^{-1}$ of the diameter of the hexagonal BZ. Therefore, only $\sim 10^{-2}$ of all phonon wavevectors directly interact with the electrons. Accordingly, the heat capacity of the hot phonons is that of graphite reduced by the same factor. Therefore, the maximum temperature increase of the hot phonons is $\sim 10^2 \cdot \Delta T \sim 100$ K where $\Delta T \approx 3$ K is the expected final temperature increase of the excited graphite, see Eq. (4.12).

This estimate is in good agreement with the experimental data in Fig. 4.15(a). Thus, our measurements reflect the ultrafast generation of hot phonons and their subsequent slow cooling.

**SCOPs Dominate the Energy Transfer**

As seen above, the phonons cool the laser-excited electrons within 0.5 ps although only $\sim 10^{-2}$ of all phonon wavevectors directly take part in this process.

We now show that the SCOPs dominate the energy loss of the electrons by employing the following gedankenexperiment: Since cold phonons result in a faster electron cooling than hot phonons, we first assume the SCOPs to be cold and the only lattice modes interacting with the electrons. We use the 2-temperature model of Section 1.3.2 and the theoretical matrix elements of e-ph coupling in graphite to calculate the temporal decay of $T_e$; technical details are described in Appendix C.2. With a fixed phonon temperature of 300 K and an initial electronic temperature of 380 K at $\tau = 0.5$ ps, we obtain the dashed curve in Fig. 4.15(a). Note that this hypothetical decay is much faster than that measured. Therefore the assumption of cold SCOPs at $\tau = 0.5$ ps has to be wrong, and we have found further evidence for ultrafast phonon heating. It should be noted that other $\Gamma$ and K phonons in graphite lead to similar decay curves only if comparable or even larger e-ph matrix elements are assumed, which is in contradiction to theoretical results [Pis04].

In summary, the electron cooling within only few 100 fs is dominated by the generation of hot SCOPs. It proceeds significantly faster than in doped semiconductors [Els89, Pel98] as a consequence of the strong e-ph coupling and the large phonon quantum energies of up to 0.2 eV. Metals also can dissipate the electronic energy quickly but this is due to their large Fermi surface which involves the generation of all phonon wavevectors. The slow decay of $T_e$ back to 300 K provides an estimate of the SCOP lifetime of 5.4 ps.
4. Graphite: Strongly Coupled Optical Phonons in Action

![Graph](image.png)

**Figure 4.16.:** Pump-induced changes $\Delta \Gamma$ in the Drude scattering rate ($\bigcirc$) vs. electronic temperature $T_e$. Velocity relaxation of the electrons due to scattering with the SCOPs can explain a significant part of the observed striking increase of $\Delta \Gamma$ as shown by the calculated $\Delta \Gamma^{e-SCOP}$.

### 4.8.5. Drude Scattering Rate

While $\partial T_e/\partial \tau$ is a measure of electronic energy relaxation, the classical Drude rate $\Gamma$ quantifies the decay of an electronic current when the driving electric field is switched off, see Section 1.5.1. In Fig. 4.16, $\Gamma$ shows a remarkable increase from $\Gamma_\infty = 10$ THz by more than 3 THz, although $T_e$ has increased by less than 80 K. This is in contrast to comparable measurements on n-doped InAs where similar electronic temperatures but an order of magnitude smaller effect on $\Gamma$ were found [Els89].

What processes cause this significantly different behavior in graphite? As detailed in Section 1.6, the Drude absorption is due to IOTs which require some wavevector source. Among these, phonons are more sensitive to temperature changes than impurities. We calculate the contribution of the SCOPs to the increase of $\Gamma$ with electronic temperature $T_e$ by using Eq. (1.24), the SWM band structure (4.4), and the e-ph matrix elements from DFT calculations [Pis04]. Moreover, the SCOP occupation numbers are assumed to follow the Bose-Einstein distribution (1.5) at a temperature that equals the instantaneous electronic temperature $T_e$. Computational details are described in Appendix C.3. The result of this calculation is shown in Fig. 4.16. It demonstrates that the hot optical phonons can explain about 25% of the observed increase of the current relaxation rate although their occupation numbers are still small at 380 K. The reason is mainly the strong coupling between SCOPs and electrons. Dominating contributions to $\Delta \Gamma$ by other phonons near $\Gamma$ and $K$ are not expected, since they are only weakly coupled to the electronic system [Pis04].

The question arises why the measured $\Delta \Gamma$ is even larger than the calculated SCOP contribution.

1. The theoretical curve in Fig. 4.16 should be considered as a lower limit of the true contribution $\Delta \Gamma^{e-SCOP}$ of the SCOPs to $\Delta \Gamma$ since the theory used is expected to underestimate the current relaxation. As discussed in Section 1.7, it does not account for IOTs where the photon changes the electron Bloch state. However, in graphite, resonant intermediate states in other bands can make additional contributions [Dum61]. Furthermore, IOTs involving more than 1 phonon are not accounted for.
2. As mentioned in Section 1.7, electron-electron (e-e) scattering is suggested to be quite effective in graphite. Assuming that the contribution of e-e scattering is the remaining contribution to the observed $\Delta \Gamma = \Delta \Gamma^{\text{e-SCOP}} + \Delta \Gamma^{\text{e-e}}$ and using [Mal79, Kav84]

$$\Gamma^{\text{e-e}} = AT_e^2$$

one obtains $A = 3.7 \cdot 10^7 \text{s}^{-1} \text{K}^{-2}$. This value is about 1 order of magnitude larger than those reported for noble metals [Kav84] which is a reasonable result: First, e-e interaction in graphite is much less screened than in noble metals due to the lower electron density. Second and in contrast to quasifree electrons, the band structure of graphite allows to change the total band velocity of 2 colliding electrons without involving umklapp processes [Mal79, Kav84], see Section 1.7. In contrast, n-doped InAs exhibits only 1 parabolic band around $\epsilon_F$ and shows a much smaller increase of the Drude scattering rate under excitation conditions similar to our experiment [Els89]. Thus, our results are consistent with strong e-e scattering as a further source of current relaxation in graphite.

4.9. Conclusion and Outlook

The ultrafast dynamics of optically excited charge carriers in graphite have been investigated by time-resolved THz spectroscopy. We find an ultrafast energy transfer from the excited electrons to only few strongly coupled optical phonon (SCOP) modes within 0.5 ps. The decay of the resulting nonequilibrium population of hot phonons provides an estimate for the lifetime of these vibrational modes of 5.4 ps. Their occurrence was not considered in previous reports on carbon nanotubes where a fast and slow decay of the measured signal was assigned to e-e and e-ph coupling, respectively [Her00, Zam05]. Our work, however, underlines the importance of hot optical phonons which also contribute significantly to the striking increase of the Drude scattering rate. Therefore, they might limit the performance of carbon nanotubes circuits not only at high electric fields [Jav04], but also at elevated temperatures and high frequencies. We expect the electronic energy relaxation by those strongly coupled optical phonons to play an important role also in other areas like phonon-mediated surface chemistry [Bon99]. The selective excitation of only few phonon modes may influence the desorption dynamics and products remarkably.

Future experiments will involve the amplified laser system to measure the THz response of graphite at much higher pump fluences. It is an interesting question how the electron dynamics changes close to the melting point [Mal86].

A possible experiment to isolate the significance of e-e scattering in the velocity relaxation would employ a sample of n-doped graphite with completely filled $\pi^*$ valence bands. Then electrons from bands of only positive curvature should be involved in an e-e collision, and the total electron velocity should change much less than in undoped graphite.
4. Graphite: Strongly Coupled Optical Phonons in Action
5. Carbon Nanotubes: Excitons, Localized and Delocalized Carriers

In this chapter, the mid-infrared response of an optically excited carbon-nanotube film is investigated. In contrast to graphite, the data lack a free-carrier response which clearly indicates that strongly bound excitons are the main product of optical excitation in the tubes with energy gaps in the eV range. We find a spectral feature of enhanced transmission which originates from blocked optical transitions in tubes having a small or vanishing energy gap. A featureless background of increased absorption shows a large optical anisotropy and provides direct evidence for the localization of charge carriers on a length scale of $\sim 100 \text{ nm}$.

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5.1. Motivation

Single-wall carbon nanotubes (NTs) are hollow cylinders made of carbon atoms. Since their discovery in 1991, they have attracted an enormous attention in fundamental and applied research due to their unique properties [Avo04]:

- NTs have a tensile strength many times that of carbon steel, are thermally stable at temperatures of more than 1000 $\text{°C}$ in air, and have a thermal conductivity comparable to that of diamond. As a strongly bonded covalent material, they typically show only few defects.

- They are close to a true 1-dimensional system since their diameters are typically only 1 to 3 nm but they can be millimeters long. Thus, they constitute a playground for probing the properties of 1-dimensional solids.

- Depending on their geometry, NTs can be semiconducting with an electronic energy gap of $\sim 1 \text{ eV}$ or nearly metallic. For example, the semiconducting tubes can be employed to build a NT-based field-effect transistor as shown in Fig. 5.1. Soon the gate size of such devices is expected to be smaller than that of current silicon-based transistors. Moreover, NTs feature a high threshold for electrical breakdown.
5. Carbon Nanotubes: Excitons, Localized and Delocalized Carriers

Figure 5.1: Illustration of NT field-effect transistor, taken from Ref. [Avo04]. The gate voltage is applied between the metallic gate and the conducting silicon substrate. It can switch the conductance between the source and drain electrodes on and off.

In order to realize the great potential of NTs in future nanoelectronics, a comprehensive knowledge of the charge-carrier dynamics in NTs is essential. As mentioned in the introduction to this work, time-resolved THz spectroscopy is a promising approach to this issue.

5.2. General Properties

Figure 5.2 illustrates that NTs can be understood as a rolled-up graphene sheet having lattice basis vectors $b_1$ and $b_2$. The 2 integers $n_1$ and $n_2$ characterize the wrapping or chiral direction $n_1 b_1 + n_2 b_2$ and therefore completely determine the resulting NT as well, for example its diameter $d_{NT} = |n_1 b_1 + n_2 b_2|/\pi$ [Sai98]. There is still a discrete translational symmetry along the tube axis but the size of the 1-dimensional unit cell depends on $(n_1, n_2)$ and can be considerably larger than the diameter of the hexagonal unit cell of graphene. Consequently, the Brillouin zone (BZ) is also 1-dimensional, and its wavevectors $k$ refer to the direction parallel to the tube axis.

There are several methods to produce NTs. The NTs investigated in this work have been produced by the high-pressure carbon monoxide (HiPCO) method [O'C02] which employs gaseous Fe(CO)$_5$ and CO at $\approx 1000$ °C under high pressure. In this reaction, Fe(CO)$_5$ dissociates, and the resulting Fe clusters initiate the growth of NTs where the C atoms derive from the disproportionation of CO. Finally, the HiPCO material is purified to remove catalyst particles.

5.3. Electronic Structure

The NTs investigated in this work have a length of a few 100 nm. Their much smaller diameter of $d_{NT} \approx 1$ nm leads to remarkable quantum-size effects in the electronic structure.
5.3. Electronic Structure

Figure 5.2.: Structure of carbon nanotubes. They can be thought of as rolled-up sheets of graphene where the chiral vector $n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2$, with $n_1$ and $n_2$ being integers, entirely determines the wrapping direction. Depending on $(n_1, n_2)$ the resulting tube is semiconducting or metallic. This figure was taken from Ref. [Hag05a].

Figure 5.3.: Electronic band structure of NTs derived from that of a graphene sheet. The NT geometry restricts the allowed wavevectors to a series of lines in the $(k_x, k_y)$ space of graphene. Each line leads to a 1-dimensional subband in the $k$ space of the NT where $k$ is the wavevector along the NT axis. If at least 1 of these lines crosses the K or K' point, a metallic NTs without an energy gap is obtained; otherwise, the NT is semiconducting. The resulting eDOS exhibits van Hove singularities at energies where the bands have vanishing slope. This figure was taken from Ref. [Hag05a].
5. Carbon Nanotubes: Excitons, Localized and Delocalized Carriers

5.3.1. Single-Particle Picture

In a single-electron approach, one can employ tight-binding schemes as done in Section 4.3.1 for graphite to determine the electronic band structure of a NT. The simplest approach relies on the graphene bands where the NT geometry allows only for a subset of the graphene wavevectors \( \mathbf{k} \) \[Sai98\]:

- The wavevectors \( k \parallel \) to the tube axis are given by the 1-dimensional BZ of the NT under consideration.
- The wrapping of the graphene sheet is taken into account by periodic boundary conditions for the electron wavefunctions along the wrapping direction \( n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 \) which allows only for certain graphene wavevectors \( k \perp \) to the tube axis.

This so-called zone folding is demonstrated in Fig. 5.3 for 2 different NTs and shows how the geometrical structure can make a NT semiconducting or metallic. Within this framework, it generally can be shown that NTs with \( n_1 - n_2 \notin 3\mathbb{Z} \) are “large-gap NTs” since they are semiconducting with an energy gap of about 1 eV for tube diameters of \( \approx 1 \) nm. The remaining “NTs are metallic. Consequently, 2/3 of all NT types \( (n_1, n_2) \) are large-gap NTs. The electronic density of states (eDOS) in Fig. 5.3 features so-called van Hove singularities which arise from the vanishing slope of 1-dimensional energy bands \[Sai98\].

The graphene-based model does not take into account the curvature of the graphene sheet which modifies the overlap of adjacent \( p_z \) orbitals. More sophisticated tight-binding calculations \[Din02\] show that this curvature introduces additional small band gaps in all metallic NTs apart from the \((n, n)\) “armchair” tubes. These “small-gap NTs” with \( n_1 - n_2 \in 3\mathbb{Z} \) and \( n_1 \neq n_2 \) exhibit band gaps of \( \sim 20 \) meV for tube diameters of \( \approx 1 \) nm as found by scanning tunneling spectroscopy \[Ouy01\].

Strong curvature can also induce an appreciable hybridization of the \( \sigma \) and \( \pi \) bonds between the carbon atoms. Taking this effect into account makes the originally large-gap \((5, 0)\) NT metallic \[Spa04\]. In addition, environmental perturbations, for example by other NTs in NT ropes, a surrounding solution, or a substrate, can further modify the electronic structure and even open energy gaps \[Del98\].

5.3.2. Many-Body Effects

Compared to 3-dimensional solids or quasi-2-dimensional solids like graphite, the e-e interaction is expected to be much stronger in the quasi-1-dimensional NTs: In a somewhat...
naive picture, the electrons simply cannot “circumvent” each other as they can in higher-dimensional solids.

The picture of independent electrons breaks down at least in the large-gap NTs since there the Coulomb interaction is only weakly screened compared to the small-gap and metallic NTs. As a consequence, electrons and holes form strongly bound excitons with binding energies of up to 1 eV [Spa04]. This is in contrast to 3-dimensional semiconductors like GaAs where exciton binding energies of less than 10 meV are found [Mad78]. The energy spectrum of an exciton is similar to that of a hydrogen atom with discrete energy levels below and a continuum of levels above the binding energy.

The existence of excitonic resonances in NTs has been indicated by several experiments such as 2-photon fluorescence spectroscopy [Wan05] or pump-probe transmission measurements [Kor04]. This work provides additional strong evidence that excitons are the main product of photoexcitation of large-gap tubes.

Remarkably, excitons can also occur in metallic NTs although screening of the e-e interaction is much more effective there. For example, the (3, 3) tube turns out to be metallic both in a tight-binding approach and a combined approach based on density-functional theory and many-body perturbation theory [Oni02]. The latter approach, however, additionally predicts 1 bound excitonic state which has a binding energy of ≈ 0.1 eV and is embedded in a continuum of single-electron excitations [Spa04]. Nevertheless, the single-particle picture is expected to remain virtually valid in the small-gap and metallic tubes because screening by free electrons greatly reduces the Coulomb interaction in these systems [Rub05].

5.3.3. Impurity-Induced Carrier Localization

A point-like impurity or defect in a 1-dimensional solid represents a more serious perturbation than in a 3-dimensional solid: As shown in Fig. 5.4, defects in quasi-1-dimensional NTs can lead to the confinement of the electron wavefunction between these defects. Such a localization strongly decreases the dc conductivity of the NT since the conduction electrons have to “hop” over all barriers to get from the start to the end of the 1 dimensional conductor [Dyr00].

Scanning tunneling spectroscopy revealed that the dc conductance of a HiPCO-grown NT decreases exponentially as $\exp(-l_{NT}/l_{loc})$ with the NT length $l_{NT}$ rather than linearly [GN05]. This was assigned to the regime of strong Anderson localization and allowed for the extraction of the electronic localization length of $l_{loc} \approx 200$ nm. This value is verified within this work based on simple geometrical arguments.

When electric fields of higher frequencies $\omega$ are applied, each electron merely oscillates around a fixed position with a spatial amplitude of $\sim v_F/\omega$ where $v_F$ is the band velocity averaged over the Fermi surface. The defect-induced barriers do not play a role any more, if their distance $l_{loc}$ is much larger than this amplitude or, equivalently [Mau94],

$$\omega \gg \omega_{loc} := \frac{v_F}{l_{loc}}.$$
Using $v_F = 10^6 \text{ m s}^{-1}$ [Sai98] and $l_{\text{loc}} = 200 \text{ nm}$ [GN05] yields $\omega_{\text{loc}}/2\pi \approx 1 \text{ THz}$ for HiPCO tubes. Far above this frequency, localization effects are not expected to affect the absorption of light. However, it can influence the real part of the dielectric function via the Kramers-Kronig relations.

5.4. Phonons

When a graphene sheet is rolled up to a NT, the changed symmetry leads to new fundamental lattice vibrations such as twisting or radial breathing modes [Sai98]. However, the graphene and graphite phonons with their high quantum energies are still present in the resulting NT. Theory even predicts that the strong coupling between the electrons and the high-energy phonons in graphene and graphite is inherent in the NTs as well [Pis04]. As shown for graphite in Chapter 4, these strongly coupled optical phonons (SCOPs) are expected to influence the energy and velocity relaxation of electrons also in NTs substantially. For example, the decrease of the dc conductivity of a metallic NT at high applied electric fields has been attributed to the emission of SCOPs [Jav04, Pop05].

5.5. Optical Properties

The transmission spectrum of a film of bundled NTs is shown in Fig. 5.5. Here, the phonon lines are nearly invisible but show up if the spectrum between 500 and 1900 cm$^{-1}$ is magnified [Kim05]. The broad peak labeled $E_{00}^{\text{sg}}$ at $\approx 200 \text{ cm}^{-1}$ has been assigned to optical transitions across the curvature-induced band gap of the small-gap tubes [Itk02, Uga99]. This frequency corresponds to an energy of 25 meV which nicely agrees with measurements of the energy gap of comparable NTs by scanning tunneling spectroscopy [Ouy01].

The peaks $E_{11}^{\text{lg}}$, $E_{22}^{\text{lg}}$, and $E_{11}^{\text{sg}}$ in the visible spectral range were first attributed to optical transitions that symmetrically connect the van Hove singularities above and below the Fermi energy in the metallic and small-gap (sg) and large-gap (lg) NTs [Hag03]. However, these peaks rather arise from excitons as has been demonstrated by 2-photon luminescence spectroscopy [Wan05].
5.6. Ultrafast Dynamics in Optically Excited Carbon Nanotubes

The charge-carrier dynamics in optically excited NTs has been probed by several techniques such as pump-probe transmission experiments [Man05, She05, Ma05], TRPES [Her00], and time-resolved fluorescence [Hag05b, Wan04]. These experiments employed visible probe
pulses and mainly studied the exciton dynamics in large-gap tubes leading to the following picture:

1. As illustrated in Fig. 5.7(a), a pump pulse of appropriate photon energy resonantly populates the excitonic band $E_{22}^{lg}$ in a large-gap tube. The peak of this population rapidly shifts to the $E_{11}^{lg}$ band with a 40-fs time constant followed by efficient energy transfer to strongly coupled optical phonons [Man05, Rub05]. This point will be again discussed in Section 5.9.4.

2. The interaction between two $E_{11}^{lg}$ excitons can lead to the annihilation of the 1st exciton and the promotion of the 2nd exciton to an excited state [Ma05]. The rate of such exciton-exciton annihilation strongly depends on the exciton density and should play a minor role at lower exciton densities. The decay of the remaining excitons is not yet completely clear but time-resolved fluorescence suggests that defect-induced trap states play an important role in this process [Hag05b].

3. In NT bundles, an additional effective decay channel opens up: $E_{11}^{lg}$ excitons can tunnel into adjacent small-gap and metallic tubes where the resulting electrons and holes relax efficiently via phonon emission. This is suggested by the absence of fluorescence from NT bundles [O’C02, She05].

However, there are much less reports on the dynamics in small-gap and metallic tubes: Probing NT mats by time-resolved photoemission spectroscopy (TRPES) also revealed dynamics on a subpicosecond- and picosecond-time scale. Remarkably, although not explicitly mentioned in that report, a loss of $\approx 90\%$ of the energy of the excited electrons within 0.5 ps was found in Ref. [Hag04] in complete analogy to the findings in Chapter 4. This is not surprising in view of the the strongly coupled optical phonons of graphite which are also present in NTs, see Section 5.4.
5.7. Experimental and Technical Details

Figure 5.7.: (a) Excitation scheme of a large-gap NT. The pump pulse resonantly populates the 2nd excitonic band $E_{22}$. (b) Excitation and probing scheme of a small-gap NT together with a magnification of the region around the Fermi edge. The pump pulse creates electrons and holes which subsequently relax to the vicinity of the small gap. The different electronic occupation numbers are represented by various gray scales.

Figure 5.8.: (a) Topography of the NT sample taken with an atomic force microscope. The image reveals that the NT axes are bent with a mean radius of curvature of $\sim 100$ nm. (b) Side view of the NT film obtained by scanning electron microscopy. The thickness of the film is about 800 nm. The images have been provided by Carla Aguirre (École Polytechnique de Montréal).

5.7. Experimental and Technical Details

5.7.1. Sample Preparation

The NT sample was prepared by Carla Aguirre (École Polytechnique de Montréal) similar to the procedure described in Ref. [Wu04]. First, HiPCO NTs (Tubes@Rice) are dispersed in a 2%-sodium-cholate solution. Centrifuging results in a supernatant that is used to produce a suspension that contains a substantial amount of isolated NTs surrounded by sodium cholate molecules. After vacuum-filtering onto a filtration membrane and washing away the surfactant with purified water, the membrane is dissolved, and the remaining NT film is transferred to a diamond substrate. Finally, the film is annealed at 600°C under a constant flow of argon for 1 hour to remove most of the remaining contaminants.

Figure 5.8(a) shows an image of the sample surface taken by an atomic force microscope. Note that the NT axes are bent with a mean radius of curvature of 100 nm. Moreover, the NTs are preferentially oriented parallel to the sample surface and, to some extent, isolated.
from each other. Figure 5.8(b) has been obtained by scanning electron microscopy and reveals that the NT film has a thickness of $d \approx 800 \text{ nm}$. The sample contains all types of nanotubes with a diameter distribution that extends from about 0.8 to 1.2 nm [Hag03].

The optical transmission spectrum of the NT film in Fig. 5.9 looks quite similar to that of the NT solution the film is made from. In particular, the $E_{22}^{lg}$ excitonic resonances of the various tube types are still but less visible which is due to a higher degree of tube bundling [Hag05a]. Figure 5.9 also shows that the pump photon energy is located directly in the $E_{22}^{lg}$ cluster.

The power transmission of the NT film at an 800-nm wavelength is $T = 0.25$. It can be used to estimate the space filling factor $F$ of the NTs since it is related to the number density $n_C$ of the C atoms by $T = \exp(-\alpha n_C d)$ with $\alpha \approx 0.5 \cdot 10^6 \text{ cm}^2 \text{ mol}^{-1}$ [Isl04]. The resulting density $n_C = 0.035 \text{ mol cm}^{-3}$ is a factor $F = 0.27$ less than the theoretical close-packing density of 0.13 mol cm$^{-3}$ of NTs with a 1-nm diameter [Sai98].

### 5.7.2. Sample Pumping and Probing

The pump-and-probe geometry of the NT sample is the same as that of the graphite sample as described in Section 4.6.2. Note that the NT film is substantially thicker than the penetration depth of the pump pulse since the power transmission of the sample is only $T = 0.25$. Although leading to an inhomogeneous excitation profile, this is not a complication here: In contrast to graphite in Section 4.6.2, ultrafast transport processes into the depth of the NT film are not expected since the NTs are preferentially oriented parallel to the sample surface. Therefore, the excitation profile (4.5) does not change on the picosecond scale which is the time scale of interest here.

The probe polarization is parallel to the optical table which corresponds to the $x$ axis in Fig. 5.10(b). Probing the sample along the $y$ direction was achieved by keeping the probe polarization along $x$ and instead turning the pump polarization by 90°.
5.7. Experimental and Technical Details

**Figure 5.10.** (a) A bent NT can be understood as a chain of nanocylinders (NCs). (b) The orientation of a NC in the reference frame is determined by 2 angles, the azimuth \( \phi \) and the zenith \( \theta \). In the experiment, both pump and probe beam propagate along the \( z \) axis, that is normally to the sample surface. The probe beam is polarized along the \( x \) axis, whereas the pump beam is either polarized along the \( x \) or \( y \) axis.

**5.7.3. Data Analysis**

The NT film investigated here consists of nanoparticles that are embedded in a host material. Therefore, its dielectric function varies on a microscopic length scale, and the relation to the measured quantities in THz spectroscopy is more involved. Moreover, the NTs are bent, and there are different types of NTs with different optical properties. The situation becomes even more complicated after excitation by a pump pulse which produces additional anisotropies and inhomogeneities.

However, as mentioned in Section 1.4.1, the macroscopic optical polarization \( \mathbf{P} \) is obtained by spatially averaging the microscopic polarization over a length scale \( l_{\text{avg}} \). Since many NTs are contained in the averaging volume \( V_{\text{avg}} = l_{\text{avg}}^3 \), the probe light “sees” an effectively homogeneous and isotropic sample with an effective susceptibility \( \chi^{\text{eff}} \). This is the basis of the so-called effective medium approach.

In order to derive the effective susceptibility of both the unexcited and excited NT film, we consider a long bent NT as a chain of independent short straight nanocylinders (NCs) as shown in Fig. 5.10(a). If the relevant length scales fulfill the relation

\[
\text{radius of curvature of bent NT} \gg \text{NC length} \gg \text{NT diameter},
\]

each NC can be considered as a NT with corresponding properties. This condition is certainly fulfilled for a cylinder length of, for instance, 20 nm. Moreover, the NCs are assumed to be oriented randomly.

**Steady State**

The NT film is made of various sorts of NCs. Each sort \( s \) occupies the volume fraction \( F^s \) and has the diagonal susceptibility tensor \( \chi^s = \text{diag} \left( \chi^s_\parallel, \chi^s_\perp \right) \) where \( \chi^s_\parallel \) and \( \chi^s_\perp \) are the susceptibilities parallel and perpendicular to the NC axis. The depolarization tensor of this NC is simultaneously diagonal, \( L^s = \text{diag} \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \) [Kit96]. The host material “h”
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filling the space between the NCs is assumed to consist of spheres with scalar susceptibility $\chi^h$ and depolarization tensor $L^h = \text{diag} \left( \frac{1}{3}, \frac{1}{3}, \frac{1}{3} \right)$ [Kit96]. Then the effective-medium approximation results in an equation for the effective scalar susceptibility $\chi^{\text{eff}}$ [Noh91],

$$9(F - 1) \frac{\chi^{\text{eff}} - \chi^h}{2\chi^{\text{eff}} + \chi^h} = \sum_s F^s \left( 4 \frac{\chi^{s\parallel} - \chi^{s\perp}}{\chi^{\text{eff}} + \chi^{s\perp}} - \frac{\chi^{s\perp}}{\chi^{\text{eff}}} + 1 \right).$$

We assume the host material to be air with $\chi^h \approx 0$. If the total NT volume fraction $F = \sum F^s$ is small, $F \ll 1$, the effective susceptibility is comparable to that of the host and thus small compared to the susceptibilities $\chi^{s\parallel}$ and $\chi^{s\perp}$, $|\chi^{\text{eff}}| \ll |\chi^{s\perp}| \sim |\chi^{s\parallel}|$. In this case, the 1st term on the right-hand side of Eq. (5.1) is $\approx -4$ which leads to

$$F \langle \chi^{\parallel} \rangle = -3F + 9(1 - F) \frac{\chi^{\text{eff}} - \chi^h}{2\chi^{\text{eff}} + \chi^h}. \quad (5.2)$$

Here, $\langle \chi^{\parallel} \rangle = \sum F^s \chi^{s\parallel}_e / F$ is the susceptibility parallel to the nanotube axis averaged over all nanotubes. As expected from the depolarization effects, $\chi^{\perp}$ does not contribute here, but is not negligible for larger $F$ since the assumption $|\chi^{\text{eff}}| \ll |\chi^{s\perp} | \sim |\chi^{s\parallel} |$ is not valid any more. This is most likely due to NT bundling at higher NT volume fractions: A thick NT bundle has a larger polarizability perpendicular to the tube axis than a single thin NT as detailed in Section 5.5.

Again assuming once more $F \ll 1$ and in addition $\chi^{\text{eff}} \approx \chi^h$ yields the intuitive result

$$\chi^{\text{eff}} - \chi^h = \frac{1}{3} F \langle \chi^{\parallel} \rangle \quad (5.2)$$

for the effective susceptibility $\chi^{\text{eff}}$: The change of the polarizability of the host medium is proportional to that of the NTs times the volume fraction of the NTs. The factor of $1/3$ arises since the NT is polarizable along only 1 of all 3 spatial dimensions. Small changes in the prefactor of $1/3$ are possible since the NTs in our sample lie mainly parallel to the substrate surface and are therefore not completely randomly oriented. Moreover, the assumption $\chi^{\text{eff}} \approx \chi^h$ is not valid here; instead one has $|\chi^{\parallel}| \gg |\chi^{\text{eff}}| \gg |\chi^h|$ which also modifies the prefactor. However, these changes are small and not relevant for the conclusions of this chapter.

The effective dielectric function $\varepsilon^{\text{eff}} = 1 + 4\pi \chi^{\text{eff}}$ of our NT film is obtained from the experimental data analog to graphite in Section 4.6.3; one just has to replace $\varepsilon$ by $\varepsilon^{\text{eff}}$. Equation (5.2) provides the relation between $\chi^{\text{eff}}$ and $\langle \chi^{\parallel} \rangle$.

**Excited Sample**

After sample excitation by the pump pulse, the susceptibility tensor of the NT network changes by $\Delta \chi(x)$. This results in a change $\Delta p$ of the NC dipole moment $p$ induced by the probe field $E_{\text{in}}$ inside the NC via

$$\Delta p = V_N \Delta \chi E_{\text{in}} \overset{(i)}{\approx} V_N \Delta \chi_e E_{\text{line}} \overset{(ii)}{\approx} V_N \Delta \chi_e E_{\text{e}}$$
where $V_{NC}$ is the volume of the NC at position $x$. In step (i), we exploited that only the field component $E_e = (eE)e$ parallel to the axis direction

$$
e = e(\theta, \varphi) = \begin{pmatrix} \cos \varphi \sin \theta \\ \sin \varphi \sin \theta \\ \cos \theta \end{pmatrix}$$

of the NC in Fig. 5.10(b) makes the major contribution to the pump-induced polarization change. In step (ii) we employed $E_{ine} = E_e$ since depolarization effects along the NC axis are negligible, see Section 5.5.

Averaging over all NCs in the volume $V_{avg}(x)$ around position $x$ yields the pump-induced change in the polarization,

$$P_{NL}(x) = \frac{1}{V_{avg}(x)} \sum_{x_j \in V_{avg}(x)} \Delta p_j = \frac{E(x)}{V_{avg}(x)} \sum_j V_{NC} \Delta \chi_e(x_j) e_j \cdot \epsilon_j,$$

where $j$ numbers the NCs. One can now split the $j$ summation in an integration $\int |d\Omega|$ over all solid angles $d\Omega = d\varphi \, d\cos \theta$ and a summation $\sum_{j'}$ over a subset of NCs $j'$ whose orientation $e$ points to the solid angle $d\Omega$. The latter summation yields

$$\sum_{j'} V_{NC} \Delta \chi_e(x_j') = \Delta \chi_e(x) \cdot F V_{avg} \cdot w(e) |d\Omega|$$

where $w(e) |d\Omega|$ is the probability of the $e$ subset, and $\Delta \chi_e(x)$ is its mean change in susceptibility. One then obtains

$$P_{NL}(x, \omega) = F E(x, \omega) \int |d\Omega| w(e) \Delta \chi_e(x) \epsilon^* \epsilon.$$

Since the probe beam is polarized along the $x$ axis in Fig. 5.10(b), one can exploit the invariance of $w(e) \Delta \chi_e$ with respect to the transformation $\theta \rightarrow -\theta$ which enforces $P_{NLz} = 0$. Moreover, if the pump polarization is parallel or perpendicular to the probe polarization, this invariance also holds for the transformation $\varphi \rightarrow -\varphi$ implying $P_{NLy} = 0$. Therefore, the polarization change is parallel to the probe polarization, and the pump-induced change in the effective susceptibility finally is

$$\Delta \chi^e_{ij} = 0 \quad \text{for} \quad i \neq j$$

and

$$\Delta \chi^e_{xx}(x) = F \int |d\Omega| w(e) \Delta \chi_e(x) \sin^2 \theta \cos^2 \varphi. \quad (5.3a)$$

This result reflects the expectation that we mainly probe tubes parallel to the probe polarization that is $\varphi = 0$ and $\theta = 90^\circ$ in Fig. 5.10(b). The angular factor in the last expression arises because the probe field induces a dipole moment along the NC axis which involves a
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The component $\Delta \chi_{yy}^{\text{eff}}$ is simply obtained by replacing $\cos \varphi$ in Eq. (5.3a) by $\sin \varphi$,

$$\Delta \chi_{yy}^{\text{eff}}(x) = F \int |d\Omega| w(e) \Delta \chi_e(x) \sin^2 \theta \sin^2 \varphi,$$

which can be different from the $xx$ component. Such pump-induced optical anisotropy will be discussed in Section 5.9.2. Therefore, it is important to have the pump and probe polarizations either parallel or perpendicular to each other. Otherwise, the sample can cause a rotation or ellipticity of the probe polarization whose electro-optic detection will lead to more complicated results [Pla01].

In order to check the validity of the above derivation, we assume a completely isotropic and homogeneous $\Delta \chi_e(x) = \Delta \chi ||$ and an isotropic distribution of the tube directions, $w(e) = 1/4\pi$. This yields $\Delta \chi_{xx}^{\text{eff}} = \Delta \chi_{yy}^{\text{eff}} = \frac{1}{3} F \Delta \chi ||$ in agreement with Eq. (5.2).

At the pump beam intensities in our experiment, $\Delta \chi_{xx}^{\text{eff}}(z)$ is due to a 1-photon absorption and therefore decays exponentially as $\Delta \chi_{xx}^{\text{eff}}(z) = \Delta \chi_{xx}^{\text{eff}}(z = 0^+) \exp(-z/d_{\text{pen}})$ along the $z$ axis in Fig. 5.10(b). The penetration depth $d_{\text{pen}} = 580 \text{ nm}$ is derived from the sample thickness and the sample power transmission of $T = 0.25$. The extraction of the susceptibility $\Delta \chi_{xx}^{\text{eff}}(z = 0^+)$ directly behind the film surface is now straightforward with the aid of Eq. (2.16). Note that one has to use the effective susceptibility $\chi^{\text{eff}}$ for the unexcited sample.

5.8. Results: Unexcited Sample

Figure 5.11 presents the quantity

$$\varepsilon := \frac{4\pi}{F} (\chi^{\text{eff}} - \chi^h).$$

According to Equation (5.2), $\varepsilon$ is the dielectric function of the unexcited NTs between 9 and 30 THz averaged over all NT types and orientations.
Contributions from the large-gap tubes are not expected since their excitation energies in the ground state are on the eV scale and thus exceed our probe-photon energies by far. The increase of \( \text{Im} \varepsilon \) towards low frequencies arises from the broad resonance \( E_{sg00}^\text{tg} \) centered at about 6 THz in Fig. 5.5. As mentioned above, this feature has been attributed to optical transitions across the gap of the small-gap NTs [Itk02, Uga99].

Moreover, \( \varepsilon \) does not display a distinct free-carrier response which would imply a large negative real part as described in Section 1.6.1. The negligibly small \( \text{Re} \varepsilon \) is consistent with the low plasma frequency of \( h\Omega_{pl} \approx 20 \text{ meV} \) found in metallic and small-gap tubes by conductivity measurements below 5 THz [Hil00, Krö05]. A possible reason for this behavior might be the localization of charge carriers which decreases the conductivity at least below a characteristic frequency, see Section 5.3.3.

5.9. Results: Excited Sample

We now consider the changes in the dielectric function of the NT sample after pump pulse excitation with an incident fluence of 30 \( \mu \text{J cm}^{-2} \). From the absorption cross sections for 1.6-eV photons [Isli04], we estimate that \( \sim 10^{-4} \) photons per carbon atom are absorbed close to the front surface of the NT sample. This excitation density is comparable to that of graphite in Section 4.8.

The pump-induced change in the dielectric function plotted in the following is defined as

\[
\Delta \varepsilon_{xx,\tau} := \frac{4\pi}{F} \Delta \chi_{xx,\tau}(z = 0^+).
\]

According to Eq. (5.3a), \( \Delta \varepsilon_{xx,\tau} \) describes an excited NT directly behind the sample surface and averaged over all possible NT types and directions. If not otherwise mentioned, the \( xx \) component, that is the component along the pump polarization, is considered.

All types of NTs are excited by the 1.6-eV pump pulse as sketched in Fig. 5.7. Transient transmission measurements with pump-photon energies above and below the \( E_{11}^\text{lg} \) band indicate that roughly half of the absorbed 1.6-eV pump photons resonantly populate the \( E_{22}^\text{lg} \)-exciton bands of the large-gap tubes [Ell05]. The remaining portion resonantly excites the small-gap and metallic NTs.

5.9.1. No Response of Free Charge Carriers

Figure 5.12(a) shows \( \Delta \varepsilon_\tau \) for 3 different pump-probe delays \( \tau \). Note that \( \Delta \varepsilon_\tau \) is quite small and does not exhibit a distinct free-carrier response. This is in striking contrast to the model semiconductor GaAs, where excitation above the band gap creates electrons and holes [Hub01], and to graphite, which is closely related to NTs: Its corresponding \( \Delta \varepsilon_\tau \) taken under comparable excitation conditions (see above) is plotted in Fig. 5.12(a) for
$	au = 0.1 \text{ ps}$. The 2 orders of magnitude larger and negative $\text{Re} \Delta \varepsilon \tau$ is a clear signature of free charge carriers, and the lack of such a response from the NT sample has important consequences:

- It strongly supports the assertion that excitons are the main products of photoexcitation of large-gap tubes [Man05, Kor04]. These strongly bound electron-hole pairs are not directly visible in our experiment since their internal excitation energies of 0.2 eV [Wan05] exceed our probe energies of $\sim 50 \text{ meV}$ by far.

- The plasma frequency and the Drude scattering rate in the small-gap and metallic NTs do not change appreciably upon excitation. This can be traced back to Eq. (1.22) and to their peculiar eDOS as detailed in Fig. 5.13. An example of the opposite behavior is graphite in Section 4.8.3.
5.9. Results: Excited Sample

Figure 5.13.: Electronic density of states \( D(\epsilon) \) in a small-gap NT with an energy gap of 20 meV and derivative \( -\partial f / \partial \epsilon \) of the Fermi function at an electronic temperature of \( T_e = 300 \) K. The width of \( -\partial f / \partial \epsilon \) increases with rising \( T_e \) and is much larger than the energy gap. As a consequence, the squared plasma frequency \( \Omega_{\text{pl}}^2 \), which is the area under the product curve \( -D(\epsilon) \cdot \partial f / \partial \epsilon \), changes only weakly.

5.9.2. Pump-Induced Anisotropy and Carrier Localization

To identify the origin of the pump-induced signal, we now analyze the spectral structure of our data in Fig. 5.12(a): \( \text{Im} \Delta \varepsilon_\tau \) is positive above 15 THz, which implies increased light absorption accordingly labeled “A”. In contrast, \( \text{Im} \Delta \varepsilon_\tau \) is negative below 15 THz, which means decreased light absorption (bleaching) and is labeled “B”. The following arguments strongly indicate that A and B arise from distinct products in the photoexcited NTs:

- A and B exhibit significantly different temporal decays as can be seen in Fig. 5.12(c): At early times, A decreases much faster than B.
- A and B respond differently to a change in the probe pulse polarization as shown in Fig. 5.14(a,b): The pump-induced dichroism

\[
D_\tau = \frac{\text{Im} \Delta \varepsilon_{xx,\tau}}{\text{Im} \Delta \varepsilon_{yy,\tau}} = \frac{\text{Im} \Delta \chi_{\text{eff}}^{xx,\tau}}{\text{Im} \Delta \chi_{\text{eff}}^{yy,\tau}} \tag{5.5}
\]

is found to be \( \approx 1.2 \pm 0.1 \) for feature B but \( \approx 2.1 \pm 0.2 \) for feature A.

Such transient optical anisotropy has previously been observed for visible probe pulses [She05] and relies on the greatly reduced NT polarizability perpendicular to the tube axis, see Section 5.5. Therefore, and as illustrated in Fig. 5.15, the probe pulse is most sensitive to tubes parallel to the probe polarization. Likewise, the pump pulse is absorbed most effectively by tubes parallel to the pump polarization. As a consequence, parallel pump and probe polarizations should give a larger pump-induced signal than in the perpendicular case.

This effect is largest if the pump-induced excitations have a spatial extent much smaller than the mean radius of curvature \( R_c \sim 100 \) nm of the bent NT, see Fig. 5.8(a). On the other hand, a dichroism of 1 is attained when the excitations are spatially delocalized with respect to \( R_c \). Therefore, the pump-induced dichroism of A and B provides direct evidence of the existence of localized and delocalized electrons in the bent NTs.
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![Graph](image)

**Figure 5.14.** (a) Dielectric function at $\tau = 0.1$ ps parallel ($xx$) and perpendicular ($yy$) to the pump polarization. The difference between the $xx$ and $yy$ curves directly shows the pump-induced optical anisotropy. It is most pronounced in the imaginary part above 20 THz where feature $A$ dominates. Such dichroism is a direct consequence of excitations in the NTs which are localized on a length scale smaller than the radius of curvature of the bent tube. (b) Temporal dynamics of the pump-induced dichroism (5.5) at 10 THz (mainly feature $B$) and 25 THz (mainly feature $A$). (c) Expected pump-induced dichroism as a function of the localization length of the corresponding excitation. Lines mark the measured dichroism of feature $A$ and $B$.

**Estimate of the Electron Localization Length**

In order to estimate the localization length of the electrons, we assume the NTs to be bent to circles with radius $R_c$ as shown in Fig. 5.15(b). Moreover, they are assumed to be parallel to the ($x, y$) plane defined in Fig. 5.10. In other words, the orientational distribution of the nanocylinders is

$$w(e) = w(\theta, \varphi) \propto \delta(\theta - 90^\circ).$$

Exciting the NTs with a pump-beam polarization along the $x$ axis will induce a susceptibility change $\Delta \chi_e = \Delta \chi_\varphi \propto \cos^2 \varphi$ provided the excited carriers are perfectly localized. However, a finite localization length $l_{loc}$ leads to a “smearing” or convolution (B.2) of the carrier position by a function of width $l_{loc}$. Equivalently, $\Delta \chi_\varphi$ is convolved by a function $s(\varphi)$ of width $\varphi_{loc} = l_{loc}/R_c$ which leads to an angular distribution $\Delta \chi_\varphi \propto \cos^2 \varphi \ast s(\varphi)$. When the smearing $s$ has Gaussian shape, $s(\varphi) = \exp(-\varphi^2/2\varphi_{loc}^2)$, the change in the effective susceptibilities (5.3) parallel and perpendicular to the pump polarization can be
5.9. Results: Excited Sample

**Figure 5.15.** Illustration of the origin of the pump-induced anisotropy. The pump beam mainly excites tube segments parallel to its polarization along the \( x \) direction. These segments are drawn brighter than the less strongly excited regions. Similarly, the probe beam is most sensitive to tube segments parallel to its polarization. (a) Parallel pump and probe polarization. The probe pulse is most sensitive to the tube segments with a maximum change in the susceptibility provided the pump-induced excitations are localized with respect to the tube radius of curvature \( R_c \). (b) Perpendicular pump and probe polarization. The probe beam is most sensitive to the less excited tube segments and therefore less affected by the pump-induced changes than in case (a).

Calculated analytically and yields

\[
\frac{\Delta \chi_{xx}^{\text{eff}}}{\Delta \chi_{yy}^{\text{eff}}} \propto \Delta \chi_{\phi=0} \left[ 2 \pm \exp(-2\varphi_{\text{loc}}^2) \right].
\]

Here, \( \Delta \chi_{\phi=0} \) is the susceptibility change of the NT segments parallel to the pump polarization. The resulting pump-induced dichroism (5.5) becomes

\[
D_\tau = \frac{2 + \exp(-2\varphi_{\text{loc}}^2)}{2 - \exp(-2\varphi_{\text{loc}}^2)}
\]

which is plotted in Fig. 5.14(c).

As expected, a complete delocalization with \( \varphi_{\text{loc}} = 0 \) implies a dichroism of 1, whereas perfect localization with \( \varphi_{\text{loc}} = \infty \) leads to a dichroism of 3. As to our data in Fig. 5.14(b), the excitations correlated with feature A have a localization length of \( \approx 0.4R_c \sim 40 \text{ nm} \) and are substantially more localized than those related to feature B having a twice as large localization length of \( \approx 0.9R_c \sim 90 \text{ nm} \). The localization lengths found here agree reasonably with those extracted by scanning tunneling spectroscopy of HiPCO NTs [GN05]. Note that the transient dichroism remains constant in Fig. 5.14(b) showing that carrier transport is negligible during the 1st picosecond after sample excitation.

It should be mentioned that the derivation of Eq. (5.6) assumes that only 1 type of excitations induces the pump-induced signal whereas in our case at least 2 types, namely A and B, contribute. However, B completely dominates the signal at 10 THz since the dichroism still remains at \( \approx 1.2 \) when A has already reduced to small values. Conversely, B has only little spectral weight above 25 THz and thus does not interfere with feature A in this spectral region.
To summarize, the pump-induced dichroism allows for a direct observation of pump-induced excitations $A$ and $B$ that are localized and delocalized with respect to a length scale of $\sim 100$ nm. The dichroism is based on the greatly reduced polarizability of the NTs perpendicular to the tube axis whereas the spatial resolution comes into play due to the radius of curvature of the bent NTs. The remaining sections are dedicated to a discussion of the origin of $A$ and $B$.

5.9.3. Bleaching in Small-Gap Tubes

Phononic contributions as a cause of the bleaching feature $B$ are excluded, since broad phonon bands are neither predicted [Ye04] nor observed [Kim05] in the probed spectral region. Consequently, $B$ must arise from electronic transitions. Stimulated emission from excited excitonic levels in large-gap tubes can be ruled out because the lowest $E_{11}^{lg}$ state is attained within $40 \text{ fs}$ after optical excitation [Man05]. We conclude that $B$ is due to metallic and small-gap tubes.

The single-electron approach in Fig. 5.7(b) can qualitatively explain the observed effect: After pump pulse absorption, the excited electrons thermalize to a Fermi-Dirac distribution within $\approx 0.2 \text{ ps}$ [Her00]. This results in additional electrons and holes around the Fermi energy. Similar to graphite in Section 4.8.2, these hot carriers block originally possible optical transitions connecting the van Hove singularities near the band gap. The contributions of various tube types lead to an inhomogeneously broadened bleaching feature $B$ as seen in our experiment [Shy02].

Similar to graphite in Section 4.8.4, the small Fermi surface and the strong e-ph interaction suggest a very rapid cooling of the excited electrons via phonon emission which finally leads to a non-equilibrium distribution of hot phonons. Indeed, although not explicitly mentioned in Ref. [Hag04], a loss of $\approx 90\%$ of the electronic energy within $0.5 \text{ ps}$ after optical excitation has been found. Consequently, the decay of feature $B$ in Fig. 5.12(c) with a $1\text{-ps}$ time constant must be due to the cooling of the hot phonons. This is considerably faster than in graphite where a $5.4\text{-ps}$ time constant was found and may point to a stronger ph-ph coupling in NTs.

5.9.4. Increased Absorption by Intraexcitonic Transitions?

As detailed above, feature $B$ derives from rather delocalized electrons in the small-gap and metallic NTs. It is, however, rather unlikely that these tubes are also the origin of feature $A$, since this would imply the existence of electrons with 2 different localization lengths in the same tube type.

We propose the following explanation: Directly after excitation, the exciton population peaks sharply at the excitation energy in the $E_{22}^{lg}$ band as shown in Fig. 5.16. This peak relaxes to the bottom of the $E_{11}^{lg}$ band with a $40\text{-fs}$ time constant [Man05]. Note that
5.10. Conclusion and Outlook

In conclusion, time-resolved THz spectroscopy has been used to study single-wall carbon nanotubes. First, our data lack a distinct free-carrier response which is ascribed to the instantaneous generation of strongly bound excitons instead of free charge carriers as seen in graphite. Second, the transient dichroism directly displays the existence of charges that are spatially delocalized and localized with respect to a length scale of $\sim 100$ nm. The more delocalized excitations are attributed to carriers in the small-gap and metallic tubes.
5. Carbon Nanotubes: Excitons, Localized and Delocalized Carriers

whereas the more localized excitations may arise from transitions between continuum states of excited excitons which decay with a 150-fs time constant.

The fact that all types of nanotubes compose our sample complicates the assignment of the features in the THz spectra. Meanwhile, the preparation of samples containing only large-gap tubes is possible [Rub05]. By investigating such a sample, the origin of the absorption feature \( A \) could be clarified. Alternatively, one can pump the present sample with THz radiation in order to excite only small-gap and metallic tubes. The amplified laser system in principle allows for the generation of sufficiently intense THz-pump pulses. At present, this setup is used to study the THz response of NTs excited with more intense visible pump pulses.
6. Optically Ionized Gases: Long- and Short-Lived Electrons

This chapter presents the first application of the THz spectrometer driven by the amplified laser: The intense pulses of this laser system are used to ionize various gases. The THz signal of the resulting gas plasma is dominated by the Drude response of the quasifree electrons and yields the dynamics of their density and Drude collision rate. The electron decay in Ar is found to be much slower than in O\textsubscript{2} due to a lack of internal dissipation channels for the electron energy. However, it can be accelerated enormously by adding the electron scavenger SF\textsubscript{6} to Ar. The Drude collision (or current-relaxation) rate decreases monotonously with the decaying electron density. We discuss 2 possible scenarios which can account for this behavior: The 1st scenario assumes that electron-ion scattering is the dominating mechanism for the current relaxation whereas the 2nd favors electron-electron scattering.

Parts of this chapter have been submitted to Physical Review Letters and Chemical Physics Letters.

6.1. Motivation

Free charge carriers in gases play an important role in everyday life, for example in fluorescence tubes, lightnings during a thunderstorm, and sparks in electrical equipment.

- Sparks in high-voltage devices can lead to short-circuits of the device and material corrosion. In order to prevent or interrupt such short-circuits, the devices are flooded with insulating gases such as the electron scavenger SF\textsubscript{6} [Chr00]. To date, the decay of free electrons in the presence of SF\textsubscript{6} has not been observed on an ultrashort time scale.

- It has been a longstanding dream to trigger lightnings in a thunderstorm in a controlled way [Zha95]. In this context, laser pulses are suggested to produce a channel of ionized air between the ground and the clouds which should lead to a controlled discharge of the clouds along that channel. As shown in Fig. 6.1, the potential of this scheme has been demonstrated in laboratory over distances of few meters [Kas03]. In order to cover much larger distances, knowledge on the lifetime and mobility of the induced quasifree electrons is highly desirable.
6. Optically Ionized Gases: Long- and Short-Lived Electrons

Figure 6.1: High-voltage discharge controlled by femtosecond-laser pulses. (a) Schematic of the experimental setup. A voltage of up to 2 MV is generated between the 2 electrodes having a distance of 3 m. (b) Free discharge along an erratic path. (c) Straight discharge along a filament of ionized air generated by an intense laser pulse. This figure was taken from Ref. [Kas03].

Femtosecond time-resolved studies of gas plasmas employ powerful and short laser pulses to ionize a gas such as air. Several methods have been used to probe the free-electron dynamics of the plasma. One of these schemes involves the interferometrical or diffractive measurement of the phase shift a visible probe pulse accumulates by transmitting the plasma at a certain time after generation [Fon99, Tzo00]. In principle, this method yields the electron density $n_e$. However, according to the linearized Drude formula (1.18), the electron collision rate $\Gamma$ is much more difficult to obtain since absorption effects are weaker than phase-shift effects by a factor $\Gamma/\omega \sim 10^{-2}$ for visible probe radiation of frequency $\omega$. Another possibility is to detect the total light emission of a plasma that was reexcited by a delayed probe pulse [Mar04]. However, this approach is quite indirect since the functional relation between emitted light intensity and plasma quantities such as $n_e$ is not known.

THz radiation is a promising alternative probe because $\Gamma$ and the plasma frequency of optically ionized gases lie in the THz range. For example, the plasma frequency $\Omega_{pl}$ of a plasma consisting of electrons and singly ionized molecules with a number density of ambient air is $\Omega_{pl}/2\pi = 45$ THz according to Eq. (1.13). THz spectroscopy has already proven useful to characterize a He discharge plasma on a $\mu$s-time scale [Jam03] or to study the mechanism of oxygen ionization by femtosecond laser pulses [Mic05]. However, these reports investigated only a single gas in the frequency range from 1 to 3 THz and did not cover its decay dynamics comprehensively.

6.2. Partially Ionized Gases and Plasmas

In our work, laser pulses are used to ionize a fraction of the atoms or molecules in a gas. Such a partially ionized gas is also called a plasma when the effective interaction length $\lambda_D$ of 2 charged particles is much smaller than the linear dimensions of the system under
6.3. Dynamics of Optically Ionized Gases

consideration [Hol65]. Such effective interaction between “test charges” $q_1$ and $q_2$ is due to the screening of the bare Coulomb force by the surrounding electrons or ions and can often be written as an exponentially damped Coulomb potential

$$V_{q_1q_2}(x_1, x_2) = \frac{q_1 q_2}{|x_1 - x_2|} \exp\left(-\frac{|x_1 - x_2|}{\lambda_D}\right).$$ \hspace{1cm} (6.1)

In a nondegenerate plasma with electron density $n_e$ and electron temperature $T_e$, the screening length is the Debye length [Hol65]

$$\lambda_D = \sqrt{\frac{k_B T_e}{4\pi e^2 n_e^2}}$$

which represents a special case of the Thomas-Fermi screening length in solid-state physics. Note that Eq. (6.1) quantifies the screening of a static charge; dynamic screening may be different and is described for example by the Lindhard dielectric function [Ash76].

Further important plasma parameters are

$$\Theta = \frac{k_B T_e}{\epsilon_F} = \frac{2m_e k_B T_e}{\hbar^2 (3\pi^2 n_e)^{2/3}}$$ and $$G_{ee} = \frac{Z e^2}{a k_B T_e},$$

where $a = (4\pi n_e/3)^{-1/3}$ is the “electron-sphere radius” [Sty02]. An electron-degeneracy parameter of $\Theta \gg 1$ indicates that the Fermi energy $\epsilon_F$ of the quasifree electrons is much smaller than their thermal energy such that the electrons can be described by Maxwell-Boltzmann statistics. In the opposite case, exchange effects become important which requires Fermi-Dirac statistics. The electron-coupling parameter $G_{ee}$ quantifies the coupling strength between the electrons, and $G_{ee} < 0.1$ indicates that the electron-electron interaction can be considered as a small perturbation of the free-electron gas [Ger05].

6.3. Dynamics of Optically Ionized Gases

As mentioned in Section 1.1, the electron dynamics in ionized gases is in principle quite similar to that in metals. However, the generation of the free electrons in gases requires intense laser pulses which ionize the atoms and molecules by promoting the electron with the lowest binding energy $W_b$ to an unbound or “free” state. $W_b$ is also called ionization energy. An important parameter for the description of the ionization process is the Keldysh parameter [Bra00]

$$\gamma_K = \frac{\omega \sqrt{2m_e W_b}}{e|E_0|}.$$ \hspace{1cm} (6.2)

$\gamma_K^2$ can be interpreted as the ratio of the electron binding energy $W_b$ and the peak kinetic energy $m_e v_{\text{max}}^2/2$ a free electron would acquire in a laser field of amplitude $E_0$ and frequency $\omega$ due to acceleration to a peak velocity $v_{\text{max}} = e|E_0|/m_e \omega$. 

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6. Optically Ionized Gases: Long- and Short-Lived Electrons

For $\gamma_K \gg 1$, the ionization can be described by multiphoton absorption based on higher-order perturbation theory [Bra00] which results, for example, in the perturbation series (1.9). On the other hand, for $\gamma_K \approx 1$ and linearly polarized light, the laser field starts to lower the Coulomb potential of the nucleus such that the electron with the binding energy $W_b$ can tunnel through the reduced Coulomb barrier. At even higher laser fields, $\gamma_K \ll 1$, the Coulomb barrier is so low that the electron can escape classically [Pos04]. At our pump photon energy of $\hbar \omega = 1.6 \text{ eV}$, the crossover region with $\gamma_K \approx 1$ is reached at laser intensities of $10^{14} \text{ W cm}^{-2}$.

After generation of the quasifree electrons, electron-electron scattering leads to a thermalization of the electronic system on a subpicosecond-time scale [Ger05]. Electron cooling occurs via energy transfer from the electronic system with temperature $T_e$ to the ions described by temperature $T_i$. If there is only one sort of singly charged ions of mass $m_i$ the inverse time constant of this process is given by the Spitzer formula [Spi56]

$$\frac{1}{\tau_{ei}} = \frac{3m_em_i}{8\sqrt{2\pi n_i}e^4 A_C} \left( \frac{k_BT_e}{m_e} + \frac{k_BT_i}{m_i} \right)^{3/2}.$$  

Here, the electron-ion interaction comes into play via the so-called Coulomb logarithm $A_C = \ln(12\pi n_e\lambda_D^0)$. The Spitzer formula can be considered as an analog of the equations of the 2-temperature model in solids, see Section 1.3.2. Cooling by heat transfer to the neutral particles is usually substantially slower especially in noble gases due to the much smaller cross section for scattering between the electrons and neutral particles [Ger05].

Finally, the recombination of an electron and an ion requires a sink for the binding and the kinetic energy of the electron which is, for example, provided by internal excitations of the ion or a 3rd particle like another electron or an emitted photon. The great variety of reactions between the plasma constituents leads to a complete “zoo” of recombination reactions. It is one of the tasks of plasma physics to determine the weight of the possible reaction channels in the plasma investigated [Hol65].

6.4. Optical Properties of a Plasma

A plasma consists of quasifree electrons, ions, and neutral particles. Due to their small mass, the motion of the free electrons is expected to make the dominating contribution to the optical properties.

In the simplest approach, one can use the Drude model of Section 1.5.1 to describe the dielectric function $\varepsilon$ of a plasma. Note that according to Eq. (1.12), $\text{Re} \varepsilon$ becomes negative for frequencies $\omega$ below the plasma frequency $\Omega_{pl}$ which makes the plasma highly reflecting. When, in addition, the penetration depth of the electromagnetic wave into the plasma is smaller than the mean free path of an electron, the anomalous skin effect becomes operative [Ich73]. As a consequence, the electrons can create a nonlocal coherent polarization in plasma regions deeper than the penetration depth. However, this regime is not important.


Table 6.1.: Ionization energy $W_b$ and purity of the gases investigated. As to the gas mixture $0.9 \text{Ar} + 0.1 \text{SF}_6$, the coefficients represent the volume fractions of the constituting gases. The values for $W_b$ are taken from Ref. [oS05].

<table>
<thead>
<tr>
<th>gas</th>
<th>Ar</th>
<th>$O_2$</th>
<th>$\text{SF}_6$</th>
<th>gas mixture</th>
<th>0.9 Ar + 0.1 $\text{SF}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_b$ (eV)</td>
<td>15.8</td>
<td>12.1</td>
<td>15.3</td>
<td>$W_b$ (eV)</td>
<td>-</td>
</tr>
<tr>
<td>purity (%)</td>
<td>99.998</td>
<td>99.9</td>
<td>99.9</td>
<td>Ar content (%)</td>
<td>90 ± 2</td>
</tr>
</tbody>
</table>

in the work presented here since the probe frequencies used are always above the plasma frequency resulting in a penetration depth much larger than the plasma thickness. The Boltzmann approach of Section 1.5.2 gives a more sophisticated description of the dielectric function of a weakly coupled plasma [Sty02]. As shown later it also leads to a Drude-like dielectric function but relates the Drude collision rate $\Gamma$ to microscopic quantities such as the momentum-transfer cross sections for the scattering of electrons with ions or neutral particles.

6.5. Experimental and Technical Details

The optical ionization of gases requires large light intensities. Therefore, the measurements of this chapter require light pulses from the amplified laser system which is described in Section 3.1.2.

6.5.1. Sample

All gases are obtained from Linde and Aldrich in high-pressure bottles; their purity and ionization potential $W_b$ are listed in Table 6.1. The setup for the sample preparation consists of a gas cell which is connected to a gas bottle with a pressure regulator in-between. In order to always guarantee a fresh sample, the gas enters the gas cell at a pressure slightly above the ambient pressure of 1 bar which is the pressure at the cell outlet.

6.5.2. Sample Pumping and Probing

The gas cell is placed in the standard sample position of Fig. 3.3, but a modified pump geometry is used here: As shown in Fig. 6.2, the visible and linearly polarized pump pulse enters the gas cell through a glass window. Before, the beam is focused by 2 cylindrical lenses whose symmetry planes are perpendicular to each other leading to an elliptical beam cross section. The gas is ionized around the focal plane of lens 2 where the intensity is highest; Fig. 6.3(a) shows that the beam cross section at this position is a strongly elongated ellipse.
6. Optically Ionized Gases: Long- and Short-Lived Electrons

**Figure 6.2.** Schematic of the sample geometry. The pump beam is focused into the gas cell by two cylindrical lenses. The resulting plasma sheet around the focal plane of lens 2 is probed by a THz beam propagating perpendicularly to the pump beam.

**Figure 6.3.** (a) Gray-scale plot of the intensity profile $I$ of the pump-beam focus acquired by a charge-coupled device (CCD). The THz probe pulse propagates along the $z$ axis. Note the different axis scaling. (b) Line plot along the $z$ direction. Here, the full width at half maximum (FWHM) of the intensity profile comes close to the CCD-pixel size of 5.5 $\mu$m. (c) Line plot along the $y$ direction. It shows that there is nearly no intensity variation around the maximum in this direction such that the THz probe pulse sees a homogeneously excited sample perpendicular to its direction of propagation.
6.5. Experimental and Technical Details

The THz probe beam travels in a direction perpendicular to that of the pump beam, enters the gas cell through a silicon window, transmits the plasma, and leaves the cell through another silicon window. Note that the THz probe pulse sees a homogenously excited gas perpendicular to its propagation direction \( z \): As shown by Fig. 6.3(c), the pump intensity \( I \) along the \( y \) axis is nearly constant over the 50-\( \mu \)m diameter of the probe-beam focus. The same holds true along the \( x \) direction where the focal length of the pump focus is at least 400 \( \mu \)m.

However, as seen in Fig. 4.12(c), \( I \) varies strongly along the propagation direction \( z \) of the probe pulse and can be described by a Gaussian

\[
I(z) = I(0) \exp \left(-4 \ln 2 \frac{z^2}{\text{FWHM}^2}\right) \tag{6.3}
\]

with a full width at half maximum of \( \text{FWHM} = 25 \mu \text{m} \).

For the largest pump-pulse energies of 0.4 mJ we estimate a peak intensity of \( 3 \cdot 10^{13} \text{ W cm}^{-2} \) in the center of the focus. With a pump-photon energy of 1.6 eV, this corresponds to a Keldysh parameter (6.2) of \( \gamma_K \approx 15 \) indicating that the regime of field ionization is not yet completely reached. In addition, we can exclude double ionization which comes into play at much higher intensities around \( 10^{18} \text{ W cm}^{-2} \) [Pos04].

The pulse shaper in the amplified laser system is employed to maximize the bandwidth of the THz pulses and the plasma-induced signal. We made sure that the latter did not depend on the THz intensity showing that the THz pulse can be still considered as a linear probe despite its high electric fields, see Section 3.2.4. Our temporal resolution of about 200 fs is estimated by the rise of the pump-induced signal. It is limited by the 90° beam geometry since different sample positions along the \( x \) direction in Fig. 6.2 are excited at different times.

6.5.3. Data Analysis

Unexcited Sample

Since the gas cell and its Si windows are thick, multiple reflections do not play a role in the detection window of the THz pulse, and the THz electric field propagating along the \( z \) axis through the gas long after or before excitation is

\[
E_{\infty}(z, \omega) = E_{\text{inc}} \exp \frac{i\omega\sqrt{\varepsilon}z}{c}.
\]

In this way, the dielectric function \( \varepsilon \) of SF\(_6\) in the THz range can be measured where Ar or O\(_2\) serve as the reference with \( \varepsilon = 1 \). The result is shown in Fig. 6.4 where a peak in \( \text{Im} \varepsilon \) at about 18 THz is due to the \( \nu_4 \) vibration of the SF\(_6\) molecule [Her66].
6. Optically Ionized Gases: Long- and Short-Lived Electrons

![Figure 6.4: Dielectric function of an SF$_6$ between 12 and 24 THz under normal conditions. Note the distinct peak in the imaginary part at about 18 THz. It originates from the $\nu_4$ vibration of the SF$_6$ molecule [Her66]. The real part is offset for clarity.]

**Excited Sample**

Exciting the sample with a pump pulse creates a change $\Delta \varepsilon_\tau$ in the dielectric function of the gas which is seen by the probe pulse at time $\tau$ after excitation. Concerning the extraction of $\Delta \varepsilon_\tau$, we are confronted with several problems: As suggested by the intensity profile of the pump-beam focus in Fig. 6.3(b), $\Delta \varepsilon_\tau(z, \omega)$ varies along the propagation direction $z$ of the THz probe pulse. Moreover, Fig. 3.5(b) shows that the measured pump-induced changes $\Delta S_\tau$ in the THz signal are too large to justify a linear relationship like Eq. (2.15) between $\Delta S_\tau$ and $\Delta \varepsilon_\tau$.

However, since the dynamics after sample excitation takes place on a time scale of at least 10 ps, a quasistatic approach to the data analysis is justified. Therefore, we use the WKB approximation (2.19) to calculate the transmitted THz field at a point $z_1$ after the ionized region. The relative change in the THz field referenced to the unexcited sample is then

$$Q_\tau(\omega) = \frac{S_\tau(\omega)}{S_\infty(\omega)} = \frac{E_\tau(z_1, \omega)}{E_\infty(z_1, \omega)} = \exp \left[ \frac{i}{c} \int_{-\infty}^{z_1} dz \Delta n_\tau(z, \omega) \right]$$ (6.4)

with $\Delta n_\tau = \sqrt{1 + \Delta \varepsilon_\tau} - 1$ being the pump-induced change in the refractive index.

The quality of this approximation is checked by numerically solving the wave equation (2.18) for a large variety of test functions $\Delta \varepsilon_\tau$. The numerical procedure involves the summation of the perturbation series (2.5) up to the 100th order or more until convergence is achieved. The agreement between this solution and Eq. (6.4) is excellent even for spatially narrow profiles of $\Delta \varepsilon_\tau$ where the WKB approximation is expected to fail.

How can one deal with the unknown spatial variation of the dielectric function? In contrast to the measurements on graphite and carbon nanotubes, $\Delta \varepsilon_\tau(z, \omega)$ does not follow the intensity profile $I(z)$ of the pump beam. Here, we assume a power law for the change in the refractive index with respect to the pump intensity,

$$\frac{\text{Re } \Delta n(z, \omega)}{\text{Re } \Delta n(0, \omega)} = \left[ \frac{I(z)}{I(0)} \right]^{p_{\text{Re}}} \quad \text{and} \quad \frac{\text{Im } \Delta n(z, \omega)}{\text{Im } \Delta n(0, \omega)} = \left[ \frac{I(z)}{I(0)} \right]^{p_{\text{Im}}}.$$ (6.5)
6.5. Experimental and Technical Details

As a consequence, real and imaginary part of the auxiliary quantity

\[ h(W) := -i \ln Q_{\tau} = \frac{\omega}{c} \int_{-\infty}^{z_0} dz \Delta n_{\tau}(z, \omega) \quad (6.6) \]

should obey the corresponding power law with respect to the pump pulse energy \( W \),

\[ \frac{\text{Re} h(W)}{\text{Re} h(W_{\text{max}})} = \left( \frac{W}{W_{\text{max}}} \right)^{p_{\text{Re}}} \quad \text{and} \quad \frac{\text{Im} h(W)}{\text{Im} h(W_{\text{max}})} = \left( \frac{W}{W_{\text{max}}} \right)^{p_{\text{Im}}} \quad (6.7) \]

Indeed, as seen in Fig.6.5(a) for Ar at \( \tau = 5 \) ps after excitation, the left-hand sides of both equations (6.7) do not depend on frequency. Moreover, Fig.6.5(b) shows that they can be adequately described by a power law with exponents \( p_{\text{Re}} = 3.9 \) and \( p_{\text{Im}} = 5.3 \), respectively. We conclude that the ansatz (6.5) for the spectral shape of the pump-induced change \( \Delta n_{\tau} \) in the refractive index is reasonable. For \( \text{O}_2 \), we find exponents of \( p_{\text{Re}} = 2.9 \) and \( p_{\text{Im}} = 4.5 \); the exponents for \( \text{SF}_6 \) are assumed to agree with those of Ar because of the similar ionization potential.

We now employ Eqs. (6.3), (6.6), and (6.5) to obtain

\[ \text{Re} (i \ln Q_{\tau}) = - \frac{\omega}{c} \frac{\text{FWHM}}{\sqrt{0.88 p_{\text{Re}}}} \text{Re} \Delta n_{\tau}(z = 0, \omega) \quad (6.8) \]

and an analog expression for the imaginary part which both allow for the extraction of the dielectric function \( 1 + \Delta \varepsilon_{\tau}(z = 0, \omega) \) in the center of the pump-induced plasma.

We assume that the ansatz (6.5) is still valid at longer delays \( \tau \). This assumption is justified since transport effects are not expected to play an important role during the first 200 ps after plasma generation according to Ref. [Dun94]. They measured the expansion of
6. Optically Ionized Gases: Long- and Short-Lived Electrons

Figure 6.6.: Pump-induced changes $\Delta \varepsilon_\tau = \varepsilon_\tau - 1$ in the dielectric function. (a) $\Delta \varepsilon_\tau$ of Ar at $\tau = 1$ ps after ionization. The Drude model excellently reproduces the experimental data. (b) Same as (a) at $\tau = 200$ ps. Note that the pump-induced changes have slightly increased. (c) $\Delta \varepsilon_\tau$ of the gas mixture 0.9 Ar + 0.1 SF$_6$ at $\tau = 0.3$ ps after ionization. The Drude model works fine also at this early delay. (d) Same as (c) at $\tau = 100$ ps. Note that the signal has already greatly reduced.

a laser-generated plasma channel in a N$_2$ gas jet and found a plasma expansion of 10 $\mu$m in 200 ps. However, this length should be considered as an upper limit of our experiment since their gas density was a factor of 100 lower than ours which greatly increases the mean free path and thus the plasma-expansion velocity. Moreover, their electron temperatures of $k_B T_e = 25$ eV are larger than the temperatures of $k_B T_e \approx 2$ eV suggested by our data (see below) which implies an increase of the electron velocity and the plasma-expansion velocity by another factor of 3 with respect to our experiments.

6.6. Results: Dynamics of the Free-Electron Density

The raw data are analyzed according to the procedure of the preceding section in order to obtain the dielectric function $\Delta \varepsilon_\tau(z = 0, \omega)$ in the center of the plasma. Figure 6.6 shows the pump-induced changes in the dielectric function of Ar and the gas mixture 0.9 Ar + 0.1 SF$_6$ at various delays $\tau$ after excitation.

Upon excitation, the sample contains free electrons, ions, and neutral particles. As men-
tioned in Section 6.4, the free electrons are expected to make the dominating contribution to the THz response. Indeed, all real parts \( \text{Re} \Delta \varepsilon \) in Fig. 6.6 are negative, and their magnitude increases with decreasing frequency. According to Section 1.6.1, this is a clear signature of free charge carriers. Note that the real part \( \text{Re} (\Delta \varepsilon + 1) \) of the total dielectric function is always positive which excludes any complications of the anomalous skin effect as mentioned in Section 6.4.

Therefore, we employ the Drude formulas (1.12) and (1.13) to fit the measured dielectric function in which the fit parameters are the free-electron density \( n_e \) and the collision rate \( \Gamma \) of the free electrons. As seen in Fig. 6.6, the classical Drude model provides a nearly textbook-like reproduction of the experimental data. It should be emphasized that uncertainties of the exponents \( p_{\text{Re}} \) and \( p_{\text{Im}} \) of the data analysis in Section 6.5.3 lead to relatively moderate variations of the fit parameters \( n_e \) and \( \Gamma \) since \( p_{\text{Re}} \) and \( p_{\text{Im}} \) enter Eq. (6.8) in the radicand of the square root.

The temporal evolution of the fit parameters \( n_e \) and \( \Gamma \) is the main outcome of the preceding data analysis, and we start with a discussion of the dynamics of the density \( n_e \) of the free electrons.

### 6.6.1. Ar: Long-Lived Free Electrons

Figure 6.7(a) shows the temporal dynamics of the free-electron density \( n_e \) in the laser-ionized noble gas Ar. Note that \( n_e \) still increases during the first 50 ps after plasma generation and reaches a maximum of \( n_e = 2.5 \times 10^{17} \text{cm}^{-3} \) which corresponds to 1% of the total particle density of a gas under normal conditions. The additional generation of free electrons is most likely due to impact ionization of preexcited Ar atoms by fast electrons [Hol65]. After this increase, the electron density remains nearly constant up to \( \tau = 200 \text{ps} \). These extremely long-lived electrons are typical for monatomic gases and are also observed for the noble gas Kr (data not shown). Although binary collisions are the most frequent interaction events they are very ineffective for the recombination of an Ar\(^+\) ion with an electron e\(^-\) due to a lack of internal degrees of freedom: Apart from spontaneous photon emission there is no sink to absorb the kinetic and the binding energy of the electron. For this reason, the dominating recombination process is the 3-body collision [Bul02, Hol65]

\[
\text{Ar}^+ + 2\text{e}^- \rightarrow \text{Ar} + \text{e}^-.
\]  

(6.9)

As a consequence, the rate equation for the electron population can be written as \( \partial n_e / \partial \tau = -Kn_e^3 \) where equal densities of electrons and Ar\(^+\) ions are assumed, \( n_e = [\text{Ar}^+] \). The reaction constant of this reaction is given by the phenomenological relation \( K = 4.2 \times 10^{-29} \times (T_e/10000 \text{K})^{-8.29} \text{cm}^6 \text{s}^{-1} \) [Bul02]. According to this formula and the slow electron decay found here, the electronic temperature must be significantly larger than 5000 K.

It should be mentioned that also sequential reactions like \( \text{Ar}^+ + 2\text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar} \), \( \text{Ar}_2^+ + \text{e}^- \rightarrow \text{Ar} + \text{Ar}^* \) can lead to an electron decay. However, \( \partial n_e / \partial \tau \) scales with \( n_e \) for
6. Optically Ionized Gases: Long- and Short-Lived Electrons

Figure 6.7: (a) Temporal decay of the free-electron density $n_e$ of laser-ionized gases of Ar and O$_2$. In Ar, $n_e$ increases during the first 50 ps after excitation and remains constant afterwards. The electron decay in O$_2$ is much faster than in Ar as a consequence of the dissociative recombination (6.10) which does not occur in Ar. (b) The linear increase of the inverse electron density $1/n_e$ with time $\tau$ is a clear signature of the dissociative recombination in O$_2$.

this reactions instead of $n_e^3$. Therefore, the recombination reaction (6.9) is the dominating reaction at the elevated electron densities in our experiment [Bul02].

Before discussing the electron decay in O$_2$, we estimate the plasma parameters introduced in Section 6.2 for $n_e = 3 \cdot 10^{17}$ cm$^{-3}$ and $T_e = 10000$ K which reflect the conditions in our laser-ionized gases. The electron degeneracy parameter of $\Theta \approx 500$ means that one can apply Maxwell-Boltzmann statistics. The electron-electron coupling parameter of $g_{ee} = 0.16$ indicates that the electron-electron interaction can still be considered as a perturbation of the free-electron gas. The Debye screening length amounts to $\lambda_D = 12$ nm which is comparable to the mean distance $n_e^{-1/3} = 15$ nm of adjacent electrons. The electron cooling proceeds very slowly as shown by the inverse Spitzer rate $\tau_{ei}$ of more than 1 ns.

6.6.2. O$_2$: Dissociative Recombination

Figure 6.7(a) shows that the free electrons in laser-excited O$_2$ decay much faster than in Ar, namely on a time scale of roughly 50 ps. The reason for this behavior are the internal excitations of the O$_2^+$ ion which can dissipate the kinetic and the binding energy of the recombining electron [Hol65]. This energy leads to a breaking of the O$_2^+$ bond in the so-called dissociative recombination [Hol65]

$$\text{O}_2^+ + e^- \rightarrow \text{O} + \text{O}^*.$$  \hspace{1cm} (6.10)

At least 1 of the oxygen atoms is in an excited state after this reaction.

The rate equation for this process is $\partial n_e / \partial \tau = -Kn_e^2$ if equal densities of electrons and O$_2^+$ ions are assumed, $n_e = [\text{O}_2^+]$. This yields the linear relationship

$$\frac{1}{n_e} = \frac{1}{n_e(0)} + K\tau \hspace{1cm} \text{slope: } 3.5 \cdot 10^{-8} \text{ cm}^3 \text{s}^{-1}$$

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6.6. Results: Dynamics of the Free-Electron Density

![Graph](image)

**Figure 6.8.** (a) Temporal decay of the free-electron density $n_e$ of laser-ionized SF$_6$ and the mixture 0.9 Ar + 0.1 SF$_6$. The dynamics is much faster than in pure Ar. (b) Logarithmic plot of the dynamics in (a) together with monoexponential fits.

which indeed well reproduces the measured $1/n_e$ vs. $\tau$ for a reaction constant of $K = 3.5 \cdot 10^{-8}$ cm$^3$s$^{-1}$ as can be seen in Fig. 6.7(b).

The same temporal behavior has been also observed on much longer time scales: For example, Mehr et al. ionized O$_2$ by microwave radiation and measured a linear increase of $1/n_e$ with a temporal resolution of $\sim 1$ ms [Meh69]. Similar to Ar, such experiments led to a phenomenological formula for the reaction constant $K = 2 \cdot 10^{-7} \cdot (T_e/300$K$)^{-0.5}$ cm$^3$s$^{-1}$ as a function of electronic temperature $T_e$ [Pet05]. The application of this formula to our $K$ yields an electronic temperature of about $T_e = 9000$ K. However, due to the uncertainty in the absolute values of $n_e$ this value can be only considered as an estimate. The discussion of the free-electron decay in the remaining gases will permit a more accurate determination of the electronic temperature.

### 6.6.3. SF$_6$ in Ar: Electron Scavenger in Action

The man-made molecule SF$_6$ is known as a very effective electron scavenger due to its positive electron affinity of 1.1 eV and very large cross sections $\sigma_{\text{att}}$ for electron attachment, see Fig. 6.9(a) [Chr00]. For these reasons and due to its chemical stability, it is used as insulating gas and arc interrupter in high-voltage devices. In order to study the influence of SF$_6$ on the lifetime of free electrons we add a small amount of SF$_6$ to the pure Ar gas. Figure 6.8(a) shows that there is nearly no decay of the quasifree electrons in pure ionized Ar but this situation changes dramatically when we replace 10% of the Ar by SF$_6$: Now the free-electron density decays *exponentially* with a time constant of 79 ps as demonstrated by the logarithmic plot in Fig. 6.8(b). Indeed, the attachment reaction

$$\text{SF}_6 + e^- \rightarrow \text{SF}_6^- \tag{6.11}$$

implies the rate equation $\partial n_e/\partial \tau = -K \cdot [\text{SF}_6]n_e$ and thus a simple exponential decay

$$n_e(\tau) = n_e(0) \exp (-[\text{SF}_6] K \tau) \tag{6.12}$$

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![Figure 6.9](image)

**Figure 6.9.**: (a) Total cross section $\sigma_{\text{att}}$ for electron attachment to SF$_6$ as a function of the electron kinetic energy. Data are taken from Ref. [Chr00]. (b) Reaction constant $K$ for electron attachment to SF$_6$ as a function of electronic temperature $T_e$ according to Eq. (6.13). The 2 horizontal lines represent the measured reaction constants.

provided the reaction constant $K$ and the number densities [SF$_6$] and [Ar$^+$] do not change in the course of the reaction.

The free-electron decay in pure SF$_6$ is shown in Fig. 6.8(a) and exhibits a time constant of 12 ps which is a factor of $\approx 7$ faster than the decay in the Ar-SF$_6$ mixture. However, a factor of 10 is expected from the 10 times higher density of SF$_6$ molecules in the pure SF$_6$ gas, see Eq. (6.12). The slight difference between the observed and predicted time constant may be related to uncertainties of the SF$_6$ content in the Ar-SF$_6$ mixture, which is specified as 10$\pm$2\% by the supplier, and to different electron temperatures in the excited pure SF$_6$ gas and the mixture. Thus, we obtain values of $3.3 \times 10^{-9}$ and $5.1 \times 10^{-9}$ cm$^3$s$^{-1}$ for the reaction constant $K$ in pure SF$_6$ and the Ar-SF$_6$ mixture, respectively.

To the best of my knowledge, direct measurements of the ultrafast free-electron decay induced by the electron scavenger SF$_6$ are performed here for the first time.

**Estimate of the Electronic Temperature**

The exponential decay (6.12) of the electron population in pure SF$_6$ and the mixture $0.9\text{ Ar} + 0.1\text{ SF}_6$ permits to determine the corresponding time constants [SF$_6$] $K$ without knowing the absolute values of the electron density $n_e$. Therefore, the electronic temperature $T_e$ can be determined with better accuracy than in the cases of Ar and O$_2$ provided a functional relationship between $T_e$ and the reaction constant $K$ is known. The latter can be derived with the aid of the cross section $\sigma_{\text{att}}$ for electron attachment to SF$_6$ presented in Fig. 6.9(a). Note that $\sigma_{\text{att}}$ strongly increases with decreasing kinetic energy of the electron. This fact also explains the increasing slope of the electron decay in the logarithmic plot of Fig. 6.8(b) when the electrons cool down in the course of time.

Similar to the considerations in Section 1.5.2, the change in the density $f(\mathbf{v}, t)$ of electrons...
6.7. Results: Electron Collision Rate

Figure 6.10: (a) Temporal dynamics of the Drude collision rate $\Gamma$ in laser-ionized Ar and O$_2$. (b) Same as (a) for pure SF$_6$ and the mixture 0.9 Ar + 0.1 SF$_6$. Note that these dynamics resemble those of the free-electron densities in Figs. 6.7(a) and 6.8(a), respectively.

with a velocity within the interval $[\mathbf{v}, \mathbf{v} + d\mathbf{v}]$ is given by

$$\frac{\partial f}{\partial \tau} = -[SF_6] \sigma_{\text{att}} |\mathbf{v}| \cdot f.$$ 

If $f$ can be described by a Maxwell-Boltzmann distribution (1.14), the temporal change in the total electron density $n_e = \int d^3\mathbf{v} f$ is reduced to an integration over all kinetic energies $\epsilon$ of the electrons and yields the reaction constant [Jen01]

$$K = \frac{8\pi}{m_e^2} \left( \frac{m_e}{2\pi k_B T_e} \right)^{3/2} \int_0^\infty d\epsilon \sigma_{\text{att}} \epsilon \exp \left( -\frac{\epsilon}{k_B T_e} \right). \quad (6.13)$$

The derivation of this relation presumes a thermalized system of the free electrons.

The reaction constants $K$ calculated in this way are plotted in Fig. 6.9(b) as a function of electronic temperature together with the constants measured in pure SF$_6$ and the Ar-SF$_6$ mixture. This graph allows to infer an electronic temperature $T_e$ of 17000 to 23000 K which is of the same order of magnitude as the estimates based on the electron decay in Ar and O$_2$.

6.7. Results: Electron Collision Rate

We now discuss the Drude collision rate $\Gamma$ of the free electrons whose temporal dynamics is plotted in Fig. 6.10 for all gases investigated. For example, the value $\Gamma \approx 15$ THz found for Ar implies a mean free path of roughly 30 nm for the electrons in this gas if their average kinetic energy is $k_B \cdot 10000$ K. This mean free path is comparable to the approximate mean distance $n_e^{-1/3} \approx 15$ nm of adjacent electrons or Ar$^+$ ions.
6. Optically Ionized Gases: Long- and Short-Lived Electrons

Figure 6.11: (a) Plot of the collision rate $\Gamma$ vs. the electron density $n_e$ for all gases investigated. The temporal evolution is indicated by the arrow marked with “$\tau$”: A point $[n_e(\tau), \Gamma(\tau)]$ walks from the right to the left and from the top to the bottom of this diagram in the course of time. (b) Modeled Drude collision rates $\Gamma$ as a function of electron density $n_e$ and temperature $T_e$ based on the procedure described in the text and Fig. 6.12. Note that the experimental values exceed those modeled by a factor of 3 for SF$_6$ and the Ar-SF$_6$ mixture.

Note that the evolution of the collision rate $\Gamma$ in Fig. 6.10 is quite similar to that of the free-electron density in Figs. 6.7(a) and 6.8(a). This behavior appears most clearly for the fast free-electron decay in laser-excited SF$_6$ [Fig. 6.8(a)] and the corresponding decay of the collision rate [Fig. 6.10(b)]. For better comparison, Fig. 6.11(a) plots the collision rate $\Gamma$ vs. the electron density $n_e$ for all gases investigated and seems to reveal a nearly universal behavior: All curves have the same slope and, apart from that of O$_2$, even agree. This observation should not be overrated since the $n_e$ axis involves some systematic error as mentioned in Section 6.6. Nevertheless, this graph clearly demonstrates that the collision rate $\Gamma$ of the free electrons decreases with decreasing density $n_e$.

Within the framework of the Boltzmann approach to the dielectric function in Section 1.5.2, an increased collision rate is due to an increased number of scattering events of some “test electron” with other electrons (e), ions (i), and neutral particles (n). Since the number of neutral molecules remains virtually constant, the increase of $\Gamma$ with $n_e$ has to arise from e-e and e-i scattering.

Before modeling the dielectric function of our plasmas it should be mentioned that Mics et al. employed TRTS to measure the dielectric function of a cylindrical channel of ionized O$_2$ in the range from 1 to 3 THz [Mic05]. They found a scattering rate of 7 THz at an electron density of $1 \cdot 10^{16}$ cm$^{-3}$ which compares well to the data in Fig. 6.11(a).

6.7.1. Modeling the Dielectric Function

In order to estimate the contribution of e-i and e-n scattering to the dielectric function we now model the dielectric function of a partially ionized gas. We have to neglect e-e scattering such that Eq. (1.15) for the calculation of the dielectric function becomes
6.7. Results: Electron Collision Rate

applicable. Rewriting this equation in terms of the electron kinetic energy \( \epsilon = m_e v^2 / 2 \) instead of velocity \( v \) leads to

\[
\epsilon(\omega) - 1 = \left( \frac{2}{m_e} \right)^{3/2} \frac{(4\pi e)^2}{3m_e \omega} \int_0^\infty d\epsilon \frac{\partial f}{\partial \epsilon} \epsilon^{3/2} \frac{1}{\omega + i\gamma} \tag{6.14}
\]

where \( f \) is the Maxwell-Boltzmann distribution (1.14). Since e-i and e-n scattering are considered as the relevant mechanisms for the current relaxation, Eq. (1.16) yields the collision rate

\[
\gamma = v n_i \sigma_{ei} + v n_n \sigma_{en} \tag{6.15}
\]

of electrons moving with velocity \( v \). Note that \( \gamma \) is the collision rate of electrons moving with a velocity from a narrow interval \([v, v + dv]\). It should not be confused with the Drude scattering rate \( \Gamma \) which to some extent can be understood as an average of \( \gamma \) since Eq. (6.14) involves an integration over all kinetic energies \( \epsilon = m_e v^2 / 2 \) of the electrons.

We assume that there are only positive ions with a density \( n_i \) that equals the electron density, \( n_i = n_e \). This implies a neutral-particle density of \( n_n = n_{n0} - n_e \) with \( n_{n0} = 2.5 \times 10^{19} \text{ cm}^{-3} \) being the particle density of a gas under ambient conditions. The approximate momentum-transfer cross section \( \sigma_{en} \approx 10^{-15} \text{ cm}^2 \) for scattering between electrons and neutral atoms or small neutral molecules is taken from Ref. [Mit73].

Concerning the cross section \( \sigma_{ei} \) for e-i scattering, we assumed the screened Coulomb potential (6.1) to be the interaction potential between an electron and a positive ion. Dirk Gericke (Universität Greifswald) numerically solved the resulting 1-particle Schrödinger equation to provide us with the momentum-transfer cross sections \( \sigma_{ei} \) [Ger99]. This exact approach to the cross sections of the screened Coulomb potential is an improvement with respect to approaches involving the Born approximation [Sty02] or cut-off schemes [Ich73] which may lead to erroneous results [Sty02].

Figure 6.12 shows exemplary results of this modeling: The energy-dependent collision rate \( \gamma \) is plotted in Fig. 6.12(a) together with the weighting factor \( \epsilon^{3/2} \partial f/\partial \epsilon \) of the integral (6.14) for an electron density of \( 3 \times 10^{17} \text{ cm}^{-3} \) and an electron temperature of 10000 K. Note that \( \gamma \) is large for electrons with kinetic energies below 0.5 eV. However, the weight of these scattering rates is small and rather peaks at about 1 eV where e-n scattering contributes already more than 40% to the total collision rate of \( \gamma \approx 5 \text{ THz} \). Therefore one cannot expect an averaged scattering rate \( \Gamma \) much larger than 5 THz.

Figure 6.12(b) presents the resulting dielectric function for the same parameters \( n_e = 3 \times 10^{17} \text{ cm}^{-3} \) and \( T_e = 10000 \text{ K} \). In order to get a direct comparison to the experimental data, we fit the modeled dielectric function (6.14) to the Drude formula (1.12). As seen in Fig. 6.12(b), the fit excellently reproduces the electron density which was used as an input of Eq. (6.14). We repeat this procedure over a wide range of electron densities \( n_e \) and temperatures \( T_e \). The resulting Drude collision rates are plotted in Fig. 6.11(b) for comparison with the measured rates which is used as a basis of the following final discussion.
Figure 6.12: (a) Collision rate $\gamma$ for electrons with a kinetic energy $\epsilon$ together with the weighting factor $e^{\epsilon / 2} \partial f / \partial \epsilon$ of the integral (6.14). Curves are calculated for an electron density of $3 \times 10^{17}$ cm$^{-3}$ and an electron temperature of 10000 K. Note that for $\epsilon > 1$ eV e-n scattering more and more dominates the total scattering rate $\gamma$. (b) Dielectric function of a plasma calculated according to Eq. (6.14) for the same conditions as in (a). Thick solid lines mark a fit according to the Drude formula which excellently reproduces the input parameter $n_e = 3 \times 10^{17}$ cm$^{-3}$.

6.7.2. Indication of Strong Electron-Electron Scattering?

Figure 6.11 shows that we only get agreement between the measured and modeled scattering rates when we assume an electronic temperature below 2000 K. Such a temperature seems very unlikely in view of the decay rates found in Section 6.6. This is especially true for SF$_6$ and the Ar-SF$_6$ mixture where the exponential decay of the free electrons convincingly indicated an electronic temperature of more than 15000 K. We conclude that the model for the dielectric function used in the last section greatly underestimates the electronic scattering rate by a factor of up to 5 for the case of SF$_6$.

The question arises whether e-i scattering really dominates the electron collision rate in our laser-ionized gases. There are 2 possible scenarios:

1. Electron-ion scattering is the major contribution to the electron collision rate $\Gamma$ and is just underestimated by the model used in the preceding section. However, this assertion appears to be in contradiction to the dynamics of $\Gamma$ in SF$_6$: In this gas, the attachment reaction (6.11) should result in a decrease of the electron density but in an increase of the number of negative ions SF$_6^-$. As a consequence of the increased number of scattering centers, $\Gamma$ should also increase and lead to a curve of negative slope in Fig. 6.11(a).

Such behavior is not observed and either indicates a strong contribution of e-e scattering to the Drude collision rate $\Gamma$ or is due to a very efficient neutralization of the negative and positive ions by recombination reactions like

$$\text{SF}_6^+ + \text{SF}_6^- \rightarrow 2 \text{SF}_6.$$  \hspace{1cm} (6.16)

In the most optimistic case, when adjacent positive and negative ions move directly towards each other, it takes about 10 ps to cover their mean initial distance of $n_e^{-1/3} \approx$
6.8. Conclusion and Outlook

15 nm such that a recombination can occur. This time is comparable to the 12-ps time constant of the free-electron decay in the SF\textsubscript{6} plasma and may explain why the Drude collision rate does not increase with decreasing $n_e$.

For the above estimate, the kinetic energy of the SF\textsubscript{6} ion was set to the mean kinetic energy $k_B T_e \approx 2$ eV of the attached electron. Taking the Coulomb attraction between the ions into account does not substantially shorten the recombination time. Nevertheless, more thorough approaches are required to calculate the neutralization rate of positive and negative ions in reactions like (6.16) which for example also account for the occurrence of ion fragments such as SF\textsubscript{5}$^-$ [Chr00].

2. In the 2nd scenario, e-e scattering is assumed to make the major contribution to the electron collision rate $\Gamma$. Such a scenario would immediately explain why the modeled rates $\Gamma$ in Fig. 6.11 are substantially lower than those observed: Electron-electron interaction is simply not included in this model.

In literature [Sty02], e-e scattering is usually considered as a minor contribution to the velocity relaxation of the electrons based on an argument similar to that in Section 1.7: A collision between 2 electrons, for example shown in Fig. 1.3, involves the conservation of the total momentum $m_e v_1 + m_e v_2$ of the 2 electrons; as a consequence, the electronic current does not change, either.

However, e-e scattering can become operative in the current relaxation when higher-order processes are considered [Sty02, Ger05]: For example, 2 electrons from a Maxwell-Boltzmann distribution with comparable velocities scatter with each other resulting in the velocities $v_1$ and $v_2$. In case of $v_1 \ll v_2$, the electron with velocity $v_1$ suffers a much larger collision rate with ions as seen in Fig. 6.12. This is not compensated for by the electron with the large velocity. As is known from calculations of the dc conductivity of plasmas, this effect can make up to 40% of the contribution of e-i scattering to the current relaxation [Sty02]. This is still not enough to explain the discrepancy between the curves in Fig. 6.11(a) and Fig. 6.11(b) for electron temperatures of about 15000 K. Improved calculations of the ac conductivity may have to include, for example, dynamical screening effects which are not yet accounted for by the static Debye screening of Eq. (6.1) [Rei00].

We conclude that the present arguments are not sufficient to decide which of the 2 scenarios corresponds to reality. If the 1st scenario is true, the Drude collision rate $\Gamma$ represents a measure of the ion density making time-resolved THz spectroscopy an easy-to-interpret and useful tool to study the dynamics of optically excited gases.

6.8. Conclusion and Outlook

In conclusion, we employed time-resolved THz spectroscopy to study the electron dynamics in optically ionized gaseous Ar, O\textsubscript{2}, SF\textsubscript{6}, and the gas mixture 0.9 Ar+0.1 SF\textsubscript{6}. The measured
6. Optically Ionized Gases: Long- and Short-Lived Electrons

transient dielectric function allows for an excellent description by the simple Drude model leading to the temporal dynamics of the free-electron density $n_e$ and the Drude collision rate $\Gamma$. The electrons in Ar decay much slower than in O$_2$ due to a lacking dissipation channel for the kinetic and binding energy of the electron. However, the decay can be accelerated enormously by adding the electron scavenger SF$_6$ to Ar. In pure SF$_6$, the free-electron decay occurs with a time constant as short as 12 ps which directly demonstrates the ultrafast extinction of free electrons in SF$_6$ and allowed for a quite reliable estimate of the electronic temperature of 17000 to 23000 K. The Drude scattering rate $\Gamma$ was found to increase with the electron density. Assuming only collisions between electrons and ions and electrons and neutral particles underestimates the measured rates significantly. This and the fact that the electron attachment does not result in a temporal increase of $\Gamma$ might point to a dominant contribution of electron-electron scattering to the current relaxation.

Future work requires a more thorough modeling of the dielectric function of optically ionized gases in the THz range. The same applies to the recombination of positive and negative ions in SF$_6$. Regarding the experimental setup, the somewhat unknown sample structure could be improved by employing a supersonic gas jet in a small vacuum chamber. Then one deals with a thin and homogeneous gas film and can both pump and probe the sample from the same side. The resulting increased temporal resolution may be used to look for effects in the early stage after plasma generation. An example is the build-up of the screening in an initially uncorrelated plasma which was already observed in optically excited semiconductors [Hub01].
Summary

This thesis deals with the dynamics of charge carriers in optically excited solids and gases. The manner in which the excited electrons relax their energy and their average velocity is of particular importance in terms of technical applications. For example, graphite and, in particular, carbon nanotubes are potential alternatives to traditional semiconductors as base material for smaller and faster electronic devices. Therefore, electrons in these materials should relax their energy as slowly as possible and maintain an electronic current as long as possible when the driving electric field is switched off. The opposite behavior is required for insulating gases in high-voltage devices: Quasifree electrons should decay quickly and exhibit a low mobility in order to prevent short-circuits.

The conductivity of a material is determined by the electrons with the lowest excitation energies, for instance the electrons around the Fermi energy of a metal. Therefore, THz radiation is particularly sensitive to these charge carriers due to its very low photon energy \(2\pi \hbar \cdot 1 \text{ THz} = 4.1 \text{ meV}\). In this thesis, time-resolved THz spectroscopy is the method of choice in which an ultrashort visible laser pulse excites the charge carriers in the sample. After a variable temporal delay, they are probed by a THz pulse.

Two THz spectrometers were built in the course of this work. One of them is driven by a laser oscillator delivering 10-fs laser pulses with a 10-nJ pulse energy. It is used for the measurements of graphite and carbon nanotubes. However, the optical ionization of gas molecules requires much higher intensities and therefore another spectrometer driven by 20-fs laser pulses with a 1-mJ pulse energy. The THz pulses obtained have a duration of about 100 fs and cover the spectral range from 10 to 25 THz. It should be emphasized that the electric field of the THz pulse is detected which allows to determine the instantaneous dielectric function of the excited sample. The extraction of the dielectric function in a pump-probe experiment has to take the THz propagation through the excited sample into account. Corresponding relations have been derived in this work.

In the semimetal graphite, the analysis of the transient dielectric function is based on linear-response theory and yields the temporal evolution of 3 important observables of the excited system: The electronic temperature, the plasma frequency, and the Drude scattering rate. Our data exhibit a twofold dynamics: Within the first 500 fs, the electrons thermalize and lose more than 90% of their initial excess energy. This is an amazing result since the small Fermi surface of graphite implies that only \(\sim 1\%\) of all phonon modes can directly dissipate the electronic heat. Our simulations based on the 2-temperature
model reveal that strongly coupled optical phonons with quantum energies of up to 0.2\,eV dominate the energy transfer until they have heated up. The remaining slow decay of the electronic temperature is due to the cooling of these hot phonons by other, cold vibrational modes with a 5.4-ps time constant. In addition, the Drude collision rate of the electrons is found to increase by more than 30\% during the first ps after excitation. This is at least one order of magnitude larger than found in comparable experiments on doped semiconductors. Numerical estimates show that the hot phonons can explain a significant part of this rise. Therefore, they might limit the performance of graphite and carbon-nanotube circuits at elevated temperatures and high frequencies. On the other hand, these results show a route to populate certain phonon modes selectively which might be exploited in fields like surface femtochemistry.

In our carbon-nanotube sample, the pump pulse excites all types of tubes which can be metallic or exhibit electronic energy gaps of $\sim 20\,\text{meV}$ or $\sim 1\,\text{eV}$. The THz spectra lack a signature of free charge carriers which clearly indicates that strongly bound excitons are the main product of photoexcitation of the tubes with an energy gap of $\sim 1\,\text{eV}$. We find a spectral feature of enhanced transmission which is caused by the blocking of optical transitions in tubes with an energy gap of $\sim 20\,\text{meV}$. Similar to the dynamics in graphite, the decay of this feature is assigned to the cooling of hot optical phonons by other, cold phonons with a time constant of 1\,ps. This is significantly faster than in graphite and points to a stronger anharmonic coupling between the phonon modes of the nanotube. Finally, a small and featureless background of increased absorption exhibits a remarkable optical anisotropy. By using simple geometrical arguments, this can be directly traced back to the localization of charge carriers on a length scale of 100\,nm. We can consistently assign the localized excitations to optical transitions between higher-lying intraexcitonic levels in the tubes with energy gaps of $\sim 1\,\text{eV}$. These levels are rapidly depopulated with a time constant of 150\,fs due to the emission of optical phonons. These findings may be of great importance for the application of carbon nanotubes in photoconductive and nanoelectronic devices.

In the experiments with optically excited gases, the pump pulse is found to ionize about 1\% of all molecules. The THz response of the quasifree electrons is well described by the Drude model and yields the temporal evolution of the electron density $n_e$ and the Drude collision rate $\Gamma$. The electrons in ionized Ar decay on a time scale of more than 1\,ns which is an order of magnitude slower than in O$_2$ and due to a lacking dissipation channel for the kinetic and the binding energy of the electron. However, the electron decay can be accelerated enormously by adding the electron scavenger SF$_6$ to Ar. In pure SF$_6$, the free-electron decay occurs with a time constant as short as 12\,ps which directly demonstrates the ultrafast extinction of free electrons in SF$_6$. It allows for a reliable estimate of the electronic temperature of 17000 to 23000\,K. The Drude scattering rate $\Gamma$ was found to increase with the electron density. A model based on the Boltzmann equation which only accounts for collisions between electrons and ions and electrons and neutral particles underestimates the measured collision rates significantly. This and the fact that the electron capture by SF$_6$ does not increase $\Gamma$ might point to a dominant contribution of electron-electron scattering.
to the current relaxation. The measurements demonstrate that THz spectroscopy provides new and important information on the dynamics of quasifree electrons in gases.
Summary
A. Frequently Used Quantities and Abbreviations

Quantities

\[ \begin{align*}
    b & : \text{Bose-Einstein distribution function; band index} \\
    b_Q & : \text{occupation number of phonon mode } Q \\
    c & : \text{vacuum light speed} \\
    \epsilon & : \text{single-electron energy} \\
    f & : \text{Fermi-Dirac or classical distribution function} \\
    f_k & : \text{occupation number of electronic Bloch state } k \\
    k & : \text{electronic Bloch state} \\
    k & : \text{wavevector} \\
    n & : \text{refractive index} \\
    D & : \text{electronic density of states} \\
    E & : \text{electric field} \\
    P & : \text{induced electric polarization} \\
    Q & : \text{phonon mode} \\
    T & : \text{temperature} \\
    \epsilon & : \text{dielectric function} \\
    \tau & : \text{temporal delay between pump and probe pulse} \\
    \omega & : \text{angular frequency} \\
    \omega/2\pi & : \text{frequency}
\end{align*} \]
A. Frequently Used Quantities and Abbreviations

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>DFG</td>
<td>difference-frequency generation</td>
</tr>
<tr>
<td>DFT</td>
<td>density-functional theory</td>
</tr>
<tr>
<td>DOT</td>
<td>direct optical transition</td>
</tr>
<tr>
<td>e</td>
<td>electron</td>
</tr>
<tr>
<td>eDOS</td>
<td>electronic density of states</td>
</tr>
<tr>
<td>HiPCO</td>
<td>high-pressure carbon monoxide</td>
</tr>
<tr>
<td>HOPG</td>
<td>highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>i</td>
<td>ion</td>
</tr>
<tr>
<td>imp</td>
<td>impurity</td>
</tr>
<tr>
<td>interDOT</td>
<td>direct optical interband transition</td>
</tr>
<tr>
<td>intraDOT</td>
<td>direct optical intraband transition</td>
</tr>
<tr>
<td>IOT</td>
<td>indirect optical transition</td>
</tr>
<tr>
<td>n</td>
<td>neutral particle</td>
</tr>
<tr>
<td>NC</td>
<td>nanocylinder, short straight segment of a NT</td>
</tr>
<tr>
<td>NT</td>
<td>single-wall carbon nanotube</td>
</tr>
<tr>
<td>ph</td>
<td>phonon</td>
</tr>
<tr>
<td>SCOP</td>
<td>strongly coupled optical phonon</td>
</tr>
<tr>
<td>SFG</td>
<td>sum-frequency generation</td>
</tr>
<tr>
<td>TRTS</td>
<td>time-resolved THz spectroscopy</td>
</tr>
<tr>
<td>TS</td>
<td>THz (time-domain) spectroscopy</td>
</tr>
<tr>
<td>2TM</td>
<td>2-temperature model</td>
</tr>
<tr>
<td>N</td>
<td>set ( {1, 2, \ldots } ) of all positive integer numbers</td>
</tr>
<tr>
<td>Z</td>
<td>set ( {0, \pm 1, \pm 2, \ldots } ) of all integer numbers</td>
</tr>
</tbody>
</table>
B. Mathematical Definitions and Theorems

Fourier Transformation

\[ x(\omega) = \mathcal{F}[x(t)](\omega) = \int_{-\infty}^{\infty} dt \, x(t) \frac{\exp(i\omega t)}{\sqrt{2\pi}} \]  

(B.1)

\[ x(t) = \mathcal{F}^{-1}[x(\omega)](t) = \int_{-\infty}^{\infty} d\omega \, x(\omega) \frac{\exp(-i\omega t)}{\sqrt{2\pi}} \]

Convolution

\[ (x * y)(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt' \, x(t - t') \, y(t') \]  

(B.2)

Convolution Theorem

\[ \mathcal{F}(x * y) = \mathcal{F}(x) \mathcal{F}(y) \]
\[ \mathcal{F}^{-1}(x * y) = \mathcal{F}^{-1}(x) \mathcal{F}^{-1}(y) \]

Comparison

\( x \approx y: \quad \text{x is approximately equal to y} \)
\( x \sim y: \quad \text{x and y are of the same order of magnitude} \)
B. Mathematical Definitions and Theorems
C. Details of Numerical Calculations for Graphite

C.1. Direct Optical Transitions in Graphite

The contribution \( \varepsilon_{\text{inter}D\text{OT}} \) to the dielectric function of graphite is given by Eq. (1.19). The integration over \( \mathbf{k} \) can be reduced to the vicinity of the HKH line where 1 Fermi surface pocket is located. The other pocket around H’K’H’ is accounted for by a factor of 2.

The eigenenergies \( \epsilon_k \) required are obtained by diagonalizing the SWM Hamiltonian (4.4); the momentum matrix elements are obtained by applying the unitary transformation, which diagonalizes (4.4), to the 2nd term on the right-hand side of Eq. (4.4).

The diagonalization and integration are performed numerically for a mesh of frequencies \( \omega \) and electronic temperatures \( T_e \) whereas \( \varepsilon_{\text{inter}D\text{OT}} \) for all other \( \omega \) and \( T_e \) is obtained by 2-dimensional interpolation.

For the contribution \( \varepsilon_{\text{intra}D\text{OT}} \), the calculation of the plasma frequency (1.22) is sufficient which requires the knowledge of the velocity-weighted eDOS (1.23). For this purpose, the \( \epsilon \) axis was divided in intervals \([\epsilon_j, \epsilon_j + \Delta \epsilon]\). Scanning the \( \mathbf{k} \) space and the band structure \( \epsilon_{kb} \) point by point, the resulting band velocity \( \mathbf{v}_{kb} \) was added to the \( j \)th interval fulfilling \( \epsilon_{kb} \in [\epsilon_j, \epsilon_j + \Delta \epsilon] \). The ordinary eDOS (1.7) was calculated similarly.

C.2. 2-Temperature Model for Graphite

The temporal dynamics of the electron temperature \( T_e \) is obtained from that of the total electronic energy \( E_e \) by

\[
C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{\partial E_e}{\partial t}.
\]

The electronic heat capacity \( C_e \) is taken from Ref. [Nih03], and \( \partial E_e/\partial t \) is given by Eq. (1.6) which requires the evaluation of the Eliashberg function

\[
H(\epsilon, \epsilon', \Omega) = \sum_{kk'rr} |M_{k'k}^{\epsilon}_{\epsilon'}|^2 \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}) \delta(\Omega - \Omega_Q). \tag{C.1}
\]

In graphite, the usual approximation \( \epsilon = \epsilon' = \epsilon_F \) [All87] is not justified because of the strongly varying eDOS at the Fermi edge. To avoid the 6-dimensional integration over
### C. Details of Numerical Calculations for Graphite

<table>
<thead>
<tr>
<th>transition ((k_{\perp}, b) \rightarrow (k'_{\perp}, b'))</th>
<th>(r = \text{LO})</th>
<th>(r = \text{TO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\Gamma K + \kappa, \pi) \rightarrow (\Gamma K + \kappa', \pi^*))</td>
<td>(g_f^\pi [1 - \cos(\alpha - \alpha')])</td>
<td>(g_f^\pi [1 + \cos(\alpha - \alpha')])</td>
</tr>
<tr>
<td>((\Gamma K + \kappa, \pi^<em>) \rightarrow (\Gamma K + \kappa', \pi^</em>))</td>
<td>(g_f^\pi [1 + \cos(\alpha - \alpha')])</td>
<td>(g_f^\pi [1 - \cos(\alpha - \alpha')])</td>
</tr>
<tr>
<td>((\Gamma K' + \kappa, \pi) \rightarrow (\Gamma K' + \kappa', \pi^*))</td>
<td>(\approx 0)</td>
<td>(g_K^\pi [1 + \cos(\alpha - \alpha' - 60^\circ)])</td>
</tr>
<tr>
<td>((\Gamma K + \kappa, \pi^<em>) \rightarrow (\Gamma K' + \kappa', \pi^</em>))</td>
<td>(\approx 0)</td>
<td>(g_K^\pi [1 - \cos(\alpha - \alpha' - 60^\circ)])</td>
</tr>
</tbody>
</table>

Table C.1.: Electron-phonon matrix elements for the relevant electronic transitions in graphene taken from Ref. [Pis04]. The \(k_z\) component can change arbitrarily. Transitions within the \(\pi\) band are assumed to have the same matrix element as those within the \(\pi^*\) band.

In \(k\) space some simplifications are introduced: We assume that the e-ph coupling and the phonon dispersion of the SCOPs is the same like in graphene. Moreover, we neglect trigonal warping of the electronic \(\pi\) and \(\pi^*\) bands. It is important to take care of all prefactors since the absolute values of \(H\) are required.

According to Section 4.4, the small Fermi surface of graphite allows only for wavevector changes \(\Delta k_{\perp}\) close to the \(\Gamma\) or \(K\) point. In Eq. (C.1), this is enforced by the first two \(\delta\) functions together with \(\epsilon \approx \epsilon' \approx \epsilon_F\). In other words, the electron either stays in the pocket around \(K\) or \(K'\), or it jumps into the other pocket. We choose the electron BZ (eBZ) and phonon BZ (phBZ) differently such that umklapp processes do not occur for scattering from the \(K\) to the \(K'\) pocket. For reasons of symmetry, transitions from the \(K'\) to the \(K\) pocket give identical results and will be taken into account by a factor of 2. The eBZ used is the alternative eBZ in Fig. 4.6(a); the phBZ should be chosen such that \(\Gamma\) and \(K\) point are far away from the BZ boundary. Then, the sum in (C.1) is split up by using

\[
\mathbf{k} = \mathbf{k}_c + \mathbf{k}_{\perp} = \mathbf{k}_c + \mathbf{\Gamma}X + \kappa \quad \text{with} \quad X \in \{\text{K, K}'\}
\]

where \(\mathbf{k}_c = (0, 0, k_c)\) and \(\mathbf{k}_{\perp}\) are parallel and perpendicular to the \(c\) axis, respectively. The small translation \(\kappa\) is expressed in cylindrical coordinates as

\[
\kappa = \kappa \begin{pmatrix}
\cos \alpha \\
\sin \alpha \\
0
\end{pmatrix}
\]

where \(\alpha\) is the angle between \(\kappa\) and \(\mathbf{\Gamma}K\). The definitions for \(k'\) are analog. This yields

\[
H = \frac{1}{A^2} \sum_{bb'} \sum_{jj'} \sum_{k_z k'_z} \int \int \int \int d\kappa' d\kappa' \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}) \sum_{r} \delta(\Omega - \Omega_Q) |M_{kk'rr}|^2,
\]

where the summation over the \(\kappa\) mesh has been approximated by an integration with \(A\) being the volume of a cell in the 2-dimensional \(\kappa\) space.

We now make the following assumptions for the labeled terms in Eq. (C.2): (i) We neglect the \(\alpha\)-dependence of the electron bands which is reasonable since trigonal warping is weak...
C.3. Indirect Optical Transitions in Graphite

at the energies considered here. (ii) We neglect phonon dispersion along \( q_z \) and around \( \Gamma \) and \( K \) which implies \( q_z \rightarrow -X'X \in \{ \Gamma, K \} \). (iii) The matrix elements \( |M_{kk'}|^2 \) are those of graphene and listed in Table C.1. This implies their independence of \( k_z \).

Consequently, the angular integration in (C.2) affects only the e-ph matrix elements. Together with \( \sum_r \), this yields \( 4\pi^2 g_r^2 \) for the \( \Gamma \) phonons since the angular dependence of LO and TO branch cancel each other, whereas the \( K \) phonons yield \( 4\pi^2 g_K^2 \) and 0 for the LO and TO branch, respectively. Going back to Cartesian coordinates gives

\[
H = 2 \sum_{bb'} \sum_{rr} \left[ g_r^\Gamma \delta(\Omega - \Omega^\Gamma_r) + g_K^\Gamma \delta(\Omega - \Omega^\Gamma_K) \right] \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'})
\]

where

\[
g^\text{LO}_\Gamma = g^\text{TO}_\Gamma = 0.0405 \text{ eV}^2, \quad g^\text{LO}_K = 0.0994 \text{ eV}^2, \quad \text{and} \quad g^\text{LO}_K \approx 0
\]

have been introduced [Pis04]. Since these quantities do not depend on the electron band indices \( b \) and \( b' \) we finally obtain

\[
H(\epsilon, \epsilon', \Omega) = \frac{1}{8} \sum_r \left[ g_r^\Gamma \delta(\Omega - \Omega^\Gamma_r) + g_K^\Gamma \delta(\Omega - \Omega^\Gamma_K) \right] D(\epsilon) D(\epsilon')
\]

where we have exploited \( \sum_\kappa \delta(\epsilon - \epsilon_k) = D(\epsilon)/4 \); the factor \( \frac{1}{4} \) is due to the spin degeneracy and summation over only 1 of the 2 Fermi surface pockets.

This analytic formula for the Eliashberg function may have applications in all areas where the coupling between SCOPs and electrons in graphite is important. In particular, the 2TM (1.6) now reduces to an integration over 1 energy \( \epsilon \) only which can be performed numerically without further ado.

C.3. Indirect Optical Transitions in Graphite

The IOT contribution of e-ph coupling to the dielectric function is, according to Eqs. (1.24) and (1.25),

\[
\text{Im} \varepsilon^\text{IOT}_{\beta\beta} = 2 \left( \frac{2\pi \hbar e}{\hbar \omega} \right)^2 \sum_{kk'} \sum_{\pm} \sum_{\pm} S_{\pm\pm}(k, k', Q) |M^r_{k'k}|^2 \left( v_{k\beta} - v_{k'\beta} \right)^2
\]

and can be transformed into

\[
\text{Im} \varepsilon^\text{IOT}_{\alpha\alpha} = 2 \left( \frac{2\pi \hbar e}{\hbar \omega} \right)^2 \sum_{\pm} \int \int \int d\epsilon \, d\epsilon' \, d\Omega S_{\pm\pm}(\epsilon, \epsilon', \Omega) H^r_{\beta\beta}(\epsilon, \epsilon', \Omega).
\]

Here, \( \pm \) is related to photon absorption/emission and \( \pm \) to phonon emission/annihilation, respectively, and the factor

\[
S_{\pm\pm}(\epsilon, \epsilon', \Omega) = \left[ b(\Omega) + \frac{1}{2} \pm \frac{1}{2} \right] f(\epsilon) \cdot \left[ 1 - f(\epsilon') \right] \cdot \left[ \epsilon' \delta(\epsilon' - \epsilon \pm h\Omega^\pm) \right]
\]
C. Details of Numerical Calculations for Graphite

embraces all electronic and phononic occupation numbers. The auxiliary function

\[ H^{tr}_{\beta\beta}(\epsilon, \epsilon', \Omega) = \sum_{kk'} |M_{kk'}^r|^2 (v_{k\beta} - v_{k'\beta})^2 \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}) \delta(\Omega - \Omega_Q) \]

is proportional to the Eliashberg function \( \alpha_{tr}^2 F(\epsilon, \epsilon', \Omega) \) for transport which contains all information on electron-phonon-photon interaction [Gri81, All71]. Its evaluation is very similar to that of \( H \) in Appendix C.2 and results in

\[ H^{tr}_{\beta\beta}(\epsilon, \epsilon', \Omega) = \frac{1}{8} \sum_{r,X} g^x_{\beta} \delta(\Omega - \Omega_X^r) \left[ (v^2_{\beta} D)(\epsilon) D(\epsilon') + D(\epsilon)(v^2_{\beta} D)(\epsilon') + \Pi_X(u_{\beta} D)(\epsilon)(u_{\beta} D)(\epsilon') \right]. \]

Here, \( v^2_{\beta} D(\epsilon) \) is the velocity-weighted eDOS (1.23) in \( \beta \) direction with \( \beta \in \{x, y, z\} \), and \( u_{\beta} D(\epsilon) := \sum_k u_{k\beta} \delta(\epsilon - \epsilon_k) \). In the last expressions one has \( u_{k\beta} := v_{k\beta}/\cos \alpha \). The latter term only contributes for \( \Pi_X = \frac{1}{2} \) which happens if \( X = K \). Since the THz probe pulse is polarized perpendicularly to the graphite \( c \) axis only the \( x \) direction is relevant.

Now the summation over \( k \) space is reduced to an integral over an energy which can be performed numerically without further ado.
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Bibliography
Publications


Publications
Deutsche Kurzfassung


In den Experimenten mit Gasen ionisiert ein intensiver Anregungspuls etwa 1% aller Moleküle. In Ar verschwinden die freien Elektronen auf einer Zeitskala von mehr als 1 ns. Dies ist eine Größenordnung langsamer als in O2 und auf fehlende Dissipationskanäle für die
Akademischer Lebenslauf

11.07.1973 geboren in Chemnitz
1980–1989 Besuch der Polytechnischen Oberschule “A. Becker”, Chemnitz
1994–1995 Wehrdienst in Sonthofen
1995–1997 Grundstudium Physik, Universität Erlangen
seit 01.08.2001 Wissenschaftlicher Mitarbeiter in der Gruppe Prof. Wolf im Fachbereich Physik der Freien Universität Berlin
Akademischer Lebenslauf
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