A Gas-Based Terahertz Range Time-Domain Spectrometer

By: Filippos Kapsalidis

Supervisor: Prof. Dr. Steven Johnson

Advisor: Lucas Huber

Zürich
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Email: fkapsali@student.ethz.ch
Abstract

Most of the interesting low-energy dynamic processes in solid-state materials occur at energies that correspond to the mid- and far-infrared parts of the electromagnetic spectrum. A time-domain spectrometer that has access to this frequency range would be an extremely useful experimental tool for studying these processes. For that purpose, a gas-based terahertz time-domain spectrometer, capable of spanning the frequency range from 1 to 15 THz, was designed and built. With it, probing of mid- and far-infrared active excitations is possible. The generation of the THz radiation is realised through nonlinear interaction of a two-colour laser field in a laser-induced gas plasma, while the detection is accomplished with an Air Biased Coherent Detection (ABCD) scheme. In contrast to typically used solid-state THz emitters and detectors, whose bandwidth is limited by phonon resonances in the THz region or carrier lifetime, gases do not show any phonon absorption or etalon effects from surfaces, they show hardly any dispersion and are continuously replenishable. A gas-cell was specifically designed and built to house the relevant components used for the ABCD technique, as well as for the purpose of studying the effect and the contribution to the detection of THz radiation of various gases with high values of third-order nonlinear susceptibility $\chi^{(3)}$. In addition, a single-shot autocorrelator was built and included in the setup, with which the estimation of the probe pulse duration is possible. A systematic study of its performance with focus on determining and optimizing the efficiency of the ABCD scheme was initiated.

In this thesis, initially a detailed outline of the physical models behind gas-based THz generation and detection is given. Then, the setup of the gas-based THz time-domain spectrometer along with the relevant designed components and devices are described in detail. The thesis concludes with the measurement and analysis of the performance and ideas of optimization are presented.
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Chapter 1

Introduction - Motivation

1.1 Terahertz Radiation

Terahertz (1 THz = 10^{12} Hz) radiation is a form of electromagnetic radiation with frequencies within an approximate range from 0.1 to 30 THz, situated between the microwave and infrared parts of the electromagnetic (e.m.) spectrum [1,2], as shown in figure 1.1. In contrast to its well-studied neighbouring microwave, IR and visible regions, for which a plethora of sources, detectors and devices have been developed (such as lasers, masers, high-frequency electronics etc.), the THz region had remained for a long time unexplored. This was due to the difficulties of producing efficient and reliable THz sources and detectors. The THz band was therefore known in the past as the “THz Gap”.

![Figure 1.1: The place of the THz band in the electromagnetic spectrum. Located between the microwave and IR parts.](Source: uni-konstanz.de/FuF/Physik/terahertz/research.htm)

Due to the technological advancements of the last decades however, the gap started to be filled, as new schemes of generating and detecting THz waves were developed [3,4]. This sparked a lot of interest about the potential applications of THz waves, especially in materials science and spectroscopy, as THz photon energies (4 meV at frequency of 1 THz) coincide with and thus allow the study of numerous low-energy excitations in solid-state materials, for example lattice vibrations or spin waves. Therefore, terahertz radiation can be used as a tool for chemical recognition, as well as for the study of dynamic processes occurring at those frequencies [5].

1.2 Overview of Intense Tabletop THz Sources

There are several sources available that generate radiation of THz frequencies, each with its own advantages and disadvantages. These include large-scale facilities such as synchrotron accelerators and free-electron lasers to laboratory-sized equipment and table-top sources. In the following, a brief overview of conventional table-top THz sources will be given, with a focus on those most commonly used in THz spectroscopy.

Common, intense table-top THz sources can be distinguished into two major groups, based on their operational concept. These are, sources that involve nonlinear media within which incident laser waves experience a nonlinear optical process known as frequency conversion and sources that make use of photo-induced charges and time-varying currents which radiate in that regime. A schematic overview is given in figures 1.2 and 1.3.
Optical rectification (OR) and difference frequency generation (DFG) are the two main frequency down conversion mechanisms used \[6,7\]. They are second-order nonlinear optical processes, in which two optical photons of frequencies \( \omega_1 \) and \( \omega_2 \) interact with a nonlinear crystal and generate a THz photon of frequency \( \omega_T \) such that: \( \omega_T = \omega_1 - \omega_2 \). With OR, if broadband femtosecond (1 fs = \( 10^{-15} \) s) pulses are used (typical bandwidth of a fs-pulse \( \sim 10 \) THz), THz pulses whose shape resembles the optical pulse envelope can be generated. For the case of DFG, two superimposed optical beams of slightly different frequencies create an optical beat, and produce continuous wave (CW) THz radiation.

Other THz sources involve accelerating charges, induced by fs laser pulses in semiconductor devices, which in turn radiate electromagnetic radiation at THz frequencies. Usually that device is a biased photoconductive (PC) antenna (also known as PC switch) which is excited by fs-laser pulses \[8,9\]. A PC antenna consists of a semiconductor substrate with a short carrier lifetime, and a metal electrodes structure deposited on it, usually gold or aluminium, which have a gap between them on the order of \( \mu m \). The electrodes are biased with a voltage of 10-50 V, resulting in an electric field strength of a few kV/cm across the switch. When a laser pulse illuminates the biased gap of the device, charge carriers are created and immediately accelerated by the bias field. This rapid change in polarization induced by the ultrafast acceleration of the carriers generates a subpicosecond broadband THz pulse. A variation of this technique is photomixing, which produces CW THz radiation by using two laser beams with slightly different frequencies to form an optical beat \[10\].

### 1.3 Overview of Common THz Detectors

Detection of THz radiation is essentially divided in two categories: coherent and incoherent techniques. The main difference between these two is that in coherent detection both the amplitude and the phase
of the THz field are measured, allowing to subsequently accurately reconstruct the field, while with
incoherent detectors only the intensity of the field can be measured. Coherent detection schemes are very
similar to the THz generation techniques, in the sense that the concepts used are analogous.

In figure 1.4 an overview of commonly employed coherent detection schemes is shown. The most
widely used technique for coherent, broadband THz pulse detection is the free-space electro-optic (EO)
sampling [11–13]. This technique is based on the Pockels effect: the THz field induces birefringence in a
nonlinear crystal, proportional to its amplitude. Then, using a weak probe pulse to measure the induced
birefringence as a function of a time delay between the THz and probe pulses, the whole waveform of the
THz pulse can be determined.

![Figure 1.4: Overview of coherent THz radiation detection schemes.](source: Y-S Lee, "Principles of Terahertz Science and Technology"
)

Coherent detection can also be realised with a PC antenna [14]. Without a bias field, an incident THz
pulse induces a current in the gap between the electrodes, after a probe fs-laser pulse has created the
carriers. The induced current is proportional to the THz field amplitude. The THz pulse waveform can
then be determined in the time domain by measuring the photocurrent as a function of the time delay
between the THz pulse and optical probe.

### 1.4 Time Resolved Pump-Probe Spectroscopy

For the study of processes occurring on subpicosecond time scales, fs-pulsed lasers have proven to be an
extremely useful experimental tool [15]. This can be attributed to two characteristics of fs-lasers: firstly,
to the ultrashort pulses they produce, which primarily define the temporal resolution of such studies, and
have made probing of these processes possible. In addition, to the high energies these pulses carry, which
when they interact with a sample can excite dynamic phenomena and processes. These can be excitations
such as photoionization, lattice vibrations, etc.
Figure 1.5: Schematic of a typical setup of a time-resolved pump-probe experiment. On the right, it is shown how the pump pulse induces a change in a sample, and a weaker probe pulse is used to resolve that change. $\Delta t$ is the relative time delay between the pump and the probe. [Source: Y-S Lee, “Principles of Terahertz Science and Technology”]

Based on these characteristics, pump-probe techniques have been developed for time-resolved studies of dynamic processes [16]. A typical setup is illustrated in figure 1.5. A fs-laser beam is split in two parts, named thereafter the pump and probe beam. The time delay is adjusted by a mechanical translational stage which changes the path length of one of the two beams. At the sample position, the pump beam is used to induce changes and start dynamical processes in the sample, which are detected by measuring the probe beam’s transmission or reflection properties. By modulating the time delay, the whole induced dynamic process can be examined over its whole time scale of existence, as shown on the right side of figure 1.5.

1.5 Terahertz Time-Domain Spectroscopy

Terahertz time-domain spectroscopy (THz-TDS) is a spectroscopic technique, which uses pulses in the THz frequency range to study the optical properties of materials in that regime [17][18]. A typical THz-TD spectrometer is comprised of the THz pulse generation and detection components, usually operating with the assistance of fs-laser pulses, similar to a pump-probe technique. In figure 1.6 a schematic of a basic THz-TDS setup is shown.

The fs-laser beam is split into two parts, the pump and probe. One of these parts propagates through a mechanical translational stage that provides the time delay between the two. The pump pulse is incident to the emitter which generates the THz pulse. The THz pulse is then guided to a sample, with which it interacts. Depending on the configuration of the spectrometer, the reflected or transmitted through the sample THz field, is collected and illuminates the detector. The probe pulse is used to measure the THz-induced changes in the detector.

If a coherent detection scheme is applied, with which both the amplitude and phase of the THz pulse field are determined, then by scanning the time delay between...
the pulses, the entire waveform of the pulse can be obtained. Information acquired in the time domain can be Fourier transformed to the frequency domain, from which spectral information can be obtained.

### 1.6 THz Gas Photonics

The terahertz pulse generation by the nonlinear interaction of two-colour fs-laser fields within laser-induced plasmas in gases, is a recently developed, simple, yet promising technique that can be used to obtain short single-cycle, high-field strength, broadband and coherent THz pulses [4,19–23]. An illustration of a typical experimental realisation is shown in figure 1.7: a fundamental fs-laser beam of frequency $\omega$ is focused by a lens. Before the focal point, the second-harmonic of the fundamental beam is generated by a nonlinear crystal. The combined field of the two then ionizes the air and creates a plasma with which it nonlinearly interacts. Due to this interaction, a coherent THz beam is generated.


This technique of generating THz waves has several advantages over conventional solid-state THz wave emitters. Pump beams of much higher power can be used, as there is no damage threshold for a gas THz-emitter, since it is continuously replenishable. Therefore, THz pulses of very high field strengths can be generated, typically on the order of a few tens of kV/cm, with a record high of 4.4MV/cm as reported by Clerici and co-workers [24]. In addition, the bandwidth of the gas-plasma generated THz pulses is essentially only limited by the duration of the pump pulses. Gases do not have phonon resonances in the THz band, an attribute that semiconductors and nonlinear crystals usually exhibit, and which result in dark areas and undesirable features in the measured THz spectrum. Spectra of THz pulses obtained with this technique display a bandwidth that continuously spans the full THz region, from 0.1 to 15 THz and beyond. Moreover, there are no reflections of the THz radiation from any surfaces, which would lead to complicated interference patterns, as in the case of solid emitters.

![Waveform and spectrum obtained using THz gas photonics.](Source:N. Karpowicz et al. "Terahertz gas photonics")

Gases can also be used as a sensor to detect THz waves [25,26]. The Air Biased Coherent Detection (THz-ABCD) technique, based on the nonlinear process of THz field-induced second-harmonic generation
can provide superior bandwidth (0.1 to 15 THz and higher) and detection sensitivity, since it is also a
cohherent heterodyne detection scheme [27]. Its advantages over solid-state detectors are more or less
similar as for the case of THz emitters. In figure 1.8 the waveform and spectrum of a THz pulse emitted
and detected using a typical THz gas photonics setup as in figure 1.9 is illustrated.

![Figure 1.9: Schematic of a gas based setup for generation and detection of THz pulses using fs optical

### 1.7 Motivation for this Project

Considering the advantages of THz gas-photonics over conventional THz sources and detection schemes,
we worked towards the realisation of a THz time-domain gas-based spectrometer, capable of spanning the
frequency range from 0.1 to 15 THz. The terahertz pulses are generated through the nonlinear interaction
of near-infrared two-colour laser pulses in laser-induced plasma, while for the detection of the THz pulses
an Air Biased Coherent Detection scheme is employed. In principle, the constructed spectrometer allows
access to the majority of far- and mid-infrared active phonons in solid-state materials.

The gas-based time-domain THz spectrometer could work as an experimental tool for time-resolved
pump-probe spectroscopy studies in the range from 0.1 to 15 THz to which it has access. These studies
include:

- Spin-phonon coupling in transition-metal oxides and spin density wave systems [28].
- Plasmon and transient multi-particle states in semiconductor materials [29].
- Insulator-to-metal transitions in transition-metal oxides [30].

The thesis is structured as follows: in the next chapter, an introduction to the basic principles and
theory regarding THz gas-plasma photonics is given. After the basic foundations have been laid, in
Chapter 3 the governing mechanisms and physical models that describe the generation and detection of
THz radiation in gases are discussed in detail. In chapter 4, the experimental setup of the spectrometer
is thoroughly described, as well as the constructed devices and used experimental methods. In chapter
5, the results of the various experimental tests of the behaviour and performance of the spectrometer are
presented. Finally, in chapter 6 these results are analysed and the conclusions drawn from this analysis
are discussed.
Chapter 2

Principles of Terahertz Gas-Plasma Photonics

In this chapter, a brief description of the fundamental concepts and basic theory that concern THz radiation generation, propagation and detection, as well as the optical nonlinear phenomena associated with plasma physics and gas plasma induction will be given.

2.1 Maxwell’s Equations

When discussing electromagnetic radiation, it is wise to start from the basic foundations \[31\]. These are Maxwell’s equations, which in their in macroscopic (and differential) form are:

\[
\nabla \cdot \vec{D}(\vec{r}, t) = \rho_f \tag{2.1}
\]

\[
\nabla \cdot \vec{B}(\vec{r}, t) = 0 \tag{2.2}
\]

\[
\nabla \times \vec{E}(\vec{r}, t) = -\frac{\partial \vec{B}(\vec{r}, t)}{\partial t} \tag{2.3}
\]

\[
\nabla \times \vec{H}(\vec{r}, t) = \vec{J}_f + \frac{\partial \vec{D}(\vec{r}, t)}{\partial t} \tag{2.4}
\]

where $\rho_f$ and $\vec{J}_f$ are the free charge density and free current density respectively. Together with Lorentz’ force law,

\[
\vec{F}(\vec{r}, t) = q(\vec{E}(\vec{r}, t) + \vec{v} \times \vec{B}(\vec{r}, t)) \tag{2.5}
\]

these equations establish the whole theoretical framework of classical electromagnetism.

The macroscopic electric displacement field $\vec{D}$ and magnetic field $\vec{H}$ are related to the fundamental microscopic electric and magnetic fields $\vec{E}$ and $\vec{B}$ as:

\[
\vec{D}(\vec{r}, t) \equiv \epsilon_0 \vec{E}(\vec{r}, t) + \vec{P}(\vec{r}, t) = \epsilon_0 \epsilon_r \vec{E}(\vec{r}, t) = \epsilon_0 (1 + \chi) \vec{E}(\vec{r}, t) = \epsilon \vec{E}(\vec{r}, t) \tag{2.6}
\]

\[
\vec{H}(\vec{r}, t) \equiv \frac{1}{\mu_0} \vec{B}(\vec{r}, t) - \vec{M}(\vec{r}, t) = \frac{1}{\mu} \vec{B}(\vec{r}, t) \tag{2.7}
\]

where $\epsilon_0$ and $\mu_0$ are the permittivity and the permeability of vacuum, $\epsilon$ and $\mu$ the permittivity and permeability of the medium, and $\vec{P}$ and $\vec{M}$ are the polarization density and magnetization vectors respectively. These vectors contain the information of macroscopic-scale electromagnetic properties of matter.

In general, magnetic responses in matter are small, $|\mu - \mu_0| < 10^{-4}\mu_0$, compared to their electric counter part, mainly due to the non-existence of magnetic monopoles.
2.2 The Electromagnetic Wave Equation

In the previous section it became apparent that the electric and magnetic fields described by Maxwell’s equations are coupled. By calculating the curl of equations (2.3) and (2.4), the wave equation for the fields $\vec{E}$ and $\vec{H}$ can be derived:

$$\nabla^2 \vec{E}(\vec{r},t) - \epsilon \mu \frac{\partial^2 \vec{E}(\vec{r},t)}{\partial t^2} = 0$$

(2.8)

and the speed at which light propagates in this medium is:

$$v = \frac{1}{\sqrt{\epsilon \mu}} = \frac{c}{n}$$

(2.9)

where $c$ is the speed of light in vacuum, given by $c = 1/\sqrt{\epsilon_0 \mu_0}$, and $n$ is the refractive index of the medium, defined as $n = \sqrt{\epsilon/\epsilon_0}$, assuming $\mu = \mu_0$.

The Plane Wave Solutions of the Wave Equation

One of the solutions of the electromagnetic wave equation, are the so-called plane waves:

$$\vec{E}(\vec{r},t) = \vec{E}_0 e^{i(k \cdot \vec{r} - \omega t)} \text{ and } \vec{H}(\vec{r},t) = \vec{H}_0 e^{i(k \cdot \vec{r} - \omega t)}$$

(2.10)

which describe linearly-polarized, monochromatic (single frequency) plane waves, where $k$ is the wavevector and $\omega$ the angular frequency. Using Maxwell’s equation one can prove that the fields $\vec{E}$ and $\vec{B}$ are perpendicular to $k$, and thus to the direction of propagation:

$$k \cdot \vec{E} = 0 \text{ and } k \cdot \vec{H} = 0.$$  

(2.11)

For non-magnetic media, where the magnetic permittivity $\mu = 1$, the wavevector magnitude $k$ is related to wavelength $\lambda$ by the dispersion relation:

$$k = \frac{2\pi}{\lambda} = \frac{n \omega}{c}$$

(2.12)

The flow of energy of an electromagnetic wave is represented by the Poynting vector $\vec{S}$, calculated from the cross product of $\vec{E}$ and $\vec{H}$:

$$\vec{S}(\vec{r},t) = \vec{E}(\vec{r},t) \times \vec{H}(\vec{r},t)$$

(2.13)

The optical intensity $I(\vec{r},t)$, defined as the power flowing through a unit area perpendicular to the Poynting vector $\vec{S}$, is equal to the magnitude of the time-averaged Poynting vector. It is given as:

$$I = | < \vec{S} > | = \frac{1}{2} v e |E_0|^2 = \frac{1}{2} c \epsilon_0 |E_0|^2$$

(2.14)

Optical intensity is the quantity that is usually measured by light detectors, as the electric fields of optical frequencies oscillate too fast for a detector to be able to resolve. Since intensity is proportional to the square of the electric field, any phase information is lost and therefore direct reconstruction of the electric field of an optical wave is not possible. However, electric field amplitude and phase information recovery can be done using other methods, as it will be shown later in this thesis. The units typically used for measuring light intensity are Watts per square centimetre, $W/cm^2$. 

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Helmholtz Equation and Gaussian Beams

Assume now that the solution of the wave equation of an electric field \( \vec{E}(\vec{r},t) \) in a sourceless medium is monochromatic and linearly polarized independent of position \( \vec{r} \) in space towards a direction \( \hat{E}_0 \), varying in time as \( e^{i\omega t} \), and that can be written as:

\[
\vec{E}(\vec{r},t) = \vec{E}(\vec{r}) e^{i\omega t} = \hat{E}_0 U(\vec{r}) e^{i\omega t}
\]  

(2.15)

Inserting this to the wave equation, it changes it to another well-studied form, the Helmholtz equation:

\[
\left( \nabla^2 + k^2 \right) \vec{E}(\vec{r},t) = 0
\]

(2.16)

where \( k \) is the wavevector as already defined. One of the most interesting and relevant to laser physics solution of the Helmholtz equation is the Gaussian beams [31]. The transverse profile of the electric field strength and optical intensity distributions of such beams can be identified as Gaussian. Most laser beam profiles can be approximated by this type. The complex electric field of a Gaussian beam propagating along the \( z \)-axis is given by:

\[
E(\vec{r},z,t) = \frac{E_0}{1 + iz/z_R} e^{\left( \frac{-\vec{r}^2}{w^2(z)} - ikz - ik \frac{\vec{r}^2}{2R(z)} + i\zeta(z) \right)} e^{i\omega t}
\]

(2.17)

where \( \vec{r} \) is now the radial distance from the propagation axis \( \hat{z} \) and \( z \) is the distance along the propagation axis, starting from where the beam is the narrowest. The evolution of a Gaussian beam near that area is illustrated in figure 2.1. The rest of the parameters appearing are:

- The width of the beam \( w(z) \), which is given by:
  \[
w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}
  \]
  (2.18)

  where \( w_0 \) is the minimum value of the width, known as beam waist.

- The radius of curvature of the wavefronts which comprise the beam \( R(z) \), as a function of position \( z \):
  \[
  R(z) = z \left[ 1 + \left(\frac{z_R}{z}\right)^2 \right]
  \]
  (2.19)

Figure 2.1: Gaussian beam width as function of distance \( z \). [Source:optique-ingenieur.org]
The Rayleigh length $z_R$, given by:

$$z_R = \frac{\pi w_0^2}{\lambda} \quad (2.20)$$

which defines the distance from the beam waist position along the direction of propagation, where the beam area cross section doubles. Finally, the Gouy phase $\zeta$:

$$\zeta = \tan^{-1}\left(\frac{z}{z_R}\right) \quad (2.21)$$

The presence of the Gouy phase factor causes a Gaussian beam to gain an additional amount of phase whenever the beam is focused, in addition to the predicted plane wave $e^{-ikz}$ phase shift. The overall Gouy phase shift for a Gaussian beam going through a focus is $\pi$.

## 2.3 Electromagnetic Waves in Matter

### 2.3.1 Optical Properties of Matter

The absorption of light by a medium is quantified by its absorption coefficient $\alpha$ \[32\]. This quantity is defined as the amount of optical power absorbed per unit length of the medium. The intensity of an electromagnetic wave after it has propagated to a position $z$ in a medium is given by Beer’s law:

$$I(z) = I_0 e^{-\alpha z} \quad (2.22)$$

Most of the optical properties of a medium, such as absorption and refraction, can be described by the complex refractive index $\hat{n}$, defined as:

$$\hat{n} = n + i\kappa \quad (2.23)$$

The real part of the above relation is the same as the one given by relation \[2.9\]. The imaginary part includes the extinction coefficient $\kappa$, which is related to the absorption coefficient $\alpha$ as:

$$\alpha = \frac{2\kappa \omega}{c} = \frac{4\pi \kappa}{\lambda} \quad (2.24)$$

Both quantities $\alpha$ and $n$ are strongly dependent on the frequency of the electromagnetic wave.

The complex refractive index is also linked to the complex dielectric function $\hat{\epsilon}_r$ of the medium as:

$$\hat{\epsilon}_r = \hat{n}^2 = \epsilon' + i\epsilon'' \quad (2.25)$$

These optical quantities can give useful information about the composition and other physical properties of material samples. It is possible to obtain these quantities by employing spectroscopic techniques, such as transmission spectroscopy, as will be discussed in later sections.

### 2.3.2 Reflection and Transmission of electromagnetic waves - Fresnel Equations

An electromagnetic wave propagating from a medium with refractive index $n_1$, incident at an angle $\theta_i$ on another with refractive index of $n_2$ will transmit through the other medium at an angle $\theta_t$ and/or reflect from the interface between the two media. The behaviour of the electromagnetic wave is described by the so-called Fresnel equations \[33\]. The Fresnel equations can be used to calculate the reflected and transmitted waves’ electric fields $E_r$ and $E_t$ using the electric field $E_i$ of fundamental incident wave. Two extreme cases can exist:
If the electric field of the incident wave is polarized perpendicularly to the plane of incidence on the interface, the reflection and transmission coefficients are given by:

\[ r_s = \frac{E_r}{E_i} = \frac{n_1 \cos \theta_i - n_2 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_i} \quad \text{and} \quad t_s = \frac{E_t}{E_i} = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_i} \]  

(2.26)

For parallel polarization of the electric field to the plane of incidence, the coefficients are given by:

\[ r_p = \frac{n_2 \cos \theta_i - n_1 \cos \theta_i}{n_2 \cos \theta_i + n_1 \cos \theta_i} \quad \text{and} \quad t_p = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_i} \]  

(2.27)

Figure 2.2: Reflection and transmission of an electromagnetic wave at an interface between two media.

### 2.3.3 Transmission Spectroscopy

Transmission spectroscopy is an experimental technique which can be applied to measure the optical properties of sample materials \[ [34] \]. By coherently measuring both the amplitude and the phase of the transmitted electric field, one can determine the complex refractive index of the material \( \hat{n}(\omega) \) and subsequently the dielectric function \( \epsilon_r(\omega) \) and absorption coefficient \( \alpha(\omega) \).

Assume for simplicity perpendicular incidence of the fundamental wave on a single-layer sample material, as shown in figure 2.3. Inside the sample material, the transmitted wave undergoes multiple reflections by the material-air front and back interfaces, before finally transmitting out of the sample. The detected, transmitted electric field \( E_t \) is then the sum of these multiple reflected components and can be expressed as:

\[ E_t = E_i t_1 t_2 e^{i\phi_d} + E_i t_1 t_2 e^{i\phi_d} \left( r_1 r_2 e^{2i\phi_d} \right) + ... = E_i t_1 t_2 e^{i\phi_d} \sum_{m=0}^{\infty} \left( r_1 r_2 e^{2i\phi_d} \right)^m = \frac{E_i t_1 t_2 e^{i\phi_d}}{1 - r_1 r_2 e^{2i\phi_d}} \]  

(2.28)

where \( \phi_d \) is the phase shift of the reflected wave as it propagates a distance \( d \) within the sample material:

\[ \phi_d = \hat{n}(\omega) \frac{\omega}{c} d \]  

(2.29)

Since perpendicular angle of incidence \( \theta_i = 0 \) was assumed, the reflection and transmission coefficients are:

\[ r_1 = r_2 = \frac{n - 1}{n + 1} \]  

(2.30)

\[ t_1 = \frac{2}{n + 1} \]  

(2.31)

\[ t_2 = \frac{2n}{n + 1} \]  

(2.32)
In the end, what is extracted is the complex transmission coefficient $t(\omega)$, calculated as the ratio of the measured transmitted and incident fields:

$$t(\omega) = \frac{E_t(\omega)}{E_i(\omega)} = \frac{4\hat{n}(\omega)e^{j\phi_d(\omega)}}{[\hat{n}(\omega) + 1]^2 - [\hat{n}(\omega) - 1]^2 e^{2j\phi_d(\omega)}}$$  \hspace{1cm} (2.33)

from which in turn the calculation of the complex refractive index $\hat{n}$ is possible.

2.4 Nonlinear Light-Matter Interaction

When an electromagnetic wave propagates through a medium, it induces a certain amount of polarization density $\vec{P}$. For lower intensities $I$, or equivalently low electric field strength amplitudes $E$, this induced polarization is directly proportional to the electric field strength of the propagating wave. However, as intensity increases, this relation holds no more: nonlinear contributions start to become more significant, and play a very important role for a large number of optical phenomena. The term “nonlinear” refers to the response of the optical properties of a material to the electric field of an applied optical wave. The field of Nonlinear Optics (NLO), which is occupied with the study of optical nonlinear phenomena, has seen an increase the last decades, due to the increasing availability of highly intense coherent laser sources [31,35].

2.4.1 Linear and Nonlinear Polarization Density

Generally, the strength of the electric field of optical electromagnetic waves is weak as compared to the characteristic inter-atomic or lattice crystalline binding fields, whose strength is typically in the order of $\sim 10^5 - 10^9 V/m$ [36]. Thus, the polarization density $\vec{P}$ induced by such waves propagating in a medium, is characterized by a linear relation to the electric field strength $\vec{E}$ as:

$$\vec{P}(t) = \epsilon_0 \chi_e \vec{E}(t)$$  \hspace{1cm} (2.34)

where $\epsilon_0$ is the permittivity of free space and $\chi_e$ the (linear) susceptibility of the medium.

However, for increasing electric field strengths, when their magnitude starts to become comparable to the inter-atomic fields, equation 2.34 starts to deviate from linearity and the expression can be expanded into a Taylor series with respect to the electric field strength, in the form:

$$P(t) = \epsilon_0 \chi^{(1)}E(t) + \chi^{(2)}E(t)^2 + \chi^{(3)}E(t)^3 + ... \equiv P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + ...$$  \hspace{1cm} (2.35)
where $\chi^{(n)}$, is the $n^{th}$ order nonlinear optical susceptibility. Obviously, the linear, first order term dominates for small electric field strengths $\vec{E}$. The second term represents a quadratic or second-order nonlinearity, the third term a third-order nonlinearity and so forth. The $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ susceptibilities are characteristic constants of the medium. The quantities $P^{(2)} = \epsilon_0 \chi^{(2)} E^2(t)$ and $P^{(3)} = \epsilon_0 \chi^{(3)} E^3(t)$ are referred to as second and third order nonlinear polarizations.

When considering the vector nature of the quantities at play, the electric polarization $\vec{P}$ relation with the applied electric field $\vec{E}$ can be expressed through its components as:

$$
P_i = \epsilon_0 \sum_j \chi^{(1)}_{ij} E_j + \epsilon_0 \sum_j \sum_k \chi^{(2)}_{ijk} E_j E_k + \epsilon \sum_j \sum_k \sum_l \chi^{(3)}_{ijkl} E_j E_k E_l + ... \quad (2.36)$$

where i,j=x,y,z. The $\chi_{xxxx}^{(n)}$ parameters are the relevant $n^{th}$ rank tensor components of the nonlinear susceptibility.

### 2.4.2 The Nonlinear Electromagnetic Wave Equation

It has already been discussed that the propagation of an electromagnetic wave in a medium is governed by the electromagnetic wave equation, as given by equation $2.8$. For propagation in a medium, due to the presence of polarization density $\vec{P}$, this polarization acts as a source of radiation, and is expressed by an additional source term in the wave equation. Hence, the wave equation for a homogeneous arbitrary medium becomes:

$$
\nabla^2 \vec{E}(\vec{r}, t) - \frac{n^2}{c^2} \frac{\partial^2 \vec{E}(\vec{r}, t)}{\partial t^2} = \mu_0 \frac{\partial^2 \vec{P}(\vec{r}, t)}{\partial t^2} \quad (2.37)
$$

Polarization density $\vec{P}$ depends linearly on the electric field $\vec{E}$, so this equation is still homogeneous and can be solved analytically.

Next it is assumed that the electromagnetic wave is intense enough to induce an additional nonlinear polarization component in the medium. The total polarization density can then be written as a sum of the linear and the nonlinear terms:

$$
\vec{P}(\vec{r}, t) = \epsilon_0 \chi^{(1)} \vec{E}(\vec{r}, t) + P_{NL} \quad (2.38)
$$

Thus, the wave equation of light propagation in a nonlinear medium can be expressed as:

$$
\nabla^2 \vec{E}(\vec{r}, t) - \frac{n^2}{c^2} \frac{\partial^2 \vec{E}(\vec{r}, t)}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P_{NL}}{\partial t^2} \quad (2.39)
$$

This new relation is a inhomogeneous, differential equation: the nonlinear response acts as a source term which drives the electric field $\vec{E}$. The time-varying polarization can behave as a source of new frequency components to the electromagnetic field.

There are two methods which one can use to derive a solution for the nonlinear wave equation: one is the iterative Born approximation which can be used to estimate fields when the nonlinear effects are weak, and the alternative option is the coupled wave theory which is used when nonlinear effects are strong.

### 2.4.3 Phase matching

Most of the optical nonlinear frequency-mixing processes are phase-sensitive, and as such, they require phase-matching in order to be efficient. This practically means that there is a certain phase relation between the interacting waves that needs to be maintained along the volume where the interaction takes place.
This is expressed by a phase-mismatch relation, which should be zero for maximum conversion efficiency of the nonlinear process. If this relation is fulfilled, then all the amplitude contributions to the generated wave from different locations of the nonlinear medium are all in phase at the end of the medium. Otherwise, these contributions are out of phase, and essentially cancel each other out. This is depicted in figure 2.4 which shows how the different contributions of the second-order nonlinearities accumulate.

Tolerable Phase Mismatch

As introduced before, the phase-matching conditions are a crucial relation that influences the efficiency of a frequency conversion process. Considering a general case, for which two waves with wavevectors $\vec{k}_1$ and $\vec{k}_2$ interact with the nonlinear medium and produce a third wave with a wavevector $\vec{k}_3$, then the phase-mismatch relation can be defined as: $\Delta \vec{k} = \vec{k}_3 - \vec{k}_1 - \vec{k}_2 = 0$. If for any reason $\Delta \vec{k} \neq 0$, then the efficiency of the conversion process is largely reduced.

It can be shown that the intensity of the generated wave is given by the relation:

$$I_3 \propto \left| \int_V \varepsilon_0 \chi^{(2)} E_1 E_2 e^{i \Delta \vec{k} \cdot \vec{r}} d\vec{r} \right|^2$$

(2.40)

where $E_1$ and $E_2$ the electric field strengths of the two fundamental interacting waves and $V$ the interaction volume in the nonlinear crystal. Since the contributions of of the various points along the interaction volume are added as phasors, the position-dependent phase $\Delta \vec{k} \cdot \vec{r}$, for $\Delta \vec{k} \neq 0$ can reduce the total intensity of the generated wave.

2.4.4 Second-order Nonlinear Phenomena

For media that posses second-order nonlinearities, which is expressed by a large non-zero second-order nonlinear susceptibility $\chi^{(2)}$ and negligible higher order nonlinearities, the nonlinear polarization density $P_{NL}$ is mainly given by a strong second-order nonlinear polarization component, as:

$$P_{NL} = P^{(2)} = \epsilon_0 \chi^{(2)} E^2$$

(2.41)

Only non-centrosymmetric media which lack inversion symmetry can exhibit second-order nonlinearities. This can be understood as follows: when spatially inverting the medium and the applied electric field, the signs of both $\vec{E}$ and $\vec{P}$ reverse. For the nonlinear polarization component $P_{NL}$ to change sign, the second-order susceptibility must also change sign with the spatial inversion. This is of course not possible, and essentially means that spatial inversion cannot be a symmetry operation of a second-order nonlinear medium. This imposes a limitation on the amount of media that posses this kind of nonlinearity, as most materials do have inversion symmetry. On the other hand, there are no limitations for third-order nonlinearities, and essentially every material exhibits some non-zero third order nonlinearity.

One characteristic second-order nonlinear phenomenon is the second-harmonic generation (SHG), firstly discovered by P. Franken, soon after the invention of the laser \[37, 38\]. With this, a fundamental input light beam, most usually a laser beam, interacts with a nonlinear material and generates a second wave that oscillates at twice the frequency of the fundamental.
General Case - Three-Wave Mixing

The most general case of the second-order nonlinear processes involves the frequency mixing of two fundamental waves with arbitrary distinct frequencies, referred to in this context as the *signal* and *idler*, and a plethora of generated components with various frequencies, compilations of the fundamental ones. Consider the superposition of these two waves, with distinct angular frequencies $\omega_1$ and $\omega_2$ such as:

$$E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c$$

(2.42)

with c.c denoting the complex conjugate.

The second-order nonlinear polarization, as defined by equation 2.41 in turn gives:

$$P^{(2)} = \epsilon_0 \chi^{(2)} \left[ E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1E_2 e^{-i(\omega_1+\omega_2)t} + 2E_1^*E_2 e^{-i(\omega_1-\omega_2)t} + c.c. \right] + 2\epsilon_0 \chi^{(2)} [E_1E_1^* + E_2E_2^*]$$

(2.43)

As expected, the induced second-order polarization density is comprised of many different components oscillating at various frequencies: the last two terms are the second-harmonic components, with frequencies $2\omega_1$ and $2\omega_2$. The rest of the terms include components oscillating at the sum ($\omega_1 + \omega_2$), and difference ($\omega_1 - \omega_2$) of the fundamental frequencies, as well as a non-oscillating contribution (*optical rectification*).

It should be noted however that, mixing two waves at different frequencies does not necessarily mean that all different frequency components will be generated, as certain phase matching conditions must be fulfilled.

![Figure 2.5: Optical Parametric processes](Source: Saleh & Teich, Fundamentals of Photonics)

In figure 2.5, some of the different types of three-wave mixing processes are shown. They are also called parametric, meaning that it is possible to tune the frequencies range by manipulating the parameters which govern the phase matching of the process. One of these processes which is also of interest to us, is the optical parametric amplification.
Optical Parametric Amplification

Optical parametric amplification is a second-order nonlinear frequency conversion process [35]. As illustrated in figure 2.5, a signal wave of frequency $\omega_1$ propagates through a nonlinear crystal together with a pump wave of higher frequency $\omega_3$. In the crystal, photons of the pump wave are divided into signal photons and into the same number of idler wave photons, which is an additional generated wave of frequency $\omega_2$, governed by the relation $\omega_2 = \omega_3 - \omega_1$.

A device of such configuration, known as an Optical Parametric Amplifier (OPA), functions as a coherent amplifier at the signal frequency $\omega_1$, with the energy for this amplification being supplied by the pump wave [39]. The amplifier gain is a function of the pump power. In addition, since the pump energy is fully converted to energy of signal and idler waves, the crystal material is not heated during this process and phase-matching is maintained.

2.4.5 Third-order Nonlinear Phenomena

For centrosymmetric media, the second-order nonlinear term vanishes, as polarization density $\vec{P}$ must be aligned according to the applied electric field $\vec{E}$. Thus, the highest nonlinear contribution usually comes from the third-order nonlinearity:

$$P_{NL} = P^{(3)} = \epsilon_0 \chi^{(3)} E^3$$ (2.44)

A medium with such properties is known as a Kerr material. Kerr media are used to generate third harmonics and sum and difference frequencies of the applied optical field frequencies.

Four-Wave Mixing

The most general case of optical nonlinear phenomena associated with the third-order susceptibility is, the so-called Four-Wave Mixing (FWM for short). It occurs when at least two optical waves, oscillating at two different angular frequencies $\omega_1$ and $\omega_2$, propagate in a Kerr medium. While interacting nonlinearly, they produce two additional waves with frequencies $\omega_3$ and $\omega_4$. These new frequency components are related to the first ones as:

$$\omega_3 = \omega_1 - (\omega_2 - \omega_1) = 2\omega_1 - \omega_2 \text{ and } \omega_4 = \omega_2 + (\omega_2 - \omega_1) = 2\omega_2 - \omega_1$$ (2.45)

However, FWM does not only involve these frequency conversion mechanisms. Basically, depending on the phase-matching conditions, many output combinations of these can occur. If all the waves have the same frequency, it is called degenerate FWM.

The $i$-component of the third-order polarization density $P^{(3)}_i$ is given in general by:

$$P^{(3)}_i(t) = \epsilon_0 \sum_{jkl} \chi^{(3)}_{ijkl} E_j(\omega_1) E_k(\omega_2) E_l(\omega_3)$$ (2.46)

2.5 Plasma Physics

Plasma is considered as the 4th fundamental state of matter, and is identified as a partially or fully ionized gas, which displays a collective behaviour [40]. It is comprised of neutral atoms or and molecules which can be in an excited or ground state, positively or negatively charged ions and free electrons. As a whole, a plasma is electrically neutral, but it also is electrically conductive. The existence of plasma was first reported by British physicist Sir W. Crookes in 1879 who first introduced the term “4th state of matter”, to describe the ionised gas in an electric discharge tube [41]. The final definition of plasma was given by
the American physicist Irving Langmuir in 1929, who was the first to use the term plasma to describe a collective of charged particles \[42\]. Since the discovery of the phenomenon, there has been a large interest for understanding the various types of plasma that are found in nature or are created in the lab. For this project, plasma is produced by focusing a high-power laser beam in nitrogen at ambient pressure, which due to confinement of its peak power in the focal volume, subsequently ionizes the gas in that area and creates the plasma.

### 2.5.1 Femtosecond Laser-induced Plasma Formation

When a high intensity laser beam is strongly focused in a gas, the gas atoms/molecules at the focal volume dielectrically collapse, are subsequently ionized and plasma is created \[43\] \[44\]. This process is usually accompanied by a bright white light flash and a noise, at the same frequency as the laser repetition rate. The laser-induced plasma might seem similar to dielectric breakdown by an electric discharge, however its characteristics differ in size, temperature, carrier density and lifetime. Depending on the laser beam intensity, which governs the ionization regime, plasma generation is a a result of two major mechanisms: multi-photon ionization (MPI) and/or tunnel ionization (TI) \[45\]. A parameter that helps to distinguish the transition from one ionization regime to the other, is the Keldysh parameter \[46\]

\[
\gamma = \sqrt{\frac{U_I}{2U_p}} \tag{2.47}
\]

where \(U_I\) is the atom ionization potential and

\[
U_p = \frac{e^2E_{\text{Laser}}^2}{4m_e\omega^2} \tag{2.48}
\]

the average kinetic energy of a free electron that oscillates driven by the laser electric field of strength \(E_{\text{Laser}}\) and frequency \(\omega\), also known as the ponderomotive energy. The parameter \(\gamma\) reflects the characteristic time scale of tunnelling under the binding potential barrier of an atom over the optical period of the laser, and \(\gamma \approx 1\) corresponds to the transition between MPI and tunnelling ionization. For the case of our experimental setup \(\gamma \ll 1\), meaning that tunnel ionization is the dominant mechanism.

### 2.5.2 Tunnel Ionization

When the electric field of the applied laser beam becomes too strong, it can drastically distort the binding field of an atom as shown in figure \[2.6\]. While previously the probability for an electron to escape the barrier through tunnelling was practically zero, the applied laser field distorts the barrier and its length can easily be surpassed by the bound electron. After the electron has been ionized, it can either recombine with the parent atom, emitting the kinetic energy it got as high harmonic light generation, or it doesn’t recombine and could further ionize other atoms through collisions (non-sequential ionization).

There are two major theoretical frameworks that can be used to calculate the ionization rate: static tunnelling (ST) model \[47\] \[48\] and the more general, quasi-static Ammosov-Delone-Krainov (ADK) model \[49\] \[50\].

For the ST model the ionization rate per atom/molecule is calculated from:

\[
W_{\text{ST}}(t) = 4\omega_{\text{au}}r_H \frac{E_{\text{au}}}{|E_{\text{Laser}}(t)|} e^{-\frac{2(r_H)^{1.5}}{3} \frac{E_{\text{au}}}{|E_{\text{Laser}}(t)|}} \tag{2.49}
\]

where \(\omega_{\text{au}} = 4.134 \times 10^{16} \text{Hz}\) is the atomic unit of frequency and \(E_{\text{au}} = 5.14 \times 10^9 V/cm\) is the atomic unit of field (defined as the electric field strength felt by the ground state electron in a hydrogen atom) and \(r_H = U_x/U_H\) with \(U_x\) and \(U_H\) being the ionization potentials of the ionized gas and hydrogen respectively.

22
Figure 2.6: The distortion of the binding potential of an atom by a strong laser field. The bound electron can now escape the atom through tunnel ionization with higher probability. [Source: Wikipedia, “Tunnel Ionization”, en.wikipedia.org/wiki/Tunnel_Ionization]

The ADK model has been primarily used for noble gases, but it can give accurate results for atom-like molecules such as neutral nitrogen found in air $N_2$. The ionization rate is given by:

$$W_{ADK}(t) = 1.61 \omega_{au} \frac{Z^2}{n_{eff}} \left( \frac{10.87 Z^3 E_{au}}{n_{eff}^4 E_{Laser}(t)} \right)^{2n_{eff} - 1.5} \cdot \exp \left( -\frac{2}{3} \frac{Z^3 E_{au}}{n_{eff}^3 E_{Laser}(t)} \right)$$

(2.50)

where $Z$ is the ionization degree of the atom/molecule. The effective quantum number $n_{eff}$ is calculated as:

$$n_{eff} = \frac{Z}{\sqrt{I_p/13.6eV}}$$

(2.51)

Regardless of the model one chooses, when the ionization rate $W(t)$ is determined, the laser-induced plasma density $\rho_e(t)$ is calculated from the rate equation:

$$\frac{\partial \rho_e(t)}{\partial t} = W(t)(\rho_0 - \rho_e(t))$$

(2.52)

where $\rho_0$ is the initial non-ionized atom/molecule gas density. The solution of the equation is calculated as:

$$\rho_e(t) = \left[ \rho_0 \int_{t_0}^{t} W(t') e^{\int_{t_0}^{t'} W(t'')dt''} dt' + \rho_e(t_0) \right] \times e^{-\int_{t_0}^{t} W(t')dt'}$$

(2.53)

where $t_0$ is the starting moment of the calculation, $t'$ the moment when ionization occurs and $t$ the final moment of the calculation.
Figure 2.7: Photograph of femtosecond laser-induced plasma, generated in the UDG lab.
Chapter 3

Physical Models for Gas-Based THz Radiation Generation and Detection

Terahertz emission from two-colour laser field interaction in a gas plasma is a rather complicated process, as it involves a number of physical phenomena, such as strong-field ionization and interaction, plasma dynamics and nonlinear frequency conversion phenomena. Due to this interplay of many different processes, there were various physical models that attempted to predict and describe the observed THz field generation. In this chapter, we shall discuss the two basic models that exist in literature. The first one is the Four-Wave Mixing model, which was also the first ever theoretical attempt to explain the phenomenon and second will be the Microscopic Photocurrents model.

In the third section of this chapter, a heterodyne coherent THz detection technique using the third-order nonlinearity of air, also employed in the experimental part of this thesis, will be thoroughly discussed, namely the Air Biased Coherent Detection technique.

3.1 Four-Wave Mixing Model

The first ever observation of THz radiation generated by intense laser-plasma interaction was made in 1993 by H. Hamster and his colleagues [19], when they used a focused pulsed laser beam of 100 fs pulse duration and 800 nm wavelength to form an air gas plasma. The source of the observed THz wave was attributed to ponderomotive forces inside the plasma, that drove it to oscillate coherently. Later in 2000, D.J. Cook and R.M. Hochstrasser [20] demonstrated that THz radiation of much higher field strengths can be generated, when a fundamental 800 nm beam is combined with its generated by a SHG crystal second-harmonic (400 nm) and both interact within the plasma. In this case, the THz wave generation mechanism was assumed to be a four-wave mixing process (FWM) (see section 2.4.5). This model was used by several others for a while after [23, 53, 54]. Despite the initial success of the model, eventually it failed to give an entirely complete and accurate description. Still, this model gives an intuitive picture of the phenomenon, and can help to better understand the underlying mechanisms for the ABCD detection scheme, which is supposed to be the opposite mechanism. In the following section, the model is explained in detail.

3.1.1 FWM THz Generation Model

As discussed in previous chapters, the general expression for the third-order nonlinear polarization is:

\[ P_i^{(3)}(t) = \epsilon_0 \chi_{ijk}^{(3)} E_j(t) E_k(t) E_l(t) \]  

(3.1)

where \( E_{j,k,l} \) is the total two-colour optical field of the fundamental plus the second-harmonic, in the form of:

\[ E_j(t) = E_j^f(t)e^{-i\omega t} + E_j^{2\omega}(t)e^{-2i\omega t} + c.c. \]  

(3.2)
Assuming $E_j^\omega$ is real, and keeping only the low frequency terms, one can derive for the polarization:

$$P_i^{(3)} = \varepsilon_0 \chi^{(3)} (3E_i^\omega E_j^\omega E_j^{2\omega *} + 2E_i^\omega E_j^\omega E_j^{2\omega} + E_j^\omega E_j^\omega E_i^{2\omega *}) + c.c.$$  (3.3)

where $i, j = x, y$ or $y, x$.

Assume the fundamental field $E^\omega$ to be polarized along the $x$-axis, such as $\vec{E}^\omega = E^\omega \hat{x}$. For type-I phase-matching in a SHG crystal, if $\theta$ is the angle between the ordinary axis of the crystal and the fundamental field's polarization, then the generated second-harmonic field is $E^{2\omega} = E^{2\omega} \cos \theta \hat{x}$ [31]. Substituting that in equation 3.3 one reaches:

$$P^{(3)} \propto \varepsilon_0 \chi^{(3)} (E^\omega)^2 E^{2\omega} \cos \theta = \varepsilon_0 \chi^{(3)} I^\omega \sqrt{I^{2\omega} \cos \theta}$$  (3.4)

Then, the expected magnitude of the THz field is proportional to the the absolute value of the third-order polarization, given as:

$$E_{THz} \propto |P^{(3)}|$$  (3.5)

The essence of the FWM framework is reflected by equation 3.4. As already mentioned, this model initially was considered as successful, on the grounds that it was verified experimentally that the generated THz field is proportional to the intensity of the fundamental beam and to the square root of the intensity of the generated second-harmonic [54], as shown in figure 3.1. In addition, the cosine dependence of the THz field strength, to the angle between the fundamental and second-harmonic field polarizations (which is controlled by rotating th SHG crystal) was also demonstrated experimentally [53].

![Figure 3.1: Dependence of the THz field amplitude on the fundamental ($\omega$) laser pulse energy with fixed the second-harmonic ($2\omega$) pulse energy and on the second-harmonic pulse energy, with fixed fundamental pulse energy.](image)

Figure 3.1: Dependence of the THz field amplitude on the fundamental ($\omega$) laser pulse energy with fixed the second-harmonic ($2\omega$) pulse energy and on the second-harmonic pulse energy, with fixed fundamental pulse energy. [Source: X. Xie et al, Phys Rev Lett (2006) 96, 075005].

However, successful predictions stop there. It is generally accepted that the third-order nonlinear susceptibility values of gases are too small to actually explain the observed high THz field-strengths [55]. In addition, while the FWM model predicted a simple linear dependence of the produced THz field on the fundamental beam intensity, there is an intensity threshold observed, which is coincident with the threshold of ionization and plasma formation [55]. This proves that the presence of plasma is necessary for THz radiation generation. These observations led to the development of the semi-classical THz generating photocurrents in plasma framework, proposed by Kim et al [56], described in the next section.
3.2 Terahertz Generation by Photocurrents Model

The photocurrents model, initially proposed by K. Y. Kim [56-58] is a semi-classical model that combines strong-field ionization and classical electron dynamics to describe what is happening during plasma formation. As seen in previous sections (see 2.5), the bound electrons of the gas atoms or molecules are subjected to fast tunnel ionization, since the combined laser field of the intense fundamental and second harmonic beams suppress the Coulomb barrier of the gas species. The freed electrons are then forced to oscillate driven by the laser field and, depending on the relative phase between the fundamental and the second harmonic pulses, these electrons can form a directional transverse current. Since this current surge occurs in the time scales of photo-ionization, this mechanism can produce electromagnetic radiation at terahertz frequencies. In the following, the model is presented.

3.2.1 Introduction to the Photocurrents Model

If an intense single frequency laser beam interacts with the atoms or molecules of a gas, there is high probability that a number of electrons will be liberated from their parent species. After they are released, these electrons are subjected to the electric field of the laser and oscillate along the direction of the laser field polarization. The drift velocity is determined by the moment of their ionization and the magnitude of the laser electric field at the time. However, since the waveform of a single frequency laser field is symmetric, there cannot be a directional current of freed electrons.

A directional electron current can arise if an additional laser field, oscillating at the second harmonic is combined with the fundamental. The combined laser field is given by the relation:

\[ E_{\text{Laser}} = E_\omega \cos(\omega t) + E_{2\omega} \cos(2\omega t + \theta) \]  

(3.6)

where \( E_\omega \) and \( E_{2\omega} \) are the amplitudes of the two fields, and \( \theta \) the relative phase between them.

![Figure 3.2: Electron drift velocity as a function of the phase of the applied laser field. The dotted line represents the laser field. On the left, the relative phase \( \theta \) is 0 on the right \( \theta \) is \( \pi/2 \). [Source: K-Y Kim, J. Glownia, A. Taylor, G. Rodriguez, Opt. Express 15, 4577-4584 (2007)]

For tunnel ionization occurring at \( t = t' \), the freed electron velocity, driven by the external laser field, at time \( t \) is given by:

\[ v(t) = -\frac{e}{m_e} \int_{t'}^{t} E_{\text{Laser}}(t) dt \]  

(3.7)
where \( e \) and \( m_e \) are respectively the electron charge and mass. These free electrons then drift at a velocity:

\[
v_{d}(t') = eE_{\omega \sin(\omega t')/m_e \omega) + eE_{2\omega \sin(2\omega t' + \theta)/(2m_e \omega)}
\] (3.8)

The effect of the relative phase \( \theta \) between the two fields is shown in figure 3.2. When the relative phase is zero, the combined electric field waveform is totally symmetric, as shown on the left side of the figure. The drift velocity function is then also symmetric, and so the total velocity of all free electrons around the laser slopes cancels out (shown by the shadowed area in the same figure). However, when the relative phase of the fields is \( \pi/2 \), due to the asymmetric shape of the combined field waveform, there is a remaining drift velocity towards one direction. This non-vanishing electron density produces then a current surge \( \vec{J} \).

The resulting electron current density \( \vec{J}(t) \) is given by:

\[
\vec{J}(t) = e \int_{-\infty}^{t} v(t')d\rho_e(t')
\] (3.9)

where \( d\rho_e(t') \) is the number of electrons per unit volume, ionized by the laser field in the time interval between \( t' \) and \( t' + dt' \). The number of electrons per volume can be calculated from the formula given by equation 2.53 and calculating the corresponding tunnel ionization rates for the ionized gas.

This current surge generates radiation \( E \) which is proportional to its derivative as:

\[
E \propto \frac{dJ(t)}{dt} = e \frac{d\rho_e(t)}{dt} v_d(t)
\] (3.10)

Calculating the spectrum of this radiation by taking its Fourier transform, it becomes apparent that there are multiple frequency components generated. Among others, there is a quasi-DC, phase-sensitive peak, which corresponds to THz frequencies. The following figure 3.3 shows the calculated spectra for the cases of relative phase 0, \( \pi/2 \) and for the case when no second-harmonic field exists. It is apparent that THz radiation intensity is enhanced when there is a phase difference \( \theta = \pi/2 \), between the fundamental and second-harmonic fields, while it is small for the case of \( \theta = 0 \) and no THz is generated for the case of a single frequency field.

![Figure 3.3: Radiation spectrum obtained by the photocurrents model. [Source: K-Y Kim, Phys. Plasmas 16, 056706 (2009)]](image)
3.2.2 Wavelength Scaling of THz Generation

It was recently demonstrated by M. Clerici et al., both theoretically and experimentally, that for a two-colour THz generating configuration there is a strong dependence of the THz emission from the wavelength of the fundamental pump beam [24]. This can be exhibited based on the plasma photocurrents THz generation mechanism: expressing the relation for the THz generating photocurrents density $\vec{J}$, given by 3.9, as a power expansion with respect to the pump electric field $E$ and looking at the first order term:

$$ J_x^{(1)} \propto e^2 \omega m_e \rho_e E_x $$

(3.11)

it is apparent that $J_x^{(1)}$ is proportional to the pump beam wavelength $\lambda$. Subsequently, this linear dependence of the photocurrent density to the wavelength of the pump results in a quadratic relation of the radiated THz energy with the pump wavelength. Note that, depending on the pump pulse energy and focusing conditions chosen, a sudden drop in THz conversion efficiency may be experimentally observed for long wavelengths. This is caused by the decreasing peak intensity with increasing wavelength, and thus the gas is not entirely ionized in that case.

In figure 3.4, the experimental results showed a wavelength dependence of $\lambda^{4.6}$, much larger that $\lambda^2$. This was attributed to the combination of the fundamental $\lambda^2$ law and the effect of the wavelength-dependent plasma volume.

![Figure 3.4: Radiated THz energy as a function of the pump beam wavelength.](Source: M.Clerici et al., Phys. Rev. Lett. 110, 253901)

Based on these findings, in order to achieve the highest possible THz field strengths for our experimental setup, it was decided to use the longer wavelength output of the UDG laboratory TOPAS Twins & HE optical parametric amplifier as the pump beam, instead of the 800nm output of the Ti:Sapphire laser.

3.3 Coherent Terahertz Wave Detection with Gases

For the full determination of the electric field in terahertz time domain spectroscopy, including both its phase and amplitude, coherent detection schemes have to be implemented, which usually involve photoconductive dipole antennas [14] or electro-optic(EO) sampling methods with the use of optical nonlinear crystals [11][13]. The time-resolved detection is usually done by splitting the laser beam into a pump part which is used to generate the THz radiation, and to a probe part which is used to temporally
sample the THz pulses. Changing the time delay between the pulses of the pump and probe parts, the
temporal information of the whole terahertz pulse trace can be obtained (see section 1.3).

However, most of the common solid-state detectors offer a limited bandwidth, as detection is restricted
by the lifetime \( \tau_f \) of the carriers in photoconductive antennas and the phonon resonances in electro-optic
crystals. For instance, the nonlinear crystals commonly used in EO sampling schemes, ZnTe and GaP,
demonstrate intense phonon absorptions at 5.3 \([59, 60]\) and 10.98 THz \([61]\) respectively, making them not attractive candidates for broadband (1-15 THz) detection schemes.

On the other hand, gas media in general do not show the before mentioned artefacts in the detected
THz spectra. In particular, gases do not have phonon resonances, and thus cannot show this kind
of absorption in the THz region, making them good candidates for broadband detection schemes. In
addition, gases are less dispersive than solids in the THz region, and thus phase-matching is easier to
achieve. Much higher resolution in the spectrum can be achieved as, there are no Fabry-Perot effects
coming from reflection on surfaces, as it is the case for the solid-state materials and crystals used in
other methods. Moreover, gases do not have an intensity-induced damage thresholds and high probe
beam intensities can be used, on contrary with expensive solid-state materials which can be burned or
damaged, and even if the laser intensity becomes high enough to start ionizing the gas, it is continuously renewed.

The First Steps Towards THz Detection with Gases

Ever since THz generation by interaction in gas plasmas was discovered, and while the FWM description
of the generation mechanism was still the dominant theoretical framework, there was speculation if the
opposite process could be realised. Terahertz field-induced second-harmonic generation (TFISH), is a
four-wave mixing process, in which one terahertz photon of frequency \( \Omega_{THz} \) mixes with two of the probe
beam photons with frequency \( \omega \), in order to generate one second-harmonic photon of the probe beam,
with frequency \( 2\omega \). This process was firstly demonstrated in solids and liquids \([62, 63]\) and later in 2006
the observation of this mechanism in gases was demonstrated by Dai and his colleagues \([25]\).

Dai and his colleagues showed that the TFISH mechanism
can be exploited to quasi-coherently detect a THz pulse using
the air as a sensor. The terahertz-induced second-harmonic
field of the probe beam can be expressed as:

\[
E_{2\omega}^{THz} \propto \chi^{(3)}_{xxxx} E_{THz} E_{\omega} E_{\omega} \propto \chi^{(3)}_{xxxx} E_{THz} I_{\omega}
\]

(3.12)

where \( \chi^{(3)}_{xxxx} \) is the relevant component of the third-order susceptibility \( \chi^{(3)} \) of the gas. From the above expression, it is apparent that \( E_{2\omega}^{THz} \propto E_{THz} \), and thus the THz-induced second harmonic signal that would be detected by a photodetector is:

\[
I_{2\omega}^{THz} \propto [\chi^{(3)}_{xxxx} I_{\omega}]^2 I_{THz}
\]

(3.13)

Obviously, this expression indicates that the detected
THz-induced second-harmonic intensity \( I_{2\omega}^{THz} \) is proportional
to the intensity of the THz beam field \( I_{THz} \). This measurement
by the photodetector is incoherent, meaning only amplitude and no phase information can be extracted by it. Without phase information, the exact THz electric field cannot be reconstructed.

![Figure 3.5: Schematic diagram of the first ever gas based THz detection setup.][1]

As a first approach to overcome the incoherence problem and achieve coherent detection, Dai and his colleagues developed a quasi-coherent THz field detection technique, by introducing a probe laser beam-induced plasma, generated at the focal point of a parabolic mirror, where both the THz and probe beams overlap, as shown the figure 3.5. This gas plasma emits white light which acts as a “local oscillator” $E_{2\omega}^{LO}$, and contributes as a background term to the measured second-harmonic signal $E_{2\omega}$ as $E_{2\omega} \propto E_{2\omega}^{THz} + E_{2\omega}^{LO}$. Then, the measured by the photodetector second-harmonic intensity is:

$$I_{2\omega} \propto (E_{2\omega}^{THz})^2 + (E_{2\omega}^{LO})^2 + 2\chi^{(3)} \omega E_{2\omega}^{LO} E_{THz}$$  \hspace{1cm} (3.14)

If the intensity of the plasma-induced second-harmonic is high enough, the detected signal can be approximated to be the cross term of the interference plus a strong background, resulting then in a quasi-coherent detection of the THz electric field:

$$I_{2\omega} \propto (E_{2\omega}^{LO})^2 + 2\chi^{(3)} \omega E_{2\omega}^{LO} E_{THz}$$  \hspace{1cm} (3.15)

Thus, in order for this particular detection scheme to coherently detect the THz pulse, the presence of an intense probe-beam induced plasma is required. However, due to the strong background introduced by the plasma, the measured THz trace appears distorted and with a low signal-to-noise ratio.

The Air Biased Coherent Detection Technique

Next followed an improved version of this scheme, developed by N. Karpowicz and X.-C Zhang [26, 27]. The role of the plasma as the local oscillator is played by an alternating DC bias provided by a pair of electrodes placed at the focal point where THz and probe beams overlap and provides a local bias-induced second harmonic oscillator. This new scheme, named the Air Biased Coherent Detection (or ABCD) scheme allows for coherent heterodyne detection, and is free of the noisy background.

The basic concept of ABCD is depicted in figure 3.6: a probe beam, of frequency $\omega$ is send to propagate along a controlled time delay path, in order to be able to manipulate the temporal distance between it and the pump beam. After the delay stage part, it is focused by a lens of long focal length. Usually as the probe beam is focused down, it propagates through a hole in a metal coated off-axis parabolic (OAP) mirror. The same OAP mirror is used to focus the THz beam. The probe and THz beams focus collinearly with overlapping focal points. Across the focal point, a pair of electrodes with a gap between them is placed, and an alternating voltage bias $V_{bias}$ is applied, with an amplitude on the order of some tens of kV and an alternating frequency half the repetition rate of the laser. If phase-matching is achieved, then the second-harmonic beam is generated, collected by a lens and focused to a light detector, usually a photomultiplier tube.

![Figure 3.6: Basic concept of ABCD: The THz and probe beams are collinearly focused down with overlapping focal points, which is between a pair of electrodes with a modulating bias field $E_{bias}$. A second-harmonic field of frequency $2\omega$ of the probe beam is induced by the THz and $E_{bias}$ fields.[Source: B. Clough et al, “Laser air photonics: beyond the terahertz gap”]](image-url)
The second-harmonic induced by the local-oscillator field is replaced now by the bias field, which for a field with strength $E_{\text{bias}}$ analogously is:

$$E_{2\omega} \propto \chi^{(3)}_{xxxx} E_{\text{bias}} E_\omega E_\omega \propto \chi^{(3)}_{xxxx} E_{\text{bias}} I_\omega$$ (3.16)

After filtering out the residual probe beam light with a low-pass filter, the detected second-harmonic intensity is the square of the sum of the two second-harmonic signals:

$$I_{2\omega} \propto \left( E_{2\omega}^{THz} + E_{2\omega}^{bias} \right)^2 \propto \left( E_{2\omega}^{THz} \right)^2 + \left( E_{2\omega}^{bias} \right)^2 \pm 2 E_{2\omega}^{THz} E_{2\omega}^{bias}$$ (3.17)

In order to remove the constant background terms in the above relation and only keep the cross term, a coherent heterodyne detection scheme [64] can be utilised: by modulating the bias field at a certain frequency, usually half the repetition rate of the pumping laser $f_{\text{rep}}$, the other two terms can be discarded and only the coherent cross term is isolated, hence the second-harmonic intensity is recorded as:

$$I_{2\omega} \propto E_{2\omega}^{THz} E_{2\omega}^{bias} \propto \left( \chi^{(3)}_{xxxx} I_\omega \right)^2 \left[ E_{THz} E_{\text{bias}} \right]$$ (3.18)

which allows coherent detection of the THz pulses.

Compared to the case where the gas plasma light was used as the local oscillator, with an external bias the air does not have to be ionized, which significantly reduces the probe pulse energy required for coherent detection, and leaves more pulse energy for the plasma THz-generation. In addition, since a heterodyne detection scheme is realized, both the signal-to-noise ratio and dynamic range are significantly improved.

Relation (3.18) is the most characteristic of the ABCD scheme. The field-induced second-harmonic signal is linearly proportional to the field amplitudes $E_{\text{bias}}$ and $E_{THz}$ and quadratically proportional to the relevant third-order nonlinear susceptibility component $\chi^{(3)}_{xxxx}$ and probe beam intensity $I_\omega$. We will attempt to optimize these parameters to maximize the detection sensitivity of the TD spectrometer.

### 3.3.1 Phase-matching and Other Considerations for ABCD Detection Schemes

In reality, the interacting waves have Gaussian profile distributions that need to be considered in the analysis (see section 2.2). The electric field of the THz and probe beams can be expressed in a Gaussian profile form as:

$$E_\omega(r, z) = \frac{E_\omega}{1 + iz/z_R} e^{-r^2/w_0^2(1+iz/z_R)}$$ (3.19)

$$E_{THz}(r, z) = \frac{E_{THz}}{1 + iz/z_{THz}}$$ (3.20)

where $E_\omega$ and $E_{THz}$ are the field amplitudes of the probe and THz beam respectively, $w_0$ the beam waist of the probe beam and $z_R$ and $z_{THz}$ the respective Rayleigh lengths. The THz beam waist is much larger than the probe beam’s, and so it is neglected.

Likewise, the second harmonic wave field could be in the form:

$$E_{2\omega}(r, z) = \frac{E_{2\omega}}{1 + iz/z_R} e^{-r^2/w_0^2(1+iz/z_R)}$$ (3.21)

Specifically in our setup, flat surface electrodes of various widths are used, with an adjustable gap of $d$ between them. For an applied bias voltage $V_{\text{bias}}$, the electric field strength in the volume between the electrodes is uniform and equal to:

$$E_{\text{bias}} = \frac{V_{\text{bias}}}{d}$$ (3.22)
It is possible to analytically calculate the THz and bias field-induced second-harmonic fields for the case of Gaussian beams, using the paraxial version of the nonlinear wave equation 35:

\[
2i k_{2\omega} \frac{\partial E_{2\omega}}{\partial z} + \nabla^2 E_{2\omega} = \frac{-16\pi \omega^2}{c^2} \chi^{(2)} e^{-i\Delta k z} \tag{3.23}
\]

The parameter \(\Delta k = 2k_{\omega} - k_{2\omega}\) is the phase mismatch wavevector. Usually for gases the second-order nonlinear susceptibility \(\chi^{(2)}\) is zero, due to the inversion symmetry of the isotropic gas. For the field-induced second-harmonic generation process however, the effective second-order nonlinear susceptibility \(\chi_{eff}^{(2)}\) is a function of the inducing field \(E_{THz}\) and the third-order nonlinear susceptibility \(\chi^{(3)}\) as:

\[
\chi_{eff}^{(2)} = \chi^{(3)} E_{THz}^* + c.c. \tag{3.24}
\]

where \(E_{THz}^*\) the complex conjugate of the THz field and c.c. denoting the complex conjugate. The reason why the conjugate of the THz field is considered will become clear: as already discussed, TFISH is a four-wave mixing nonlinear process, where two probe and one THz beam photons mix in order to generate one second harmonic photon. This is basically described by two frequency conversion processes 65:

\[
2\omega = \omega + \omega' + \Omega_{THz} \quad \text{and} \quad 2\omega = \omega + \omega' - \Omega_{THz} \tag{3.25}
\]

where \(2\omega\) is the frequency of the field-induced second-harmonic photon, \(\omega'\) and \(\omega\) the frequencies of the two probe beam photons (really close to each other) and \(\Omega_{THz}\) the frequency of the THz photon.

The nonlinear polarization density of these two processes is expressed as:

\[
P^{(+)} = \chi^{(3)} E_{\omega}^2 E_{THz} + c.c. \quad \text{and} \quad P^{(-)} = \chi^{(3)} E_{\omega}^2 E_{THz}^* + c.c. \tag{3.26}
\]

These two expressions of the polarization density have the same amplitude but are different in phase. For nonlinear phenomena phase is critical, as there are certain phase-matching conditions that need to be fulfilled in order for a conversion process to be efficient. For Gaussian beams in low dispersion gases, the Gouy phase plays the most critical role, rather than the difference in the refractive index between the three different wavelengths. As shown in section 2.2, the Gouy phase is expressed as an additional phase factor \(\exp(i\zeta) = \exp(itan^{-1}(z/z_R))\). Thus, the two processes will have different phases: the first one will have a phase of \(\exp(i3\zeta)\), while the second one due to the minus sign of \(\Omega_{THz}\) will retain the phase as it is, \(\exp(i\zeta)\). Hence, only the second process has the same spatially-varying phase as the fundamental probe beam, and as a result, is considered to dominate.

Replacing equations 3.19, 3.20, 3.21 and 3.22 into the nonlinear wave equation 3.23 the THz field-induced second-harmonic field can be derived as:

\[
E_{THz}^{2\omega} = \left( \frac{i8\pi^2 \omega \chi^{(3)}}{nc E_{\omega}^2 E_{THz}} \right) \frac{z_R z_T}{z_R + z_T} e^{z_T \Delta k} \tag{3.27}
\]

Similarly, the bias field-induced second-harmonic is calculated to be:

\[
E_{bias}^{2\omega} = \left( \frac{i8\pi^2 \omega \chi^{(3)}}{nc E_{\omega}^2 V} \right) z_R e^{z_R \Delta k} \tag{3.28}
\]

Again, since a heterodyne detection mode is applied, only the cross term with the product of the terahertz-induced second-harmonic and bias field-induced second harmonic fields is recorded, and is expressed as:

\[
I_{2\omega} \propto E_{2\omega}^{THz} E_{2\omega}^{bias} \propto \left( \chi^{(3)} I_{\omega} \right)^2 E_{THz} V \frac{z_R^2 z_T}{d} e^{(z_T + z_R) \Delta k} \tag{3.29}
\]
Similarly as before, it is apparent that the detected second-harmonic intensity is dependent on the value of the relevant component of third-order nonlinear susceptibility $\chi^{(3)}$, the probe beam intensity $I_\omega$, the terahertz field strength $E_{THz}$, the bias field strength $E_{bias} = V_{bias}/d$ and in addition, to the respective Rayleigh lengths of the terahertz and probe beam, as well as the phase-matching of the process, expressed by $\Delta k$. 
Chapter 4

Experimental Methods

4.1 Introduction

In this chapter, the setup of the gas-based time-domain THz spectrometer shall be described, along with the laser and OPA devices used, the Data Acquisition Framework, and the components and devices that were designed and constructed specifically for this application.

4.2 The Laser and Optical Parametric Amplifier Systems

A schematic overview of the laser and OPA systems is illustrated in figure 4.1. At the first stage, a Vitesse 800-2 diode-pumped Ti:Sapphire oscillator produces a 80 MHz pulse train, at a wavelength of 800 nm, with pulse duration of 100 fs and 5 nJ pulse energies. Mode-locking of this laser is achieved through Kerr-Lens mode-locking [66]: due to the nonlinear Kerr effect, as intensity in the oscillator cavity increases, the laser’s longitudinal modes begin to couple and pulsed operation becomes more favourable than the continuous-wave. The output of the oscillator is used as the seed to the following Amplifier stage.

Next follows the Legend Elite Amplifier. The main principle of operation of the whole stage is based on Chirped Pulse Amplification [67]. Essentially, the seed pulses get stretched in time, using a grating stretcher, and then they can safely be amplified until saturation is reached, and the pulse is compressed in time again. With this technique, it is made sure that the peak power does not become too high, so no damage will be done to the amplifier stage components through nonlinear effects such as self-focusing.

Figure 4.1: Schematic overview of the laser and OPA systems in the UDG lab. Vitesse: Provides the seed to the Legend Elite Amplifier, RGA: Regenerative Amplifier, SPA: Single Pass Amplifier
Amplification is done in three steps: after the seed pulses are stretched, they are coupled in to the Regenerative Amplifier (RGA) stage by a Pockels cell optical switch, at a reduced repetition rate of 1 kHz. The pulses are amplified by making several passes through a Ti:Sapphire rod, which is pumped by a Nd:YLF laser. After several round-trips, the pulses are amplified to several mJ of energy and are coupled out by an additional Pockels cell switch. Next, the pulses go through two single-pass amplification stages (SPA). There, amplification is again provided by Ti:Sapphire crystals pumped by Nd:YLF lasers. One of the SPAs is operating at cryogenic temperatures ($T = 80\,\text{°K}$), which is kept stable by a helium compressor and a vacuum pump. With this configuration, beam distortions during amplification such as thermal lensing are minimized and the result is a beam with good quality. After the SPAs, the beam is split in two branches with a polarizer and both are compressed back to 100 fs. The pulse energy then becomes 20 mJ and the central wavelength slightly shifts to 808 nm.

One of the two parts passes to the Light Conversion TOPAS Twins OPA device. The basic principles of operation of OPA devices were explained in section 2.4.4. This particular device is a combination of two OPAs into a single unit. The devices have separate outputs for the generated signal and idler waves. A small fraction ($1 - 3\mu J$) of the 808 nm pump beam is used to generate a white-light continuum in a sapphire crystal plate. The generated white light beam is collimated, split and later on focused into a nonlinear crystal along with another fraction of the pump beam. In there, a non-collinear parametric amplification process takes place. The signal beam is separated from the residual idler and pump beams of this stage, is then expanded and collimated by a telescope and then moves to the first amplification stage. Amplification power here is provided by the remaining power of the input 808 nm pump beam. The final outputs of the Twins are collinear, well collimated signal and idler beams. The pulse width is also reduced to about 65 fs.

After the TOPAS Twins, two additional HE TOPAS Stage devices follow, hereby referred to as HE1 and HE2. These devices provide additional high-power amplification. Part of the 808 nm beam is used to pump the TOPAS HE1 and HE2. The signal and idler outputs of the TOPAS Twins are used as a seed for each of the HEs. Inside, the seed and pump beams overlap collinearly in a nonlinear crystal and a large percentage of the pump wave is used to amplify the seed. The output of the HEs is then the collimated and amplified seed to some thousands of microjoules energy (or equivalently some Watts of averaged power). After calibration, the wavelength can be set using the WinTOPAS software.

4.3 The Experimental Set-up: Overview of the Gas-Based Spectrometer

In this section an accurate description of the experimental setup of the gas-based spectrometer shall be given. The top down and isometric views of the setup model are depicted at figures 4.3 and 4.4. The top down view is used as a reference guide for this description.

The two high-power outputs of TOPAS HE1 and HE2, with wavelengths set to $1.2\mu m$ and $1.5\mu m$ respectively, arrive at the setup at a height of 16 cm away from the optical table. Therefore, the two periscopes P1 and P2 are used to bring the beams down to the designated working plane, 13.5 cm above the optical table. Beam HE2 is designated as the fundamental or pump beam, and along with its second-harmonic generated by the $\beta - BB0$ crystal, is used to induce the plasma and subsequently, the THz beam. The HE1 beam is designated as the probe beam and is used at the ABCD detection section of the setup.

The whole setup is covered by a purge box which is filled by a continuous flow of Nitrogen, in order to remove the highly THz absorbing water. The humidity is monitored with a Sensirion humidity sensor.
The pump beam

As mentioned, HE2 is the beam which generates the plasma. After the periscope P2, it reaches a level of 13.5 cm away from the table, and is guided by a flat metallic mirror M1 to an 1” diameter, gold-coated 90° off-axis parabolic mirror OPM1, with an effective focal length of 8”. As the fundamental beam is focused down by OPM1, it propagates through a $\beta - BBO$ crystal, and the second-harmonic wave is generated. The $\beta - BBO$ crystal is mounted on a manual mechanical stage, which can move along the beam propagation path and it can also be rotated, in order to control the phase-matching of the SHG. Around the focal point, the ambient air is ionized by the combined fields (see figure 4.2) and a plasma filament is induced, and in addition, according to the mechanisms described in section 3.2 the THz beam is generated (see figure 4.2).

The three fields diverge from the focal point and continue to propagate towards the same direction. Then, an additional off-axis parabolic mirror OPM2, of a 2” diameter and an effective focal length of 4” collects and collimates the three beams. Immediately after it, a free standing mount with a thin sheet of teflon tape is used to filter out the residual optical light of the fundamental and second harmonic beams. Next, another pair of parabolic mirrors, OPM3 and OPM4 focuses down and recollimates the THz beam. At the focal point of this section between the two mirrors, samples can be inserted and their optical properties could be measured with transmission THz time-domain spectroscopy. After the pair, the collimated THz beam goes through a 1 mm thick HRFZ-Silicon wafer filter, which removes any residual optical light and also reduces the THz beam intensity. Then, the beam goes through a polyethylene wire grid polariser, which by rotating allows control of the transmitted THz intensity. Later on, the THz beam reaches a flat silver plated mirror, which reflects it into the gas-cell through a 3 mm thick 3” diameter silicon wafer window. In the gas-cell, the beam is focused by a 2” diameter, 2” effective focal length parabolic mirror OPM5, and proceeds to the focal point, between the two copper electrodes, which are used to deliver the bias field needed for the ABCD scheme.

The probe beam

After the HE1 probe beam is brought down to the working plane, it goes through a 90/10 beam-splitter which is used to control and remove the excess probe pulse energy. The unused part of the beam is dumped onto a beam block. After being reflected by mirror M2, the probe beam is send to a retro-reflector RR, mounted on a motor-controlled mechanical delay stage which allows precise control (minimum step size is 1 nm) of the time delay $\Delta\tau$ between the pump and probe beams. A mirror M3 is used to pick up the probe beam from the stage, and after a couple of mirrors, it is brought in front of the gas cell, and is then focused by an 1” diameter plano-convex lens L1 of a 150 mm focal length and is send through the fused silica optical window into the gas cell.

The focusing lens M4 is mounted on a stage which allows for control of the position of the focal point in the gas cell and subsequently of the overlap of the optical probe and terahertz beams focal points.
Figure 4.3: Top-down view of the gas-based THz time-domain spectrometer.
Figure 4.4: Isometric view of the gas-based THz time-domain spectrometer.
4.4 The Gas Cell

The gas cell contributes significantly to the realization of the ABCD detection scheme applied for this spectrometer. Using the SolidWorks\textsuperscript{TM} CAD software, it was specifically designed for this setup as three separate parts (walls, base plate and lid) and together with the electrodes and the electrode holders were all manufactured at the ETH Zürich Physics Department Workshop.

The gas cell was planned to fit an off-axis parabolic mirror on top of a manually controlled mechanical stage, and the bias field delivering electrode pair, with their holders on another separate mechanical stage. The stage of the mirror can move on a direction perpendicular to the direction of the probe beam propagation. By controlling this stage it can be made sure that the probe beam passes the hole of the mirror. The electrode base translation stage can move parallel along the direction of the probe beam. With this stage, it can be made sure that the electrodes are placed exactly at the spot where the focal points of the THz and probe beams overlap. In addition, the separation distance between the electrodes can also be controlled with smaller mechanical stage, on top of the base one. However, one must be cautious not to let the electrodes come in contact, or close enough to induce electric arcs.

In order to study the influence of various gases in the ABCD scheme, the cell was designed to be as airtight as possible. On the walls part, grooves were made within which a pair of standard O-rings were placed, making the connection of the walls to the base plate and the lid part practically airtight. The total volume in the gas cell is 5.2 litres.

![Figure 4.5: Section and interior of the gas cell.](image)

The flow of gases in the cell can be controlled by two hoses which can be connected with gas tubes. In the current configuration, one hose is used as the gas intake, with the option to independently purge the cell with nitrogen or fill it up with one of the two available alkane gases (propane $C_3H_8$ or n-butane $C_4H_{10}$). The second hose is currently used to remove the gas from the cell. In addition, a humidity sensor...
goes through that hose, that allows the monitoring the humidity levels in the cell, and the leaking rate. One should note that during purging there is a significant pressure build up in the cell, and therefore should not attempt to remove any screws or windows during that time, but only the gas outlet is shut.

For the beams coming in and out the cell, there are three separate windows, two 2” and one 3” diameter. The 3” one is used as a window for the THz beam, for which a HREFZ-Silicon 3 mm thick wafer is used. For the other two optical windows, standard thin fused silica windows are used.

The base plate has a double, standard honeycomb-like screw hole structure that allows the mechanical stages of the parabolic mirror and the electrodes to be firmly placed accordingly. The electrodes are made from copper, and pairs of various thicknesses were manufactured. The electrode holders are made from PEEK, an insulating polymer material that allows to keep the electrodes separate from the metallic cell.

A safe high voltage (SHV) jack connector allows to safely connect the electrodes to the high voltage output of the HV amplifier. The phase of the cable is directly connected to one of the electrodes, while the other one is connected/grounded to the gas cell itself. The cell is grounded by the optical table.

4.5 Photodetectors

Usually, the intensity of the field-induced second-harmonic generated beam is low. For most of the measurements taken, a Hamamatsu R636-10 photomultiplier tube (PMT) was used. Photomultiplier tubes are highly sensitive light detectors, which offer high gain and low noise, and which can be used to detect single photons.

In principle, when a photon strikes the photo-cathode of the PMT, an electron may be ejected due to the photoelectric effect. This photoelectron is accelerated by a high voltage bias towards other electrodes, on which it collides and generates other secondary electrons and so on. Due to this avalanche process, in the anode at the end of the tube, a detectable photocurrent signal is generated which can be further processed for the detection scheme.

In our particular case, prior to the detector, a 600 nm band pass and a 435 nm long pass filters were used to cut-off any residual optical probe and third-harmonic light coming towards the detector and allowing only the field-induced second-harmonic light on the detector.

It should be noted that if gases with large third-order nonlinear susceptibilities \( \chi^{(3)} \) are used, the field-induced second-harmonic becomes so intense that the PMT gets saturated, and cannot longer be used, but instead it is possible to do light detection with a standard silicon photodiode (PD).

4.6 Gated Integration Method

In order to acquire the signal from a PMT, it is typical to use a gated, or boxcar integrator as more commonly known. A gated integrator is an analog electronic instrument that is used to obtain electronic signals which are obscured by noise. It is suited for measurements of signals with a small duty cycle, meaning that the duration that the signal is active is just a small part of the time period of the whole measurement.

In figure 4.6 the principle of operation of the instrument is illustrated. The input signal is applied to the device, which then integrates it over a specified gatewidth. Integration starts after an also defined trigger delay, in relation to a trigger signal (in this case the electronic laser trigger 1 kHz). The gatewidth is set with respect to the input signal, as one tries to include in the gate the parts of interest and exclude parts near the noise level. When the gate is open, the input signal is integrated, and when the gate passes integration stops. Input parts and noise outside the gatewidth are neglected.

In the UDG lab, the Stanford Research SR250 gated integrator is available. The output signal from the PMT is connected to the input of boxcar integrator, together with an 1 kHz laser TTL signal, to be
used as the trigger. Gate width and trigger delay are set in order to get a satisfying signal-to-noise ratio. The single-shot output signal of the boxcar is then ready to be connected to the DAQ card for further analysis.

4.7 The Bias Field

In order to synchronise the modulating bias field with the laser pulse repetition rate, a laser triggered voltage alternator device was built by Lucas Huber. The device receives as input the 5-0 V, 1 kHz TTL electronic trigger from the laser oscillator and gives two outputs: an alternating at 500 Hz step-function-like signal with an adjustable amplitude (maximum is -10 to 10 V) and offset, and an additional TTL trigger signal, similar to the input but with a 500 Hz repetition rate instead of 1 kHz. The signal output is delivered to a TREK 2200 High Voltage (HV) amplifier, which returns it at its output, amplified at a rate of 200 volts per input volt. The HV amplifier output is connected via a SHV connector jack to the gas-cell and then to the copper electrodes.

4.8 Data Acquisition Framework

The Vitesse laser oscillator, besides seeding the regenerative amplifier with 80 MHz pulses, also generates a 80 MHz electronic TTL trigger signal, which is sent to a Synchronization and Delay Generator (SDG). This device divides the 80 MHz signal down to 1 kHz, and has 8 delay outputs, out of which one is used for the experimental setups of the UDG laboratory. This output is then fed to a delay generator, with which it is possible to set a desired delay. After setting the delay, an output from the delay generator is connected to the DAQ card.

The 500 Hz TTL trigger from the alternator is also connected to the DAQ card. This trigger is used as a reference for the measurements. For the detection of the field-induced second-harmonic the PMT tube is used. The signal from the PMT is connected to the the boxcar integrator. The averaged signal from the boxcar is fed to the DAQ card input channel. Data acquisition starts when the DAQ receives the TTL trigger from the alternator. For a duration set in Huberscope (in
seconds), the data is recorded by the DAQ software, and in particular, the difference between subsequent pulses, with the bias field changing sign.

4.9 The Single-Shot Autocorrelator

Since the probe beam pulse duration is an important parameter that determines the spectral response of the spectrometer, this information about the probe pulse is needed. The measurement of the duration of a laser pulse by commercial electronic means is currently limited to a time resolution of about 1-10ps. Direct electronic measurement for shorter pulses is not possible, as there are no electronics available that can operate so fast. For the measurement of optical pulses shorter in duration than 1ps, the optical intensity autocorrelation method can be used [68,69].

4.9.1 Designed Single-Shot Autocorrelator

A single-shot autocorrelator was designed and is included in this setup. Mirror M5 can be inserted using a magnetic mount to send the probe beam to a periscope P3 and then to the autocorrelator for the pulse duration measurement. (see the top-down schematic of the setup in figure 4.3)

The top down view of the background-free single-shot autocorrelator build for the setup is depicted in figure 4.8. The pulsed laser beam, of fundamental frequency $\omega$ enters the autocorrelator setup. After one reflection, it is then reflected and focused by a cylindrical concave metallic coated mirror, of 516.8 mm focal length. The mirror is used to increase the intensity-dependent second-harmonic generation in the later following $\beta$-BBO crystal. A 50/50 beam-splitter BS is used to split a laser beam into two parts of the same intensity. The two beams follow different paths, where the one is delayed with respect to the other by controlling the path length with a mechanical stage (two times $\Delta x$), and then are non-collinearly focused into a 30$\mu$m $\beta$-BBO SHG crystal and overlapped in space and time. The crystal then generates a beam at the second-harmonic frequency $2\omega$ of the fundamental beam that is a function of the time delay between the two overlapping beams, being zero for no temporal overlap and maximum for perfect
time overlap at zero time delay between the pulses. Using a CCD camera detector the intensity of the second-harmonic light $I_{2\omega}(\tau)$ can be estimated. This measured intensity mathematically corresponds to the autocorrelation function. To be noted, any phase information is lost with this measurement.

Figure 4.8: Topdown view of the constructed background-free single-shot autocorrelator setup.

4.9.2 Calculation of Optical Intensity Autocorrelation and Calibration

The basic principle of a single-shot autocorrelator is to transform the temporal distribution of the laser pulse into a spatial intensity distribution of the SHG signal generated from the nonlinear crystal, which then could be analysed by a CCD camera. The pair of the split pulses with electric fields $E_\omega$ overlap in the nonlinear crystal at an angle $\alpha$, as illustrated in figure 4.9. Different spatial positions in the nonlinear crystal correspond to different time delays $\tau$. This angle is responsible for the resolution and the maximum recordable pulse duration.

As shown in figure 4.9, the time delay $\tau$ between the two pulses is a function of the cross-angle $\alpha$ of the two beams and the distance $x$ from the centre of the crystal as:

$$\tau = \frac{nx\sin\alpha}{c}$$

(4.1)

The second-harmonic field $E_{2\omega}$ generated in a $\beta-BBO$ crystal with a second-order nonlinear susceptibility $\chi^2$ by the pair of the fundamental pulses is:

$$E_{2\omega} \propto \chi^{(2)} (E_\omega(t) + E_\omega(t - \tau))^2 = \chi^{(2)} (E_\omega(t)^2 + 2E_\omega(t)E_\omega(t - \tau) + E_\omega(t - \tau)^2)$$

(4.2)
Figure 4.9: Overlap in the $\beta - BBO$ crystal of the single-shot autocorrelator

At the output of the $\beta - BBO$, the three beams that are observed in figure 4.8 correspond to the three terms of equation 4.2. The first and last term are the double frequencies of the two pulses and the middle one is the mixing of the two. Since the two pulses are mixed non-collinearly, then due to momentum conservation, they are spatially separated from each other. Thus, these two components can be easily discarded. With a high-resolution CCD WinCamera, one can record the intensity profile of the middle term, which is now a function of the time delay $\tau$ known as the autocorrelation term $I_{ac}$:

$$I_{ac}(\tau) \propto \int_{-\infty}^{\infty} |E_\omega(t)E_\omega(t-\tau)|^2 dt \quad |E_\omega|^2 \rightarrow \propto \int_{-\infty}^{\infty} I_\omega(t)I_\omega(t-\tau) \quad (4.3)$$

From the full width at the half maximum (FWHM) of the autocorrelation function, given as $\tau_{ac}$ and under the assumption that the laser pulse shape is not subject of chirp, it is possible to estimate the pulse duration of the original pulses, for some analytic pulse shapes, such as Gaussian, sech$^2$ or other. As an example, for the case of Gaussian pulses, the conversion factor of the pulse FWHM from the autocorrelation FWHM is 0.7071. In most cases, a priori knowledge of the pulse shape is possible.

Calibration of the Single-Shot Autocorrelator

In order to be able to directly measure the autocorrelation trace width $\tau_{ac}$ from the intensity profile distribution recorded on the WinCamera’s CCD window, the camera must be calibrated.

The temporal overlap of the pulses is controlled by spatially translating the mechanical stage of one of the beam paths of the autocorrelator. Moving the stage by $\Delta z$ and thus changing the delay and overlap, it is observed that the autocorrelation trace is shifting its position on the camera detector. By recording at least two autocorrelation traces and noting the pixel position of the maxima on the camera, and associating the distance in pixels with the time delay we imposed:

$$\Delta t = \frac{2\Delta z}{c} \quad (4.4)$$

the time delay per pixel on the detector can be calculated. After the conversion value is obtained, the autocorrelation width can be calculated by measuring the pixels at the FWHM of each trace.
4.9.3 Some Properties and Considerations for Building an Autocorrelator

Some considerations one should have in mind when building a single-shot autocorrelator:
A property of the autocorrelation function is that it is always symmetric, such as $I_{2\omega}(\tau) = I_{2\omega}(-\tau)$. If the measured autocorrelation trace shape is asymmetric, it is due to misalignment of the autocorrelator.

The fundamental pulse electric field used in the equation 4.2 ideally is the one directly obtained from the ultrafast laser system. However, due to dispersion and other nonlinearities introduced by the beam guiding optics the pulse can change. Especially for ultrashort pulses, these effects lead to severe pulse deformation. To minimize these unwanted dispersion effects, it is recommended to use reflective optics and thin beam splitters and SHG crystals.

Group delay dispersion is another serious issue. To minimize it and therefore minimize temporal pulse walk-off between the fundamental and second harmonic signal, the nonlinear crystal thickness has to be reasonable small.

Bandwidth limitation in the nonlinear conversion efficiency is another serious issue. The conversion efficiency in the nonlinear crystal ideally should be constant over the full spectral region in the pulse. To verify this, one can compare for example the spectral intensity of the generated second-harmonic $I_{2\omega}(\nu)$ to the the incoming fundamental wave $I_{\omega}(\nu)$. If the spectral bandwidth limitations are negligible, then one would expect:

$$\sqrt{I_{2\omega}(\nu)} \propto I_{\omega}(\nu) \quad (4.5)$$

4.10 Properties of materials used for Terahertz Optics

Silicon

Silicon is a material widely used in THz system applications. It is one of the least absorbing and dispersive materials in this spectral region. For our experimental setup, a 3 mm thick and 3” diameter HRFZ-Silicon wafer is used as the THz window for the ABCD gas-cell and a 1 mm thick wafer of the same material before the gas-cell and the THz wire grid polarizer, as a filter to further attenuate the THz beam intensity and remove any residual optical light still left after the teflon sheet. As shown in the spectrum in figure 4.10, HRFZ-Si maintains 50-54% transmission for a wide range of wavelengths (and frequencies).

![Figure 4.10: Transmission and reflection spectrum of HRFZ-Silicon, 5 mm thick sample.](Source: tydex-optics.com/products/thz_optics/thz_materials)
Metals

The reflectivity of most metals in the THz region is close to unity, and hence it is very common to use metal-coated mirrors to reflect THz radiation. For this particular experimental setup, gold-coated off-axis parabolic mirrors and flat silver-coated mirrors are used.

Teflon

Teflon (PTFE) is a highly transparent material, showing transmission from 80 to 90% up to 15 $THz$. It has a characteristic phonon absorption line at around 6 THz (or 50 µm). It is a very cheap and easy to handle material and in our setup a thin layer of it was used to remove the residual optical light after the THz generation by the plasma. In figure 4.11 the transmission spectrum for a 0.1 mm thick teflon film is given.

![Transmission spectrum of a PTFE (teflon) film. Note the absorption dip at 50 µm (equivalently 6THz).](source: tydexoptics.com/products/thz_optics/thz_materials)

Polyethylene Wire Grid Polarizer

In order to control the intensity of the generated THz field, a free-standing polyethylene (PE) wire grid polarizer was used. It is a grating type polarizer and is made by forming grooves of a triangle profile on a substrate and subsequent deposition of a metal coating (aluminium) on one of the groove facets. The transmission at an angle $\theta$ between the grid direction and the polarization of the electric field of the THz beam is given by:

$$ T(\theta) = \cos^2 \theta \tag{4.6} $$

Polyethylene is a light elastic crystallizing material that shows high transmission in the THz range. It demonstrates two phonon resonances near 2.3 and 11 THz. In figure 4.12, the transmission spectrum of a 2 mm thick HDPE polyethylene sample in the THz region is illustrated.
Figure 4.12: Transmission spectrum of a 2 mm thick HDPE polyethylene sample in the THz region (the relevant 1 to 15 THz range corresponds to 20μm – 300μm). [Source: tydexoptics.com/products/thz_optics/thz_materials]
Chapter 5

Experimental Results

As most nonlinear frequency conversion processes, the ABCD technique is depended on phase-matching relations that need to be maintained for maximum efficiency. Hence, in order to be able to implement broadband THz pulse detection, phase modifying effects that contribute destructively to the process, for instance the Gouy phase shift, phase mismatch (expressed by $\Delta k$) and dispersion need to be well understood, examined and if possible suppressed \[65,70\].

With this in mind, a series of measurements and tests were made, investigating the performance of the gas-based spectrometer, mainly focused on the implemented ABCD detection scheme and working towards its optimal operation. In this chapter the results of these measurements shall be presented.

5.1 Some Reference Results and General Remarks

As an introduction to the results chapter, in figures 5.1, 5.2a and 5.2b the time trace and spectrum of a THz pulse generated and detected by the gas-based spectrometer are shown as a reference. The gas-cell and the setup were purged completely with Nitrogen to $1 \pm 1\%$ relative humidity to remove any water absorption lines. The probe pulse energy was measured to be $34.2 \mu J$ and the pulse width was $64 \pm 4 fs$ as estimated by the autocorrelator (assuming Gaussian shaped pulses, more about the autocorrelation measurement in \[5.7.1\]). The bias field strength was $14.6 kV/cm$.

In order to get better statistics, five time traces of the pulse were measured and averaged together. For every time-step of the time trace, an average was calculated out of 300 laser pulse-shots.

\[\text{Figure 5.1: A reference THz pulse time-domain trace, obtained by the photomultiplier tube, with the gas-cell purged with nitrogen.}\]
Figure 5.1 shows the time trace of the obtained THz pulse. The calculated spectrum of this pulse, illustrated in figures 5.2a, 5.2b, shows that it has a broad bandwidth, with a frequency cut-off at around 14 THz.

Figure 5.2: Spectrum of the reference THz-pulse. Detection is broad bandwidth, with a frequency cut-off at 14THz. Notice the teflon absorption dip at 6THz. The dip at around 11THz could be attributed to phonon absorption by the polyethylene wire grid polarizer.

5.1.1 Photomultiplier tube saturation

For most of the following experiments, the detection of the field-induced second-harmonic was done with the Hamamatsu R636-10 photomultiplier tube, since it can easily detect these usually low-intensity signals, as explained in 4.5. However, one should take care and make sure that the spectrum of a THz pulse that is detected by the PMT corresponds to expectations or is comparable with other reference measurements. The reason is, that above a certain limit of the THz field intensity, the THz-induced second-harmonic becomes so intense, that the PMT begins to saturate, and thus its output cannot be trusted. An example of this problem is illustrated in figure 5.3, in which the spectra for the same THz pulse, but with different attenuation of its field intensity are compared. As a solution to that problem, an additional 1mm thick HRFZ-Silicon wafer along with a polyethylene wire grid polarizer were used in order to decrease the intensity of the THz field whenever it was needed.
Figure 5.3: Two normalized spectra of the same THz pulse, taken under the same conditions, but with more and less THz beam attenuation. The difference in the detected spectra is attributed to the THz-induced second-harmonic beam that saturates the photomultiplier tube, and thus the output signal is distorted.

5.1.2 Signal-to-Noise Ratio

One of the most characteristic quantities that describes the performance of a THz time-domain spectrometer system is its signal-to-noise ratio (SNR). For this thesis, the definition given by the work of Naftal and Dudley [71] is followed, in which, for a typical THz pulse trace in the time-domain, the SNR is defined as:

\[
SNR = \frac{\text{mean magnitude of the peak-to-peak amplitude}}{\text{standard deviation of the peak-to-peak amplitude}}
\]  

(5.1)

Based upon this definition, SNR indicates the minimum detectable change in the measured signal. For the presented measurements of the signal-to-noise ratio, the above definition is used and in order to obtain the best possible statistics, the mean magnitude of the THz pulse amplitude was calculated as the average of the maximum and minimum points of the THz pulse (number of averages per time step × number of averages per THz trace). The standard deviation of the maximum and minimum points was calculated from the same amount of data, and the overall was calculated taking into account error propagation as:

\[
\sigma = \sqrt{\sigma_{\text{max}}^2 + \sigma_{\text{min}}^2},
\]
5.2 Electrode Width Scan

According to four-wave mixing theory, the field-induced second-harmonic field is given as the sum of the different contributions along the interaction length, which is defined by the width of the plate electrodes [70], as shown in figure 5.4. By increasing the electrode width, and subsequently the interaction length, there is larger build-up for the bias-field induced second-harmonic and the output intensity should be increased. There is also however the competing effect of the Gouy phase shift, which introduces a modification in the phase, that increases the phase mismatch, and thus lowers the process efficiency.

By choosing the correct electrode width for the relative beam waist and Rayleigh lengths for this particular setup, the two contradicting effects can be balanced and the four-wave mixing interaction length optimized. This should lead to enhanced output signal.

For the purpose of investigating the influence of the electrode width, six pairs of copper electrodes were used, with widths from 1mm to 6mm increasing at a step of 1mm, and for each pair the THz pulse trace was measured under the same conditions.

![Figure 5.4: Top-down view of the electrodes inside the gas cell. For this measurement, electrode pairs of various widths were used. Parameters $z_R$ and $z_T$ are the Rayleigh lengths of the probe and THz beams respectively.](image)

Probe pulse energy was measured to be $34.2\mu J$ and the pulse length was estimated with the autocorrelator to be $64 \pm 4fs$ (autocorrelation width was $89 \pm 6fs$, details about the measurement can be found in section 5.7.1). For each electrode pair, 3 time traces were measured, and for each step of the time traces, the average of 300 shots. The distance between the electrodes was set to 1.33 mm and it was kept the same for all measurements. The bias field strength between the electrodes for this configuration is $14.9kV/cm^2$. Both the setup and the gas-cell were purged with nitrogen. For the detection of the field-induced second-harmonic, the PMT was used.

Below, the results of the electrode width scan are presented: In figure 5.5, the average peak-to-peak amplitude values of the THz pulses as a function of the electrodes width is shown. The peak-to-peak signal seems to rapidly increase up to 3-4 mm widths and then starts to decrease again. The error bars were estimated by using a repetition measurement of the 3 mm wide electrodes, after the first set of measurements was completed.
Figure 5.5: The detected THz field average peak-to-peak amplitude as a function of the electrode width. The error bars were estimated using a repetition measurement of the 3 mm wide electrodes.

In figure 5.6, the signal-to-noise ratio as a function of the electrode width is shown. Similarly as before, SNR seems to improve and then goes slightly down again with increasing electrode widths. Again, the error bars were estimated using the repeated measurement. Finally, figure 5.7 shows the calculated spectra of the THz pulses for each electrode width measurement.

Figure 5.6: The signal-to-noise ratio as a function of the electrode width. The error bars were estimated using a repetition measurement of the 3 mm wide electrodes.
5.3 Electrode Position Dependence Scan

The goal of this measurement was to investigate the effect of the Gouy shift (see section 2.2) on the detected THz pulse. The optimal electrode width of 4 mm was used, as it was estimated from the experimental results presented in section 5.2. The focused THz and optical probe beams are aligned and overlapping, meaning that both beam foci are on the same spot. Using the base mechanical stage, the electrode pair is moved along the direction of propagation of the probe and THz beams, investigating the Rayleigh region and beyond, as depicted in figure 5.8. Several measurements of the THz trace were taken, for a number of positions before and after the assumed focal point.

The measurements of the THz traces were made under the same conditions: The probe pulse energy was calculated to be 57.6 µJ and its duration was 64 ± 4 fs (see section 5.7.1). Detection was done by the PMT, and the gas-cell with the setup were purged with nitrogen for every measurement. For each position, the average of 3 measured THz waveforms was calculated and for every time step, an average of 200 laser pulse-shots.
An overview of all measured THz pulse traces is given in figure 5.9. One can observe the polarity and the shape of the THz pulse shifting as it propagates towards and then away from the assumed focal point.

Figure 5.9: Overview of the electrode position scan measurement. The Gouy phase influences the detected THz waveform shape for various points before and after the focus.

In figure 5.10, the additional phase acquired with respect to a “reference” measurement, as a function of frequency for each individual measured waveform, is shown. As reference, the waveform obtained at the assumed focal point was chosen. One can observe that there is a linear dependence of the acquired phase with frequency, increasing for higher frequencies. This phase drift was attributed to a subtle spatial shift \( \delta x \) between the probe and THz beams. This spatial shift, expressed in phase means that the higher frequencies would acquire an additional amount of phase \( \delta \phi \), since \( \delta \phi \propto \delta x/\delta \lambda \).
Figure 5.10: Phase acquired via the Gouy phase shift with respect to the reference for the different positions. No correction applied for the phase drift.

In order to correct this deviation, a linear spatial drift over the time interval of the experiment was assumed and corrected for, by using a drift velocity $\nu_d$ of 1.483$\mu$m/hour. The value was extracted from an optimization MATLAB algorithm. After the data was corrected, the updated results of the previous plot are shown in figure 5.11. As a general trend now, the acquired phase remains about the same for all frequencies, with some of the measurements showing deviations.
Figure 5.11: Phase acquired via the Gouy phase shift with respect to the reference for the different positions, with applied correction.

In figure 5.12 the THz time traces are depicted next to each in a heat map image. One can see that the field strength amplitude “shifts” as the THz pulse moves over the assumed focus (were waveform n.6 is).

Figure 5.12: THz pulse waveforms heat image. The pulses are depicted next to each other, showing how the THz pulse shape changes as it propagates through the focus. Plot number is the number of the THz trace, as shown in the overview figure 5.9. The colour scaling indicates the field strength amplitude of the pulse.
In figure 5.13, the average of the phase for the frequency components between 1-2 THz as a function of the position relative to the focus is illustrated. The fit is calculated with the definition of the Gouy phase in mind, given by equation 2.21 and in this case is of the form: 
\[ \phi_G = -\arctan\left(\frac{z - z_0}{z_T}\right) + \frac{a}{\pi}, \]
where \( z_T \) the THz beam Rayleigh length, and \( z_0 \) the actual position of the focus. The error bars were estimated from the standard deviation of the average phase at each position.

---

Figure 5.13: Gouy phase shift as a function of position. The error bars were estimated from the standard deviation of the average phase at each position. The line corresponds to a fit calculated from the definition of Gouy phase. Calculated fit parameters: \( z_0 = 0.3182 \text{[mm]} \), \( z_T = 2.543 \text{[mm]} \), \( a = -0.1009 \text{[rad]} \)

5.4 Probe Energy Pulse Scan

Based on the theoretical background discussed in the previous chapters, from relations 3.18 and 3.29 it was shown that the field-induced second-harmonic intensity is quadratically dependent on the probe beam intensity. For this set of measurements, it was investigated if this relation holds, what is its effect on the detection of the THz field and the performance of the spectrometer, as described by the signal-to-noise ratio, and whether or not the saturation regime of the field-induced second harmonic intensity can be reached [72].

The THz pulse trace for various intensities of the probe beam were recorded. The power, and subsequently the pulse energy of the probe beam was controlled by adjusting a neutral density (ND) filter in its path, prior entering the purge box and the setup. The power was measured with a power meter after the ND filter, and the actual power that reaches the interaction volume, after part of it has been absorbed by filters and windows along the way, was deduced by a conversion factor. With an autocorrelation
measurement the pulse length was determined to be 64 ± 4fs (see section 5.7.1). For each measurement the average of three time traces was recorded, with 200 shots per step. The gas-cell and the setup were purged with nitrogen. The same conditions were used for every measurement.

In the following, the results of this investigation are shown: in figure 5.14 the time traces of the detected THz pulse, for the different probe pulse energies are illustrated. Clearly, the strength of the THz field is increasing with the probe pulse energy.

![Probe pulse energy scan](image)

**Figure 5.14:** Measured THz pulse trace for different probe pulse energies.

Figure 5.15 shows how the average peak-to-peak amplitude of the detected terahertz pulse is related to the probe pulse energy. The quadratic relation between the two quantities is revealed. In addition, there is no saturation behaviour of the detected field-induced second-harmonic intensity, and hence of the recorded terahertz pulse amplitude, observed for the range of probe pulse energies used in this set. The error bars were estimated from the standard deviation of the average amplitude. The red line corresponds to a quadratic fit, which is of the form \( f(x) = ax^2 \).
Figure 5.15: Measured THz pulse average peak-to-peak amplitudes as a function of the probe pulse energies. The red line represents a quadratic fit. The error bars are estimated by the standard deviation of the average amplitudes. Calculated fit parameter values: \( \alpha = 3.512 \cdot 10^{-05}[\text{a.u.}/\mu\text{J}] \)

Figure 5.16 shows the relation of the signal-to-noise ratio with the probe pulse energy. An increasing linear relation between the two quantities is apparent. The error bars were estimated using error propagation. The red line corresponds to a linear fit, of the form \( f(x) = \alpha \cdot x \).

Figure 5.16: Calculated signal-to-noise Ratio as a function of the probe pulse energy. The error bars were estimated using standard error propagation. Calculated fit parameter values: \( \alpha = 0.263[\mu\text{J}^{-1}] \)
Figure 5.17 shows the standard deviation of the average peak-to-peak amplitude of the detected THz pulse as a function of the probe pulse energy. The error bars represent the error of the standard deviation. The red line, again, represents a linear fit.

\[ \alpha = 1.354 \times 10^{-4} \mu J^{-1} \]

Finally, in figure 5.18 the corresponding spectra of the detected THz pulse for the different probe pulse energy measurements are illustrated. No significant difference between them is observed.
5.5 Bias Field Strength Scan

Considering the same arguments as for the probe pulse energy measurement set, the next investigation concerned the effect of the bias field strength $E_{bias}$, to the detection of the THz pulse trace, as described by relations 3.18 and 3.29.

The bias field strength $E_{bias}$ was controlled by modulating the output voltage from the alternator device to the High Voltage amplifier. Setting the electrode gap distance to $1.33\,mm$ and using the formula 3.22 from section 3.3.1, it was possible to calculate the bias electric field strength $E_{bias}$ for each measurement. For each bias field value, the average of three traces was recorded, and for each time step an average of 100 shots. The probe pulse energy was $50.4\mu J$ and the probe pulse width was $65 \pm 2fs$ (see section 5.7.2). The setup and the gas-cell were purged with nitrogen.

The results of this round of measurements: In figure 5.19 the time traces of the detected THz pulse for the different values of the bias electric field strength $E_{bias}$ are shown. Clearly, the detected THz pulse strength is increasing with the bias field strength.

![Figure 5.19: Detected THz pulse traces for different values of the bias electric field strength $E_{bias}$.](image)

Next, on figure 5.20 the effect of the bias field strength on the average peak-to-peak amplitude of the detected THz pulse is shown. The error bars were estimated from the standard deviation of the amplitude average. The red line represents a linear fit coming through zero, $y = \alpha \cdot x$. 

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Figure 5.20: Average peak-to-peak value of the THz pulse amplitude as a function of the bias field strength $E_{\text{Bias}}$. The error bars represent the standard deviation of the peak-to-peak amplitude. The red line is a linear fit coming through zero. Calculated fit parameter values: $\alpha = 0.0481[a.u/Volts]$

Figure 5.21 shows the calculated signal-to-noise ratio as a function of the bias field. SNR seems to increase linearly with the bias field strength. Again, the red line is a linear fit coming through zero.

Figure 5.21: Signal-to-noise ratio as a function of the bias field strength $E_{\text{bias}}$. The error bars were calculated using error propagation (of the standard deviation of the average peak-to-peak amplitude, and the standard deviation of this standard deviation). The red line is a linear fit going through zero. Calculated fit parameter values: $\alpha = 1.1004[Volts^{-1}]$
5.6 Comparison of Different Gases

5.6.1 Overview - Reference Measurement with Butane

In order to investigate the influence of the third-order nonlinear susceptibility $\chi^{(3)}$ on the field-induced second-harmonic generation, measurements with different gases of characteristic values of $\chi^{(3)}$ were made. As a first example, in figure 5.22 a THz pulse detected with the gas-cell filled with butane ($C_4H_{10}$) is shown. The enhancement of the field-induced second-harmonic intensity is so large, that the previously low intensity second-harmonic becomes intense enough to be visible (see figure 5.23). The third-harmonic is also visible. In this case, one would have to attenuate the THz field a lot, in order to be able to use the PMT for detection (see section 5.1.1).

For this reference measurement however, a Si-photodiode detector (PD) was used, in order to assure that we do not get into saturation. The probe pulse energy was measured to be 50.4$\mu$J and it duration was estimated to be $65 \pm 2\,fs$ (see section 5.7.2). The average of 5 time traces was taken, and for each time trace 100 shots per time step.

![Figure 5.22: Terahertz pulse time trace detected by a photodiode, using butane as the detection gas.](image)

![Figure 5.23: Photograph of the field-induced second and third harmonic generation, scattered by a sheet of paper.](image)
The spectrum of the detected THz pulse is shown in figures 5.24a and 5.24b. It is apparent that detection is still very broadband, with a frequency cut-off at 16 THz.

5.6.2 Influence of Third-order Nonlinear Susceptibility $\chi^{(3)}$ - First Comparison

A direct comparison of the effect on the detection capabilities of the ABCD technique by three different gases was made. Pure nitrogen ($N_2$), and the alkane gases propane ($C_3H_8$) and butane ($C_4H_{10}$) were used. Since nitrogen’s third-order nonlinear susceptibility value is not large enough to allow for intense field-induced second-harmonic generation, for this comparison measurement the photodiode could not be used. Instead, the PMT was used: the measurement procedure started with butane, which has the highest $\chi^{(3)}$ value of the three and was expected to emit the most intense field-induced second-harmonic. The wire grid polarizer’s optical axis orientation was optimized in order to avoid the saturation of the photomultiplier tube. The probe pulse energy was measured to be 50.4 $\mu$J and its duration was estimated to be $65 \pm 2$ fs (see section 5.7.2). Then for each gas, the average of 5 time traces was taken, with an average of 100 shots per time step. For the data analysis, the values of $\chi^{(3)}$ were taken from D.P. Shelton’s work [73].

In figure 5.25 the time traces of the THz pulse detected using the three gases are shown. It is apparent that the amplitude of the pulse when detected with the alkanes gases is significantly enhanced, as compared to the case of nitrogen.
In figure 5.26, the average peak-to-peak amplitude values of the detected THz pulses, normalized with the peak-to-peak value of the field detected with nitrogen, as a function of the third-order nonlinear susceptibility values of the gases $\chi^{(3)}$, normalized with the value for nitrogen $\chi^{(3)}_{\text{Nitrogen}}$ are shown. The error bars represent the standard deviation of the average amplitude. In addition, two quadratic $y = \alpha \cdot x^2$ fits are illustrated: The dotted line is bound to the value given by Nitrogen detection, while the solid line is an unbound fit.
In figure 5.27 the spectra of the measured THz pulse for the three gases are shown in a logarithmic scale.

![Spectra of the obtained THz pulses](image)

Figure 5.27: First Comparison of Gases: Spectra of the obtained THz pulses, shown in a logarithmic scale.

### 5.6.3 Influence of third-order nonlinear susceptibility $\chi^{(3)}$ - Second comparison

Due to the unexpected results, the gas comparison measurement was repeated. The conditions were estimated to be about the same as in the first comparison measurement. The probe pulse energy was $49.5\mu J$ and the pulse width was $62 \pm 2\, \text{fs}$ (see section 5.7.3). The plots here show the same quantity relations as the first measurement:

![Traces of the THz pulse detected in the three different gases](image)

Figure 5.28: Second Gas Comparison: Traces of the THz pulse detected in the three different gases.
5.7 Single-shot Autocorrelation Measurements

In this section, the autocorrelation measurements of the probe beam are shown. The basic principles are described in detail in section 4.9. In order to get better statistics, multiple autocorrelation traces were recorded per measurement, as shown in figure 5.31. Assuming that the probe pulses have a Gaussian profile distribution, which means that also the autocorrelation traces would have a Gaussian distribution, a
Gaussian curve was fitted for each trace. The fitted Gauss model was of the form: \( y = a \cdot \exp\left( -\frac{(x-b)^2}{c^2} \right) \).

After the calibration was done, the autocorrelation widths and subsequently the pulse widths were directly measured from the FWHM of the autocorrelation traces. Then, an average pulse width value from all traces was calculated, along with the standard deviation.

![Multiple single-shot autocorrelation traces.](image)

Figure 5.31: Multiple single-shot autocorrelation traces.

The autocorrelation measurements are categorized by dates, and for each date the measurement sets that were performed that day on the spectrometer are given.

### 5.7.1 Measurement Day 15.05.2015

During this day, the reference THz pulse measurements, the electrode width, electrode position and probe pulse energy scans were performed. An autocorrelation trace from that day is shown in figure 5.32. The average width of the autocorrelation trace was measured to be \( 89 \pm 6 \text{fs} \). Assuming Gaussian pulses, the pulse width was \( 64 \pm 4 \text{fs} \).

![Single-shot autocorrelation trace measurement of the probe pulse on 15.05.2015.](image)

Figure 5.32: Single-shot autocorrelation trace measurement of the probe pulse on 15.05.2015. Calculated fit parameters: \( a = 2.9498 \cdot 10^4 \text{[a.u.]} \), \( b = 0 \text{[s]} \), \( c = 5.050110^{-14} \text{[s]} \)
5.7.2 Measurement Day 18.05.2015

This pulse width measurement concerns the butane reference scan, the bias field strength scan and the first gas comparison. The average width of the autocorrelation trace was measured to be 91 ± 3 fs. The average pulse width was 65 ± 2 fs.

![Figure 5.33: Single-shot autocorrelation trace measurement of the probe pulse on 18.05.2015. Calculated fit parameters: $a = 5.6677 \cdot 10^3$ [a.u.], $b_1 = 0$ [s], $c_1 = 4.69 \cdot 10^{-14}$ [s]](image)

5.7.3 Measurement Day 21.05.2015

This measurement concerned the second gas comparison scan. The average width of the autocorrelation trace was measured to be 88 ± 4 fs. The average pulse width was 62 ± 2 fs.

![Figure 5.34: Single-shot autocorrelation trace measurement of the probe pulse on 21.05.2015. Calculated fit parameters: $a = 3.2603 \cdot 10^4$ [a.u.], $b = -3.5 \cdot 10^{-15}$ [s], $c = 5.05 \cdot 10^{-14}$ [s]](image)
Chapter 6

Result Analysis - Discussion

In this chapter, the motivation behind each measurement shall be discussed in detail, along with the expected outcomes and the analysis of the actual results of the experiments.

6.1 Towards the Realisation of the Gas-Based THz Time-Domain Spectrometer

For the purpose of studying low-energy dynamic processes in solid-state materials, occurring for energies that correspond to the mid- and far-infrared parts of the e.m. spectrum, such as spin-phonon coupling in transition-metal oxides [28], the need for a time-domain spectrometer that would have access to the respective frequencies has raised. After examining the relevant literature, it was concluded that the best option would be the realisation of a THz time-domain spectrometer for which the generation and detection of the THz radiation is done using THz gas photonics. In contrast to solid-state THz emitters and detectors, whose bandwidth is limited by phonon resonances in the THz region or carrier lifetime, gases do not show any phonon absorption or etalon effects from surfaces, have less dispersion and are continuously replenishable.

In section 4.3 the setup of the constructed THz-TDS spectrometer is described in detail. A high-resolution model is also illustrated in figure 4.3 from a top down view and in figure 4.4 from an isometric view. The generation of the THz radiation is realised through the nonlinear interaction of a two-colour laser field in a laser-induced gas plasma. The detection of THz is done using the Air Biased Coherent Detection scheme. A gas-cell was specifically designed and built to house the relevant components used for the ABCD technique, as well as for the purpose of studying the effect and the contribution to the detection of the THz of various gases with high values of the third-order nonlinear susceptibility $\chi^{(3)}$.

In addition, a single-shot autocorrelator was also built and included with the setup, with which the estimation of the probe pulse duration is possible.

After it was built, a systematic study of the performance of the gas-based THz-TD spectrometer, focused on determining and optimizing the efficiency of the ABCD scheme was initiated. As a nonlinear process, the ABCD technique is highly dependent to phase-matching. In order to realise broadband THz detection, phase effects that interference destructively, such as the Gouy phase shift, phase-mismatch and dispersion should be well-understood, their effect in this particular setup examined and, if possible, suppressed. In addition, the effect on the detection efficiency of the probe pulse energy, the bias field strength and the third-order nonlinear susceptibility $\chi^{(3)}$ for selected gases was also thoroughly investigated. Moreover, the probe pulse width was determined with the autocorrelator for each measurement.

6.2 Reference Results and Remarks

In the introductory section of the results chapter, the time domain trace (figure 5.1) and the corresponding spectrum (figures 5.2a & 5.2b) of a THz pulse, detected with the PMT, with the gas-cell purged in nitrogen, are shown. The aim of this measurement was to obtain a THz trace that could be used as a guide and reference for the rest of the experiments. From this reference measurement the advantage of THz
gas photonics, over other conventional methods of generation and detection is clear: the THz spectrum is continuous, showing a broad bandwidth of frequencies for 0.1 to 14 THz, and with no significant artefacts or absorption lines, with the exception of a subtle dip at 6 THz, which is attributed to phonon absorption by the thin teflon layer used for blocking the residual optical light after the THz generation and another one at 11 THz, attributed to absorption from the polyethylene wire grid polarizer.

Next, it was shown that special care must be taken when using the photomultiplier tube: although the PMT allows for the low-noise and efficient detection of the (usually low intensity) field-induced second-harmonic light, it was found that when the THz field strength is becoming large, its field-induced second-harmonic can become so intense that the PMT begins to saturate. Thus, its output signal, for such light intensities, cannot be trusted and/or used. As an example, the measured spectra of the same THz pulse with high and low attenuation of the THz field, controlled using the wire grid polariser, is shown in figure 5.3. Obviously, the saturated, intense-THz signal is not comparable with the reference pulse spectrum, shown in 5.2a. A solution to this problem was applied by using a combination of an additional 1 mm thick HRFZ-Silicon filter and a wire grid polariser to further attenuate and control the intensity of the THz field.

6.3 Electrode Width Scan

The first parameter that had to be determined was the optimal width of the copper electrodes used to deliver the bias field for the ABCD scheme. The electrode width defines the four-wave mixing interaction range. Hence, the larger the width, the more the accumulation of the field-induced second-harmonic generation is, and the detected signal strength should be vastly improved. However, the Gouy phase shift introduces a considerable phase change of over $\pi/2$, when the interaction range exceeds the THz beam Rayleigh range, which then causes increased phase mismatch and thus decreases the efficiency of the FMW interaction. Therefore, by choosing a suitable electrode width, these two competing effects can be balanced, and the FWM process optimized, which would lead to improved detection and signal-to-noise ratio.

In figure 5.5, the experimental results of the average peak-to-peak amplitude values of the THz pulse field as a function of the electrode width are shown. As one would expect, the detected field strength increases with increasing the interaction range. For the 3 & 4 mm wide electrodes, it seems that the mismatch effects caused by the Gouy phase shift balance out the increase from the longer interaction length. For 5 & 6 mm the nonlinear process’ efficiency drops even more and the detected THz amplitude further decreases. In conjunction with the results of the signal-to-noise ratio, shown in figure 5.6, which demonstrate a similar behaviour, it was concluded that for this particular setup, using nitrogen as the detection medium, the 4 mm wide electrodes have the optimal width.

It should be noted that the detected pulse spectrum, illustrated in figure 5.7, does not show an distinct features or change in its shape for any of the electrodes used. Only the amplitude is modulated.

6.4 Electrode Position Dependence Scan

The goal for this investigation was to study the effect that the Gouy phase shift has on the detected THz pulse. The electrodes with the optimum width of 4 mm were used, as it was determined from the previous study. The pair is mounted on a translation stage which can move along the direction of propagation. A number of measurements of the THz pulse trace were taken at points before and after the assumed focal point.

In figure 5.9 an overview of the measured waveforms is shown. It is apparent that the THz pulse is experiencing a significant phase modulation along the direction of propagation. which influences its shape.
and polarity.

In figure 5.10 the additional phase acquired at each position, with respect to the pulse recorded at the assumed focus, is illustrated as a function of frequency. One could see, that for all measurements there was an increasing linear dependence of the acquired phase with frequency. This was attributed to a small spatial shift between the THz and probe beams. A correction assuming constant linear drift was applied to the data, and the same quantities, corrected now, are shown in figure 5.11. The previously increasing linear trend of the phase with the frequency is corrected, but there are still some deviations. These deviations could be attributed to an additional spatial shift induced during the measurement procedure, for example when opening and closing the gas cell, or when moving the translation stage of the electrodes. The applied correction could be interpreted as a way to estimate the long-term phase stability of the spectrometer. Although technically this drift could be caused from the OPA warming up, during this measurement scan we had assumed that it was stabilized. The value of $1.483 \mu m/hour$ of the drift is actually rather high and it could interfere with the outcome of long duration spectroscopic measurements. In the future, care should be taken to reduce this spatial drift as much as possible. One way to deal with this issue could be to use the same OPA HE output for both pump and probe sections of the spectrometer.

In figure 5.12 the heat image of the obtained time traces are presented next to each other. This gives a good intuitive picture of the shape change that the pulse is subjected as it passes the focus.

In figure 5.13 the extracted phase values, averaged for the frequency components of 1 to 2 THz as a function of position are illustrated, together with a theoretical fit. Even though there are not enough data points that would show the entire arc-tan behaviour of the data, because the stage translation range was limited, still the phase shift around the focus is apparent. The parameter values obtained by the plotted theoretical fit function, suggest that the actual focus is 0.32 mm away from where it was assumed to be. In addition, the Rayleigh length of the THz beam is suggested to be 2.54 mm. However, the optimized electrode width smears out the underlying arc-tan behaviour, and so the extracted value of the fit parameters that concerns the Rayleigh length, does not entirely correspond to the real value.

The overall conclusion of this and the previous studies is that the Gouy phase shift has a significant effect on the efficiency of the ABCD method. By understanding this effect, it is possible to designate the correct electrodes width and position for a particular off-axis parabolic mirror configuration.

### 6.5 Probe Pulse Energy Scan

The goal for this measurement set was to determine if the quadratic dependence of the field-induced second-harmonic intensity to the probe beam intensity holds, and what the overall effect of the probe beam intensity on the detection performance is. The THz time traces were recorded for various energies of the probe pulse, which was regulated using a neutral density filter.

The THz pulse time traces are shown in figure 5.14. It is clear that with increasing the probe pulse energy, the amplitude strength of the detected THz pulse also increases. This can also be seen in figure 5.15 were the average peak-to-peak values of the THz pulse amplitude are shown as a function of probe pulse energy. The data and the corresponding fit verify the quadratic relation between these quantities.

Another interesting result of this study is that increasing the probe pulse energy will improve the detection efficiency, since the signal-to-noise ratio is increasing linearly with the pulse energies, as shown in figure 5.16. This behaviour of the SNR can be explained with the also linear relation of the standard deviation of the average THz pulse amplitude with the probe pulse energy, as shown in 5.17 while keeping in mind the given definition of the SNR (average amplitude over the standard deviation, see section 5.1.2).

The final conclusion is that increasing the probe pulse energy is a good approach to increase the signal-to-noise ratio and thus improve the detection efficiency of the spectrometer. This however cannot
be done indefinitely, as other studies \cite{26,65} have shown that at high probe beam intensities the field-induced second harmonic intensity gets saturated and does not further increase, as plasma is formed in the interaction region which introduces intensity clamping \cite{74}. In addition, the THz waveform is distorted due to absorption from the probe-induced plasma. This was not the case for this measurement set, as no intensity saturation or plasma formation was observed. Generally, it is advised to use probe energies just below the plasma induction threshold for maximum efficiency.

6.6 Bias Field $E_{bias}$ Strength Scan

After examining the effect of probe pulse energy, the next study concerned the effect of the bias field on the detection efficiency. The bias field strength was controlled with the alternator device.

In figure 5.19 where the THz pulse time traces are shown, it is clear that increasing the bias field strength, the detected signal strength increases significantly. In figure 5.20, the average peak-to-peak values of the THz traces amplitude are illustrated as a function of the bias field strength, showing that this increase is governed by a linear relation, as expected.

The calculated signal-to-noise ratio, shown in 5.21, is also increasing linearly with respect to the bias field strength. This demonstrates that applying higher bias field strengths is another convenient way to improve the SNR and thus the detection efficiency of the spectrometer. This could be done in conjunction with the modulation of the probe pulse energy: if the field-induced second-harmonic intensity saturation regime has been reached, increasing the bias field strength will further improve SNR. One should keep in mind however, not to surpass the breakdown threshold of the gas medium used (for air it is 30kV/cm).

6.7 Exploitation of the Third-order Nonlinear Susceptibility $\chi^{(3)}$ of Gases

Another way to efficiently increase the field-induced second-harmonic intensity is to use a gas with high third-order nonlinear $\chi^{(3)}$ susceptibility values as a sensor for the ABCD scheme. According to previous studies \cite{65} alkane gases show relevantly high $\chi^{(3)}$ values and low absorption in the THz range, mainly due to the symmetric and long structure of their molecules. Low-cost gases like propane ($C_3H_8$) and butane ($C_4H_{10}$) are good candidates to be used in an ABCD scheme.

6.7.1 Reference Results

During the first measurements with alkane gases it was observed that the enhancement of the field-induced second-harmonic intensity is so large, that the beam becomes visible (see the photo in 5.23). Therefore, for the first reference results instead of the PMT which would obviously get easily saturated, a silicon photodiode (PD) was preferred. In figure 5.22 a reference spectrum obtained by using butane as the gas sensor is shown. The corresponding spectrum, in figures 5.24a and 5.24b, show that the detection is broadband, with a cut-off at 16 THz.

6.7.2 Gas Detection Capabilities Comparison

We proceeded with the comparison of detection by nitrogen with that by the alkane gases, propane and butane. For this measurement set, the PMT was used, since nitrogen’s third order susceptibility value is not high enough to generate a sufficiently intense field-induced second-harmonic to allow for the use of the PD. The intensity of the THz pulse field was attenuated with the use of a wire grid polarizer polariser, making sure that PMT was not saturated, and the measurement was trustworthy.
The experiment was conducted in two rounds. From the very first results, it became apparent from the amplitude of the THz traces, shown in 5.25 that alkane gases significantly enhance the intensity of the field-induced second harmonic generation, and thus the detected THz signal. However, the first measurement show an unexpected inconsistency with previous studies [65]. It was expected that the signal detected with butane would be stronger than the one with propane, as butane has a longer molecule structure and the third-order nonlinear susceptibility is much larger. However, as illustrated in figure 5.27 for this measurement the opposite outcome is shown. A possible explanation for this inconsistency could be that since the setup was optimized for operation with nitrogen, that phase mismatch for butane is much worse as compared to propane, hence the efficiency of the FWM process is reduced. Another explanation could be that butane leaked since it took some time to set up the measurement and the gas was not replenished before or during the measurement. Even thought there are no water absorption lines shown in the spectrum 5.27, the leaks would be expected to be mainly through the THz and optical probe windows, which are both in the part of the spectrometer that was purged with nitrogen.

A repetition measurement under almost the same conditions, showed a slightly more enhanced emission for butane that propane. Again, field-induced second-harmonic generation is much more intense for the alkane gases than nitrogen. This time, it was ensured that there is enough amount of butane in the cell. Now, although the intensity is slightly higher for butane, it is not orders of magnitude higher as expected. This discrepancy could be explained with the phase mismatch, as the electrode width and position were optimized in nitrogen atmosphere and not for the alkane gases. It could also be attributed to saturation of the field-induced second-harmonic intensity, as it is possible that the probe pulse energies used, 50.4µJ and 49.5µJ for the first and second comparison respectively, could be high enough to cause intensity clamping when the alkane gases are filling the gas-cell.

6.8 Probe Pulse Duration Measurements

The detectable bandwidth by the ABCD scheme is essentially only limited by the duration of the probe pulse [72]. With that in mind, a single-shot autocorrelator was built and included to the spectrometer set-up. It will be possible for the user of the spectrometer to estimate the probe pulse length with little effort and in short time.

During our optimization tests of the setup the probe pulse duration was measured several times. The probe pulse width, assuming it had a Gaussian shape, was estimated to be: 64 ± 4 fs, 65 ± 2 fs and 62 ± 2 fs.

6.9 Suggestions for Future Work

Concluding this work, we shall make a few recommendations for the next steps and further development of the gas-based THz time-domain spectrometer.

Regarding the THz generation part, the next logical step forward would be to do a full characterization of the two-colour laser-induced plasma as a THz radiation source. This would require monitoring and controlling of the relevant parameters that influence this THz generation mechanism. These include the pump pulse energy and pulse duration [75], its wavelength [24], the pump beam diameter and the focusing conditions [76, 77]. In principle, the gas species and pressure of the environment in which the plasma is induced also influence THz generation [75], but with the current experimental setup their control is not possible. Only pure nitrogen at ambient pressure can currently be used.

After full characterization of the THz radiation source is done, it would be worth to experiment with different configurations for two-colour plasma THz generation. The multiple coherent light sources available in the UDG laboratory, which include the Ti:Sapphire 800nm light and the TOPAS Twins OPA
with HE1 and HE2, that offer a wide range of wavelengths from 1.1µm to 2.6µm, would allow for some different arrangements of the THz generating part of the spectrometer. One approach would be to use a combination of an 1.6µm output from the OPA and the 800nm leftover from the HE amplifier stage. This would presumably lead to THz generation without the need of a β–BBO crystal. However, the phase stability of this configuration would be an issue of concern.

To further improve the spectral sensitivity of the ABCD detection scheme, the available in the UDG laboratory non-collinear OPA TOPAS-White could be used [78]. This OPA device generates extremely short pulses of < 20fs, and could be used to deliver the probe pulses for the detection scheme. These short pulses would allow sampling of frequencies above 15 THz.

Different alkane gases could be used as the detection medium for the ABCD scheme. It would be worth trying out liquefied petroleum gas [79], which is a low-cost gas commonly used for cooking stoves, and is usually a mixture of propane and butane. This could be a cost-effective solution to improve the field-induced second-harmonic generation output. Another option would be to use alkane gases whose molecule size is really large. According to literature [65] using hydrocarbons such as C₆H₁₄ and C₅H₈ can lead to enhancement of the field-induced second-harmonic intensity by two orders of magnitude. However, as these are usually in liquid phase at ambient pressure, what could be done is to use a mixture of them with non-reactive gases.

One of the major limitations of the constructed spectrometer is the detector (PMT) saturation when the THz-field induced second-harmonic generation becomes too intense. A solution for the light detection would be to use an avalanche photodiode detector [80]. The detection bandwidth and dynamic range achievable with this kind of detectors is much higher than that of a PMT, and it would in principle allow the detection of multiple, different signals which vary a lot in intensity.

Closing, the spectrometer could soon be used in a pump-probe experimental scheme. In principle, the pump beam could be provided by the Ti:Sapphire 800nm output or one of the other available beams from the OPA, and it could induce dynamic changes to the far-infrared spectrum of a sample. The THz spectrometer then could be used to probe these dynamics.
Bibliography


Appendices
Appendix A

Technical Drawings

A.1 Walls Part
TOTAL PERIMETER OF GROVE IS 840mm

M6 size threading holes, 18mm deep

8x of these, 4 up and 4 down
A.2 Base Plate

SCALE 1:2

ABOVE VIEW

SECTION A-A
SCALE 1 : 2

Same as lid:
Counterbore for M6
Socket Head Cap

SECTION B-B
SCALE 1 : 2

M6 size Threading
holes, 10mm deep
BOTTOM VIEW
SCALE 1 : 2

SECTION C-C
SCALE 1 : 2
M6 size thread
holes, 10 mm deep

SECTION D-D
SCALE 1 : 2

118°
A.3 Lid Part

Counterbore holes for M6 Socket Head Cap Screw ANSI B18.3.1 M
A.4 Electrode Holder - Right
A.5 Electrode Holder - Left
A.6 Electrode Holder - Clamps
A.7 Electrode Base Extension

[Diagram of electrode base extension with dimensions and annotations]

A-A

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