Doctoral Thesis

Generation and detection of terahertz pulses in the organic crystals OH1 and COANP

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Publication Date:
2009

Permanent Link:
https://doi.org/10.3929/ethz-a-006002084

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Generation and detection of terahertz pulses in the organic crystals OH1 and COANP

A dissertation submitted to
ETH ZURICH

for the degree of
DOCTOR OF SCIENCES

presented by

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2009
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Abstract

The terahertz radiation is situated in the electromagnetic spectrum between the microwave and the infrared radiation and covers approximately the frequency range of 0.1 to 10 THz. In the past, technology in this spectral range was underdeveloped compared to that of the neighboring bands. However, many novel sources and detectors of pulsed and continuous terahertz waves have been invented and steadily improved during the last 30 years, and their potential for scientific and commercial applications was demonstrated.

This thesis is focused on terahertz time-domain spectroscopy—a technique that utilizes few-cycle terahertz pulses to measure the optical properties of a sample at terahertz frequencies. The terahertz pulses were generated and detected in electro-optic crystals using sub-picosecond laser pulses. In the search for more efficient terahertz emitters and detectors, we have investigated several organic electro-optic crystals (see Chapters 2–4). Broadband terahertz pulses could be generated in all of the investigated crystals through optical rectification of 150 fs laser pulses at the wavelength of 1300 nm. More detailed investigations of the crystals 2-[3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene]-malononitrile (OH1) and 2-cyclooctylamino-5-nitropyridine (COANP) are presented in the Chapters 2 and 3, respectively. A comprehensive investigation of an electro-optic terahertz emitter crystal includes phase-matching calculations and an estimation of efficiency in terms of a figure of merit. For these calculations, not only the refractive index and absorption coefficient at terahertz frequencies, but also the refractive index, optical group index, absorption coefficient and nonlinear optical susceptibility at near-infrared wavelengths are required. In Chapter 5, a simple and accurate method to measure the dispersion of the optical group index and the refractive index over a broad wavelength range (0.6–1.6 µm) is described. In Chapter 6, the linear and nonlinear optical properties of the organic terahertz emitter crystal 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium 2,4,6-trimethylbenzene-sulfonate (DSTMS) in the near-infrared and visible wavelength range (0.6–1.6 µm) are presented. This information was needed to find the optimum phase-matching conditions for terahertz generation in DSTMS.

OH1 crystals show a higher figure of merit for terahertz generation and detection in the optimized range than the benchmark inorganic semiconductor crystal ZnTe and the organic ionic crystal 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium tosylate (DAST).
The material shows a similarly low terahertz absorption as ZnTe at frequencies near 1 THz. A peak terahertz electric field of 100 kV/cm and a photon conversion efficiency of 11 percent have been achieved at a pump pulse energy of 45 µJ.

Broadband terahertz pulses have been generated in COANP single crystals by optical rectification of 150 fs laser pulses from an amplified Ti:sapphire laser operating at 776 nm. Due to better phase-matching and a higher figure of merit, COANP allows more efficient terahertz generation than the benchmark electro-optic crystal ZnTe at this laser wavelength.

The method for refractive index measurements we developed is especially suited for the characterization of novel organic electro-optic crystals. In contrast to the common minimum-deviation method where wedged samples are required, our method is applicable to plane samples. This allows us to determine the principal axes and the refractive indices of a single birefringent crystal. Note that at an early stage of the development process of a novel crystal, usually only a few small plane samples are available. For the measurement, the sample is placed in one of the arms of a pump-probe type setup. We utilize widely tunable 150 fs pulses from an optical parametric generator and amplifier. The correlation of these pulses is measured with and without the sample in the beam path. The optical group index is then obtained by measuring the time-retardation of the laser pulses within the sample relative to air. In a second step, the refractive index is calculated from a Sellmeier fit to the measured group index dispersion.

Terahertz time-domain spectroscopy experiments are most often performed in transmission setups, because transmission spectrometers are easier to implement and give more accurate results than reflection spectrometers. However, strongly absorbing samples can only be measured in reflection. The use of normal incidence of the terahertz beam onto the sample is favorable for terahertz time-domain spectroscopy in reflection, because it facilitates the data analysis. In Chapter 7, we present a normal incidence spectrometer in a transceiver configuration in which the terahertz pulses are generated and detected in a single electro-optic crystal. In contrast to transceivers based on zinc blende type electro-optic crystals earlier reported in literature, our system has the same dynamic range and bandwidth as a setup using two separate electro-optic crystals for terahertz generation and detection. Additionally, our spectrometer allows double pass transmission measurements without any modification of the experimental setup between the reflection and the transmission experiments. Two different modes for transmission measurements are demonstrated for precise measurements of transparent high or low refractive index materials, respectively. We could accurately measure the phonon-polariton dispersions of the ionic crystals cesium iodide and potassium bromide, since the resonance frequencies of their optical phonons lie in the accessible frequency range of our spectrometer.
Zusammenfassung

Die Terahertzstrahlung befindet sich im elektromagnetischen Spektrum zwischen der Mikrowellen- und der Infrarotstrahlung und umfasst ungefähr den Frequenzbereich von 0.1 bis 10 THz. In der Vergangenheit war die Technologie in diesem Spektralbereich unterentwickelt verglichen mit derjenigen der benachbarten Bänder. In den letzten 30 Jahren wurden jedoch viele neuartige Quellen und Detektoren für gepulste und kontinuierliche Terahertzwellen erfunden und laufend verbessert, und deren Potential für wissenschaftliche und kommerzielle Anwendungen wurde demonstriert.


OH1 Kristalle weisen einen grösseren Gütefaktor für Terahertzzeugung und -detektion
Zusammenfassung

auf als der anorganische Halbleiterkristall ZnTe und der organische Salzkristall 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium tosylate (DAST), welche man als Richtgrössen betrachten kann. Die Terahertzabsorption in OH1 bei Frequenzen um 1 THz ist vergleichbar klein wie in ZnTe. Spitzenwerte des elektrischen Feldes der Terahertzpulse von 100 kV/cm und eine Photonen-Konversionseffizienz von 11 Prozent wurden erreicht bei einer Pumppulseenergie von 45 µJ.


transparenten Materialien mit großem bzw. kleinem Brechungsindex. Wir konnten die Phonon-Polariton-Dispersionen der Salzkristalle Cäsiumiodid und Kaliumbromid genau messen, da die Resonanzfrequenzen ihrer optischen Phononen im erreichbaren Frequenzbereich unseres Spektrometers liegen.
Chapter 1

Introduction

1.1 The terahertz range of the electromagnetic spectrum

The terahertz range of the electromagnetic spectrum is situated between high frequency electronics (microwaves) and long wavelength photonics (infrared light). In terms of frequency $\nu$, it is roughly defined to be between 0.1 and 10 THz (see Fig. 1.1). Alternatively, an electromagnetic wave can be described by its vacuum wavelength $\lambda = c/\nu$, wavenumber $\tilde{\nu} = 1/\lambda$, or photon energy $E_{\text{photon}} = h\nu$, where $c$ is the speed of light in vacuum and $h$ is the Planck’s constant. Table 1.1 shows the conversion of the frequency of 1 THz into these parameters.

![Terahertz Spectrum Diagram](image)

**Fig. 1.1.** The terahertz range of the electromagnetic spectrum.

1.1.1 Interaction of terahertz radiation with matter

A part of the resonance frequencies of vibrational and rotational excitations of many polar molecules lie the terahertz range [1]. For example, water vapor has many absorption lines at terahertz frequencies [1,2]. Therefore, terahertz spectroscopy measurements are often
performed in a dry air or nitrogen atmosphere or in vacuum. In crystals, the resonance frequencies of transverse optical phonons are typically in the terahertz range. Some of the phonon frequencies of the organic electro-optic crystals studied in this thesis were in the accessible range of our spectrometer (see Chapters 2–4). A strong coupling of the terahertz electromagnetic wave with a transverse optical phonon is observed in alkali halide crystals, e.g., in sodium chloride. The photon and the polar phonon form a mixed quasiparticle commonly called phonon-polariton. This results in a strong dispersion and a reflectivity close to unity for frequencies between the transversal and the longitudinal optical phonon frequency [3]. In this thesis, we have studied the phonon-polariton dispersion of cesium iodide, potassium bromide, and sodium chloride using terahertz time-domain spectroscopy in reflection (see Chapter 7). The parameters of the Lorentz oscillator functions describing the phonon-polariton dispersion of the ionic crystals have been determined for CsI and KBr.

Many amorphous solid state materials, e.g., many glasses and plastics are well transparent in a large fraction of the terahertz spectral range [4–6]. Some of them are opaque for visible and infrared light, e.g., ultra-high molecular weight polyethylene (UHMWPE) or polytetrafluoroethylene (PTFE, Teflon; see Chapter 7). This prevents the optical inspection of defects in these materials. Today, ultrasound or x-rays are often used for non-destructive testing. Due to its better resolution compared to ultrasound and its non-ionizing nature, terahertz imaging could become an excellent alternative method for non-destructive testing of defects in plastics.

Materials with a large density of free electric carriers have a high terahertz absorption, e.g., metals or doped semiconductors [7]. Terahertz time-domain spectroscopy can be used to study the carrier dynamics in semiconductors at sub-picosecond time-resolution in an optical pump-terahertz probe experiment [8].

### 1.2 Terahertz time-domain spectroscopy

Except for the work presented in the Chapters 5 and 6, this thesis is exclusively focused on terahertz time-domain spectroscopy using electro-optic crystals [9]. In this technique, broadband terahertz pulses are generated through optical rectification of sub-picosecond laser pulses in an electro-optic crystal. These pulses are either transmitted through a

<table>
<thead>
<tr>
<th>Frequency $\nu$</th>
<th>Wavelength $\lambda$</th>
<th>Wavenumber $\tilde{\nu}$</th>
<th>Photon energy $E_{\text{photon}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 THz</td>
<td>300 $\mu$m</td>
<td>33.3 cm$^{-1}$</td>
<td>4.14 meV</td>
</tr>
</tbody>
</table>
sample or reflected from a sample. The electric field of the terahertz pulses is measured as a function of time by electro-optic sampling. Thus, the real and imaginary parts of the refractive index of the sample can be measured without the use of Kramers-Kronig relations. The coherent detection method also allows the investigation of hot samples, e.g., flames [10]. In contrast, terahertz spectroscopy of hot samples is not possible with incoherent detectors, e.g., liquid helium cooled bolometers because they measure also the incoherent radiation emitted by the hot sample.

1.2.1 Optical rectification

An intense laser beam can induce a DC polarization in a nonlinear optical medium [11]. This effect is known as optical rectification. However, if an ultra-short pulsed laser is used, not only the frequency zero is induced, but all the difference frequencies within the spectral content of the laser pulse. For a sub-picosecond laser pulse, frequencies from zero up to several terahertz are generated and a single- or few-cycle terahertz pulse is emitted. The spectrum of the terahertz pulse can be calculated from the laser parameters and the linear and nonlinear optical properties of the emitter material. In a first approach, one may use the plane wave and non-depleted pump approximation and exclude the nonlinear absorption of the pump beam and higher order and cascaded nonlinear optical processes in the derivation (see Ref. [12]). Using these approximations, the nonlinear polarization of optical rectification \( P_{\text{OR}}(\omega, z) \) at the terahertz angular frequency \( \omega = 2\pi\nu \) in the depth \( z \) of the crystal is given by [12]:

\[
P_{\text{OR}}(\omega, z) = \frac{\chi^{(2)}(\omega, \lambda)}{n_o(\lambda) c} I_0(\omega) \exp\left(-i\frac{\omega n_g(\lambda) z}{c}\right) \exp(-\alpha_o(\lambda) z),
\]

where \( n_o(\lambda), n_g(\lambda), \) and \( \alpha_o(\lambda) \) are the refractive index, optical group index, and absorption coefficient at the central wavelength of the laser \( \lambda, \chi^{(2)}(\omega, \lambda) \) is the exploited tensor element of the nonlinear optical susceptibility for optical rectification, \( c \) is the speed of light in vacuum, and \( I_0(\omega) \) is the Fourier transform of the laser intensity at the entrance of the crystal, i.e., at \( z = 0 \). The nonlinear wave equation for the terahertz electric field \( E_{\text{THz}} \) can be written as [12]:

\[
\frac{\partial^2}{\partial z^2} + \frac{\omega^2 n_T(\omega)^2}{c^2} - i \frac{\omega \alpha_T(\omega) n_T(\omega)}{c} \right] E_{\text{THz}}(\omega, z) = -\omega^2 \mu_0 P_{\text{OR}}(\omega, z),
\]

where \( \mu_0 \) is the permeability of vacuum and \( n_T(\omega) \) and \( \alpha_T(\omega) \) are the terahertz refractive index and absorption coefficient, respectively. This equation is solved for the boundary condition \( E_{\text{THz}}(\omega, z = 0) = 0 \) and a low terahertz absorption, i.e., \( \alpha_T(\omega) \ll \omega n_T(\omega)/c \). For the crystal length \( l \), the spectral amplitude \( |E_{\text{THz}}(\omega)| \) is given by [12]:

\[
|E_{\text{THz}}(\omega)| = \left| \frac{\mu_0 \chi^{(2)}(\omega, \lambda) \omega I(\omega)}{n_o(\lambda) \left[ \frac{\omega}{c} \left( \frac{\alpha_T(\omega)}{c} + \alpha_o(\lambda) \right) + i (n_T(\omega) + n_g(\lambda)) \right]} \right| l_{\text{gen}}(\omega, \lambda, l).
\]
The dependence of $|E_{\text{THz}}(\omega)|$ on the crystal length $l$ is given by the effective generation length $l_{\text{gen}}$ [12]:

$$l_{\text{gen}}(\omega, \lambda, l) = \left( \frac{\exp (-2\alpha_o(\lambda)l) + \exp (-\alpha_T(\omega)l) - 2 \exp \left( - \frac{\alpha_o(\lambda) + \alpha_T(\omega)}{2} \right) \frac{l \cos \left( \frac{\pi l}{l_c(\omega, \lambda)} \right)}{\left( \frac{\alpha_T(\omega)}{2} - \alpha_o(\lambda) \right)^2 + \left( \frac{\pi}{l_c(\omega, \lambda)} \right)^2} \right)^{1/2}, \quad (1.4)$$

where the coherence length $l_c$ of terahertz generation by optical rectification can be written as [9]:

$$l_c(\omega, \lambda) = \frac{\pi c}{\omega |n_T(\omega) - n_g(\lambda)|}. \quad (1.5)$$

The effective generation length $l_{\text{gen}}$ is equal to the crystal length $l$ in the case of ideal phase-matching ($n_T(\omega) = n_g(\lambda)$) and zero absorption ($\alpha_o = \alpha_T = 0$). However, phase-mismatch and absorption decrease $l_{\text{gen}}$ as illustrated in Fig. 1.2. In most practical cases, the linear absorption of the optical pump beam is low ($\alpha_o l \ll 1$). If the terahertz absorption can also be neglected, Eq. (1.4) simplifies to the following expression:

$$l_{\text{gen}}(\omega, \lambda, l) = \left| \text{sinc} \left( \frac{\pi l}{2l_c(\omega, \lambda)} \right) \right|. \quad (1.6)$$

If phase-matching is ideally fulfilled, we find:

$$l_{\text{gen}}(\omega, \lambda, l) = \frac{2}{\alpha_T(\omega)} \left[ 1 - \exp \left( - \frac{\alpha_T(\omega)l}{2} \right) \right]. \quad (1.7)$$

![Fig. 1.2. The effect of phase-mismatch and terahertz absorption on the effective generation length $l_{\text{gen}}$ (see text for details).](image)

### 1.2.2 Electro-optic sampling

The linear electro-optic effect can be exploited for terahertz detection as follows: The electric field of the terahertz wave $E_{\text{THz}}$ changes the refractive index $n_o$ of the electro-optic...
material by

\[ \Delta n_o = -\frac{n_0^3}{2} r \, E_{THz}, \]  

(1.8)

where \( r \) is the exploited element of the electro-optic tensor. This change in the refractive index \( \Delta n_o \) can be probed with a sub-picosecond laser pulse which co-propagates with terahertz pulse through the electro-optic detector. The probe pulse experiences the phase-modulation \( \Delta \phi \) [12]:

\[ \Delta \phi(\omega) = \frac{\pi}{\lambda} n_0^3(\lambda) r(\omega, \lambda) A(\omega) l_{det}(\omega, \lambda, l) E_{THz}(\omega), \]  

(1.9)

where \( A(\omega) \) is the normalized Fourier spectrum of the probe pulse amplitude and \( l_{det} \) is the effective detection length given by [12]:

\[ l_{det}(\omega, \lambda, l) = \left( \frac{1 + \exp(-\alpha_T(\omega)l) - 2 \exp\left(-\frac{\alpha_T(\omega)l}{2}\right) \cos\left(\frac{\pi l}{l_{c}(\omega, \lambda)}\right) }{\left(\frac{\alpha_T(\omega)}{2}\right)^2 + \left(\frac{\pi}{l_{c}(\omega, \lambda)}\right)^2} \right)^{1/2}. \]  

(1.10)

The effective lengths \( l_{gen} \) and \( l_{det} \) are equal in the limit of zero absorption of the optical pump beam (\( \alpha_o = 0 \)).

In zinc blende type electro-optic crystals, the phase shift \( \Delta \phi \) leads to a change in the polarization state of the probe pulse [9]. The spatial distribution of \( \Delta \phi \) due to the terahertz beam profile leads to a focusing or defocusing of the probe pulse. This effect can be exploited for terahertz detection using birefringent electro-optic crystals [13]. By changing the time-delay between the terahertz pulse and the probe pulse, one can measure the terahertz electric field as a function of time. This method is known as electro-optic sampling.

1.2.3 Extraction of material parameters in terahertz time-domain spectroscopy

Transmission spectroscopy

In terahertz time-domain spectroscopy in transmission, broadband terahertz pulses are generated and transmitted through a sample. The electric field of the transmitted pulse \( E_{sample}(t) \) is measured as a function of time. To gain quantitative information about the linear optical properties of the sample, it is additionally required to measure a reference waveform \( E_{ref}(t) \) without the sample in the beam path. The refractive index \( n(\omega) \) and the absorption coefficient \( \alpha(\omega) \) can be extracted from the ratio of the Fourier transforms of the terahertz transients \( E_{sample}(\omega)/E_{ref}(\omega) \). For the analysis, it is convenient to define the ratio of the spectral amplitudes \( r(\omega) = |E_{sample}(\omega)|/|E_{ref}(\omega)| \) and the phase difference
\( \phi(\omega) = \phi_{\text{sample}}(\omega) - \phi_{\text{ref.}}(\omega) \):

\[
E_{\text{sample}}(\omega) = |E_{\text{sample}}(\omega)| \exp[i \phi_{\text{sample}}(\omega)],
\]

\[
E_{\text{ref.}}(\omega) = |E_{\text{ref.}}(\omega)| \exp[i \phi_{\text{ref.}}(\omega)],
\]

\[
\frac{E_{\text{sample}}(\omega)}{E_{\text{ref.}}(\omega)} = r(\omega) \exp[i \phi(\omega)].
\]

All the samples investigated in this thesis were plane parallel and optically thick, such that multiple reflections of the terahertz pulse in the sample were well separated in time. For the measurements, we could use a time-window that contains only the main pulse, but none of the multiple reflections. The frequency resolution \( \Delta \nu \) of the Fourier spectra is given by

\[
\Delta \nu = \frac{1}{T},
\]

where \( T \) is the duration of the time-window. In order to avoid aliasing effects, the signal is sampled with a frequency higher than twice the highest frequency contained in the signal. The experiments are usually carried out in a dry air atmosphere whose complex refractive index is \( \tilde{n}_{\text{air}}(\omega) = n_{\text{air}}(\omega) + i \kappa_{\text{air}}(\omega) \approx 1 \). Taking into account the Fresnel transmission coefficients at the surfaces of the sample and the propagation and the attenuation of the pulse within the sample, the complex ratio of the spectra can be written as:

\[
\frac{E_{\text{sample}}(\omega)}{E_{\text{ref.}}(\omega)} = \frac{4 \tilde{n}(\omega)}{(1 + \tilde{n}(\omega))^2} \exp \left[ i \omega l (\tilde{n}(\omega) - 1) \right].
\]

The power absorption coefficient \( \alpha(\omega) \) is related to the imaginary part of the complex refractive index \( \kappa(\omega) \) as follows:

\[
\alpha(\omega) = \frac{2\omega}{c} \kappa(\omega).
\]

In general, Eq. (1.13) has to be solved numerically [14]. However, in most practical cases where \( \kappa \) is relatively low, i.e., \( \kappa \ll n \), the imaginary parts of the Fresnel transmission coefficients can be neglected and thus Eq. (1.13) can be solved analytically:

\[
n(\omega) = 1 + \frac{c \phi(\omega)}{\omega l},
\]

\[
\alpha(\omega) = -\frac{2}{l} \ln \left( \frac{(n(\omega) + 1)^2}{4n(\omega)} r(\omega) \right).
\]

This procedure of the extraction of the material parameters cannot be used for an optically thin sample in which the main pulse and the multiple reflections are superimposed. The multiple reflections are also recorded and cause Fabry-Pérot resonances in the Fourier transform of the terahertz signal \( E_{\text{sample}}(\omega) \). In addition, the relative error of the measured thickness of a thin sample is typically large, which leads to a large error in \( n \) and \( \alpha \) (see Eqs. (A.8) and (A.9) in Appendix A). Algorithms for the determination of the optical constants and the thickness of a thin sample are described in the Refs. [15,16].
Reflection spectroscopy

The refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$ of a strongly absorbing material cannot be measured in a transmission experiment if the amplitude of the transmitted terahertz signal is not much larger than the detection limit. However, a reflection geometry can be used to overcome this limitation. A reference measurement is also required in reflection spectroscopy for quantitative results. It is obtained by measuring the terahertz wave reflected from a gold coated mirror which is placed exactly at position of the sample. For normal incidence, the complex reflectivity of the sample is given by:

$$\tilde{r}_{\text{sample}}(\omega) = \frac{1 - \tilde{n}(\omega)}{1 + \tilde{n}(\omega)}. \quad (1.17)$$

Taking into account that gold is a nearly perfect reflector at terahertz frequencies [17], i.e., $\tilde{r}_{\text{ref.}} \approx -1$, the ratio of the sample and the reference spectra is given by

$$\frac{E_{\text{sample}}(\omega)}{E_{\text{ref.}}(\omega)} = \frac{\tilde{n}(\omega) - 1}{\tilde{n}(\omega) + 1}. \quad (1.18)$$

The solution of Eq. (1.18) is:

$$n(\omega) = \frac{1 - r(\omega)^2}{1 + r(\omega)^2 - 2r(\omega)\cos\phi(\omega)}, \quad (1.19)$$

$$\alpha(\omega) = \frac{2\omega}{c} \frac{2r(\omega)\sin\phi(\omega)}{1 + r(\omega)^2 - 2r(\omega)\cos\phi(\omega)}. \quad (1.20)$$
Chapter 2

A hydrogen-bonded organic nonlinear optical crystal for high-efficiency terahertz generation and detection†

Abstract: Broadband terahertz pulses have been generated in 2-[3-(4-hydroxy styryl)-5,5-dimethylcyclohex-2-enylidene]malononitrile (OH1) by optical rectification of subpicosecond laser pulses. We show that OH1 crystals allow velocity-matched generation and detection of terahertz frequencies in the whole range between 0.3 and 2.5 THz for a pump laser wavelength range from 1200 to 1460 nm. OH1 crystals show a higher figure of merit for terahertz generation and detection in the optimized range compared to the benchmark inorganic semiconductor crystals ZnTe and GaAs and the organic ionic salt crystal 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium tosylate (DAST). The material shows a low terahertz absorption coefficient $\alpha_3$ in the range between 0.3 and 2.5 THz, reaching values lower than 0.2 mm$^{-1}$ between 0.7 and 1.0 THz. This is similar as in ZnTe and GaAs, but much lower than in DAST in the respective optimum frequency range. A peak terahertz electric field of 100 kV/cm and a photon conversion efficiency of 11 percent have been achieved at a pump pulse energy of 45 $\mu$J.

2.1 Introduction

In the recent years, the improvement of existing and the advent of novel sources and detectors of terahertz radiation was driven by an increasing number of potential applications in many fields of science and technology [18]. One field of research is the development

of novel nonlinear optical materials specially designed for efficient terahertz generation (through difference frequency generation or optical rectification) and detection (through electro-optic sampling). The requirements for these materials are a high optical nonlinearity and a low dielectric constant, which results in small Fresnel losses at the boundaries and, more important, allows velocity-matching [19]. Particularly among organic crystals, one can find materials that exhibit both of these desired properties. The organic salt crystal 4-\(N,N\)-dimethylamino-4’-\(N\)′-methyl-stilbazolium tosylate (DAST) was proven to be an excellent terahertz emitter and detector [12,20]. However, a transverse optical phonon leads to a gap in the accessible terahertz spectrum around 1.1 THz [21]. In a recent work, the frequency and the oscillator strength of this resonance could be reduced by the use of a different anion [22]. Nevertheless, the terahertz absorption remains relatively strong near the resonance frequency. Instead of modifying the molecules of a salt crystal, one can circumvent the problem of the ionic resonance by using a different class of organic materials, namely hydrogen bonded organic crystals [23].

Recently, a very promising member of this class of materials, the configurationally locked polyene crystal 2-[3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene]malononitrile (OH1) has been developed and its linear and nonlinear optical properties have been determined [24,25]. In this article, the linear optical properties of OH1 at terahertz frequencies are presented, and a detailed theoretical and experimental investigation of OH1 as a terahertz source and detector is given, including the analysis of velocity-matching conditions.

### 2.2 Basic properties of OH1

#### 2.2.1 Crystal structure

The OH1 molecule (see Fig. 2.1) shows a large dipole moment of \(\mu = 3.44 \times 10^{-29} \text{ Cm}\) and contains an extended \(\pi\)-conjugated electron system, which leads to a large hyperpolarizability of \(\beta_z = 765 \times 10^{-40} \text{ m}^4 \text{V}^{-1}\), as measured in chloroform solution [24]. The charge transfer within the OH1 chromophore is induced by a phenolic (Ar–OH) electron donor and a dicyanomethylene (C=C(CN)\(_2\)) electron acceptor [24]. In the crystalline phase, the material has the point group symmetry \(mm2\) with an acentric packing of four molecules per unit cell with hydrogen bonds between the phenolic and the cyano group (i.e., Ar–OH...N=C) [24]. The angle between the charge transfer axis of the chromophores and the polar \(c\)-axis of the crystal is 28°, which results in a large macroscopic second-order nonlinear optical susceptibility of \(\chi^{(2)}_{333} = 240\pm20 \text{ pm/V}\) for second-harmonic generation at a fundamental wavelength of 1.9 \(\mu\)m [25]. OH1 single crystals grow as \(a\)-plates, i.e., with the largest surfaces perpendicular to the \(a\)-axis [24].
2.2.2 Near infrared linear and nonlinear optical properties

Due to the orthorhombic symmetry of the crystal, the dielectric coordinate system \((x_1, x_2, x_3)\) coincides with the crystallographic coordinate system \((a, b, c)\). OH1 crystals are highly birefringent due to a highly anisotropic linear polarizability of the chromophores and their acentric packing \((n_3 - n_2 > 0.5\) in the wavelength range between 0.6 and 2.2 µm) [25]. The absorption coefficient for the \(b\)- and \(c\)-polarizations is below 0.3 mm\(^{-1}\) in the wavelength range between 680 and 1460 nm [25]. The largest linear electro-optic coefficient \(r_{333} = 52 \pm 7\) pm/V [25] at a wavelength of 1300 nm and a modulation frequency of 1 kHz is similar to the largest electro-optic coefficient \(r_{111} = 53 \pm 6\) pm/V of DAST [26].

2.3 Terahertz spectroscopic measurements

2.3.1 Experiments

The linear optical properties of OH1 single crystals have been determined at terahertz frequencies using terahertz time-domain spectroscopy (TTDS). The samples were OH1 \(a\)-plates with thicknesses of 0.956 and 0.365 mm, respectively. The \(a\)-plates allowed the determination of the refractive index \(n\) and the absorption coefficient \(\alpha\) along the dielectric axes \(x_2\) and \(x_3\), where \(n_3\) and \(\alpha_3\) are of main interest for terahertz applications (see Section 2.4).

The source of the laser pulses for the generation and detection of the terahertz pulses was the tunable output of an optical parametric generator/amplifier (OPG/OPA) (Quantronix, TOPAS) pumped by a Ti:sapphire laser (Clark-MXR, CPA 2001). The pulses of the signal wave of the OPG/OPA at the wavelengths used in these experiments had typically an energy of 40 µJ and a duration of 150 fs full width at half maximum. The terahertz pulses have been generated by optical rectification of the subpicosecond near-infrared pulses in a nonlinear optical crystal and detected by electro-optic sampling in a second nonlinear crystal [9]. In order to obtain the refractive indices and the absorption coefficients of OH1 over the broadest possible frequency range, we used two configurations of TTDS based on different nonlinear optical materials. The first covered the ranges 0.3–0.8 THz and
1.4–4 THz with a laser wavelength of $\lambda = 1400$ nm using single crystals of DAST for both generation and detection [12, 13]. Anticipating the results presented in Subsection 2.5.1, an OH1 crystal served as terahertz source in the second configuration with $\lambda = 1460$ nm; for the detection, we used ZnTe with a frequency-doubled probe pulse [20]. The spectrum in these measurements spanned continuously from 0.3 to 2.2 THz.

### 2.3.2 Results

The results are presented in Figs. 2.2 and 2.3. We use a classical Lorentz multiple oscillator model to describe the dispersion of the complex dielectric function $\epsilon(\omega) = \epsilon'(\omega) + i \epsilon''(\omega)$ whose real and imaginary parts are given by [27]

\[
\epsilon'(\omega) = \epsilon_\infty + \sum_{j=1}^{m} \frac{\omega_j^2 f_j (\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2}, \tag{2.1a}
\]

\[
\epsilon''(\omega) = \sum_{j=1}^{m} \frac{\omega_j^2 f_j \gamma_j \omega}{(\omega_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2}, \tag{2.1b}
\]

where $\omega_j$ is the resonant angular frequency, $\gamma_j$ is the damping parameter, and $f_j$ is the oscillator strength of the $j$th oscillator. $\epsilon_\infty$ is the high frequency dielectric constant. The refractive index $n(\omega)$ and the intensity absorption coefficient $\alpha(\omega)$ can be obtained from $\epsilon'$
2.3 Terahertz spectroscopic measurements

Fig. 2.3. (a) Absorption coefficient $\alpha_2$ and (b) refractive index $n_2$ of terahertz waves polarized along the $b$-axis. Dots: measured data. Solid lines: best fit to the measured data using a Lorentz three-oscillator model [27] (see Eqs. (2.1)–(2.3) and Table 2.2).

and $\epsilon''$ by

$$n(\omega) = \sqrt{\frac{1}{2} \left[ \sqrt{\epsilon'(\omega)^2 + \epsilon''(\omega)^2} + \epsilon'(\omega) \right]}, \quad (2.2)$$

$$\alpha(\omega) = \frac{2\omega}{c} \sqrt{\frac{1}{2} \left[ \sqrt{\epsilon'(\omega)^2 + \epsilon''(\omega)^2} - \epsilon'(\omega) \right]}, \quad (2.3)$$

where $c$ is the speed of light in vacuum.

The functions with the oscillator parameters shown in the Tables 2.1 and 2.2 are plotted in the Figs. 2.2 and 2.3, respectively. They are in good agreement with the measured data. All the deviations of the theoretical curves from the data points are within the experimental errors. The features in the measured terahertz spectrum of the $c$-polarization can be described by four Lorentzian oscillators, whose parameters are listed in Table 2.1. The absorption within the terahertz frequency range between 0.7 and 1.0 THz is very low (i.e., $\alpha_3 < 0.2 \text{mm}^{-1}$) and remains lower than $4 \text{mm}^{-1}$ in the whole range between 0.3 and 2.2 THz. Due to the fourth resonance, which is the strongest in the investigated spectral range, the transmission of the terahertz wave was below the detection sensitivity for frequencies above 2.5 THz.

The parameters of the Lorentz-model function for $b$-polarized waves as shown in Fig. 2.3 are listed in Table 2.2. Here, we observed three main resonances. In the gaps at 1.7–1.9 THz and 2.5–3.1 THz, where no data points are given in Fig. 2.3, the absorption coefficient $\alpha_2$ is above the detection limit.
Table 2.1. Parameters for the refractive index $n_3$ and the absorption coefficient $\alpha_3$ of OH1 in the Lorentz-model.$^{a,b}$

<table>
<thead>
<tr>
<th>Oscillator $j$</th>
<th>Resonant frequency $\nu_j/(2\pi)$ (THz)</th>
<th>Oscillator strength $f_j$</th>
<th>Damping parameter $\gamma_j$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.368 ± 0.007</td>
<td>0.027 ± 0.013</td>
<td>0.18 ± 0.15</td>
</tr>
<tr>
<td>2</td>
<td>0.595 ± 0.004</td>
<td>0.020 ± 0.003</td>
<td>0.26 ± 0.06</td>
</tr>
<tr>
<td>3</td>
<td>1.467 ± 0.006</td>
<td>0.0175 ± 0.0012</td>
<td>0.97 ± 0.11</td>
</tr>
<tr>
<td>4</td>
<td>2.85 ± 0.03</td>
<td>0.23 ± 0.02</td>
<td>3.06 ± 0.23</td>
</tr>
</tbody>
</table>

$^a$ See Eqs. (2.1)–(2.3).

$^b$ An additional parameter used in the model calculation is the high frequency refractive index $n_\infty = \sqrt{\epsilon_\infty} = 2.227 ± 0.006$.

Table 2.2. Parameters for the refractive index $n_2$ and the absorption coefficient $\alpha_2$ of OH1 in the Lorentz-model.$^{a,b}$

<table>
<thead>
<tr>
<th>Oscillator $j$</th>
<th>Resonant frequency $\nu_j/(2\pi)$ (THz)</th>
<th>Oscillator strength $f_j$</th>
<th>Damping parameter $\gamma_j$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.820 ± 0.002</td>
<td>0.015 ± 0.001</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>2</td>
<td>1.772 ± 0.006</td>
<td>0.146 ± 0.005</td>
<td>1.84 ± 0.09</td>
</tr>
<tr>
<td>3</td>
<td>2.64 ± 0.02</td>
<td>0.127 ± 0.009</td>
<td>1.8 ± 0.2</td>
</tr>
</tbody>
</table>

$^a$ See Eqs. (2.1)–(2.3).

$^b$ An additional parameter used in the model calculation is the high frequency refractive index $n_\infty = \sqrt{\epsilon_\infty} = 1.640 ± 0.004$.

2.4 OH1 for the generation and detection of terahertz waves: Theory

In the following, the dependence of the terahertz generation and detection efficiency using OH1 crystals on the laser wavelength and on the crystal thickness is discussed in terms of velocity-matching of the optical and terahertz waves and their absorptions. For this discussion we use the theory presented in Ref. [12], which is briefly summarized in the following.

Terahertz pulses can be generated by optical rectification of subpicosecond laser pulses. The optical pulses give rise to a nonlinear optical polarization of the crystal at terahertz
frequencies, which acts as a source term in the nonlinear wave equation. The nonlinear optical susceptibility for optical rectification \( \chi^{(2)}(\omega, \lambda) \) is related to the linear electro-optical tensor \( r(\omega, \lambda) \) at terahertz angular frequencies \( \omega \) as follows [28]:

\[
\chi^{(2)}_{ijj}(\omega, \lambda) = -\frac{1}{2} n_o^4(\lambda) r_{jji}(\omega, \lambda),
\]

(2.4)

where \( n_o(\lambda) \) is the refractive index at the optical wavelength \( \lambda \). In the following, we will omit the tensor notation because we are interested here in noncritical type I interactions, where only one tensor element \( \chi^{(2)}_{ijj} \) of the nonlinear optical susceptibility is involved (note that \( i = j \) is possible in optical rectification). Using the plane wave and the non-depleted pump approximations, the spectral amplitude of the electric field of the generated terahertz wave after the crystal length \( l \) is given by [12]

\[
|E_{\text{THz}}(\omega)| = \left| \frac{\mu_0 \chi^{(2)}(\omega, \lambda) \omega I(\omega)}{n_o(\lambda) \left[ \frac{\sqrt{\omega}}{\omega} \left( \frac{\alpha_T(\omega)}{2} + \alpha_o(\lambda) \right) + i \left( n_T(\omega) + n_g(\lambda) \right) \right]} \right| l_{\text{gen}}(\omega, \lambda, l),
\]

(2.5)

where \( \mu_0 \) is the permeability of vacuum, \( I(\omega) \) is the Fourier transform of the intensity of the near-infrared pulses. \( n_T(\omega) \) and \( \alpha_T(\omega) \) are the refractive index and the absorption coefficient at the terahertz angular frequency \( \omega \), respectively. \( n_o(\lambda), n_g(\lambda), \) and \( \alpha_o(\lambda) \) are the refractive index, the group index and the absorption coefficient of the optical pulse with the central wavelength \( \lambda \). The dependence of \( |E_{\text{THz}}(\omega)| \) on the crystal length \( l \) is given by the effective generation length \( l_{\text{gen}} \) [12]:

\[
l_{\text{gen}}(\omega, \lambda, l) = \left( \frac{1}{\exp (2\alpha_o(\lambda) l) + \exp (-\alpha_T(\omega) l) - 2 \exp \left( -\left[ \alpha_o(\lambda) + \frac{\alpha_T(\omega)}{2} \right] l \right) \cos \left( \frac{\pi l}{l_c(\omega, \lambda)} \right) \right)^{1/2},
\]

(2.6)

where the coherence length \( l_c \) of terahertz generation by optical rectification can be written as [9]

\[
l_c(\omega, \lambda) = \frac{\pi c}{\omega |n_T(\omega) - n_g(\lambda)|}.
\]

(2.7)

As one can see immediately from (2.6) and (2.7), for an efficient generation of terahertz pulses, the refractive index of the terahertz wave has to be close to the optical group index of the optical beam (velocity-matching), and the absorption should be low for both terahertz and near-infrared pulses. In the limit of zero absorption, (2.6) simplifies to the following expression that is well-known from other second order nonlinear optical processes [28]:

\[
l_{\text{gen}}(\omega, \lambda, l) = \left| \frac{\pi l}{2l_c(\omega, \lambda)} \right| l.
\]

(2.8)
For each laser wavelength $\lambda$ and terahertz frequency $\nu = \omega/(2\pi)$, we can calculate the maximum effective generation length $l_{\text{max}}(\omega, \lambda)$ and the optimum crystal length $l_{\text{optimum}}(\omega, \lambda)$, which are defined as follows:

$$l_{\text{max}}(\omega, \lambda) := \max_l l_{\text{gen}}(\omega, \lambda, l),$$  \hspace{1cm} (2.9a)$$

$$l_{\text{max}}(\omega, \lambda) = l_{\text{gen}}(\omega, \lambda, l_{\text{optimum}}).$$ \hspace{1cm} (2.9b)$$

The detection of terahertz transients through electro-optic sampling is essentially the inverse process of optical rectification, and the dependence of the sampling signal on the length of the electro-optical crystal is the same as in (2.6). The sampling signal is proportional to the phase shift $\Delta \phi$ of the probe pulse induced by the terahertz electric field $E_{\text{THz}}(\omega)$ in the detection crystal which is given by [12]:

$$\Delta \phi(\omega) = \frac{\pi}{\lambda} n_0^3(\lambda) r(\omega, \lambda) A(\omega) l_{\text{gen}}(\omega, \lambda, l) E_{\text{THz}}(\omega),$$ \hspace{1cm} (2.10)$$

where $A(\omega)$ is the normalized Fourier spectrum of the probe pulse amplitude.

From a contour plot of $l_{\text{max}}(\omega, \lambda)$, one can predict the range of the pump laser wavelengths $\lambda$ where a high conversion efficiency for a certain range of terahertz frequencies can be achieved. Figure 2.4 shows $l_{\text{optimum}}(\omega, \lambda)$ with the corresponding $l_{\text{max}}(\omega, \lambda)$ for terahertz generation and detection exploiting the largest tensor element of the nonlinear optical susceptibility $\chi^{(2)}_{333}$ and the largest linear electro-optic coefficient $r_{333}$, respectively. The

![Contour plots](image_url)

**Fig. 2.4.** (a) Optimum OH1 crystal length $l_{\text{optimum}}(\omega, \lambda)$ for the generation of terahertz pulses [see Eq. (2.9b)]; (b) the corresponding maximum effective generation length $l_{\text{max}}(\omega, \lambda)$ [see Eq. (2.9a)]. The values of the contour lines are in units of mm.
refractive index and the absorption in the terahertz range are taken from the four-oscillator Lorentz function (see Fig. 2.2), and the optical data are taken from Ref. [25].

The highest conversion efficiency can be expected in the velocity-matching and transparency range for terahertz frequencies below 2.2 THz and optical wavelengths between 1200 and 1460 nm. The upper limit for the wavelength is given by the optical absorption. Above 2.2 THz, the main limiting factor is terahertz absorption.

Due to the very large birefringence \( n_3 - n_2 > 0.5 \) of OH1 in the terahertz as well as in the optical range [25], the second largest coefficient \( \chi^{(2)}_{322} \) cannot be used for velocity-matched generation of terahertz pulses. Likewise, \( r_{223} \) cannot be exploited in velocity-matched terahertz detection.

### 2.4.1 Overall figure of merit for generation and detection of terahertz pulses

For the comparison of the performance of two terahertz systems using different electro-optic crystals, one may define an overall figure of merit (FoM) for the generation and detection of terahertz pulses [29]:

\[
\text{FoM} = b \frac{4 n^7_o(\lambda_{vm}) r^2}{(1 + n_o(\lambda_{vm}))^2 (1 + n_g(\lambda_{vm}))^2},
\]

\[b = \begin{cases} 
1 & \text{for standard electro-optic sampling in cubic crystals (e.g., ZnTe or GaAs),} \\
1/4 & \text{for electro-optic sampling in birefringent crystals,}
\end{cases}
\]

where \( \lambda_{vm} \) is the velocity-matching wavelength. The overall efficiency of a terahertz system for the generation and detection of the electric field at the frequency \( \nu \) using the laser wavelength \( \lambda \) is proportional to \( \text{FoM} \times l_{\text{max}}^2 (2\pi \nu, \lambda) \). Equation (2.11) has been derived from (2.5) and (2.10) taking into account the Fresnel losses of the optical beam at the generation crystal and of the terahertz beam at the generation and the detection crystals [29].

In Table 2.3, the figures of merit of OH1 and of the commonly used electro-optic crystals DAST, ZnTe and GaAs are shown. Additionally, the terahertz absorption coefficient is given at the typical frequency \( \nu_{\text{peak}} \) of the peak spectral amplitude of terahertz pulses generated through optical rectification of 150 fs laser pulses at the velocity-matching wavelength. OH1 shows the highest figure of merit and a low terahertz absorption at the optimum conditions.
### Table 2.3. Overall figure of merit (FoM) for generation and detection of terahertz pulses and other relevant parameters of OH1 in comparison with commonly used electro-optic crystals.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{vm}$</th>
<th>$n_o$</th>
<th>$n_g$</th>
<th>$r$</th>
<th>$\text{FoM}^b$</th>
<th>$\nu_{\text{peak}}^c$</th>
<th>$\alpha(\nu_{\text{peak}})$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH1</td>
<td>1.3</td>
<td>2.16</td>
<td>2.33</td>
<td>52</td>
<td>5300</td>
<td>1</td>
<td>0.2</td>
<td>[25], and this work</td>
</tr>
<tr>
<td>DAST</td>
<td>1.5</td>
<td>2.13</td>
<td>2.26</td>
<td>47</td>
<td>4200</td>
<td>2</td>
<td>3.5</td>
<td>[12, 21, 26]</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.8</td>
<td>2.85</td>
<td>3.23</td>
<td>4</td>
<td>370</td>
<td>1</td>
<td>0.1</td>
<td>[30, 31]</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.4</td>
<td>3.40</td>
<td>3.61</td>
<td>1.3</td>
<td>86</td>
<td>2</td>
<td>0.3</td>
<td>[32–35]</td>
</tr>
</tbody>
</table>

$a\lambda_{vm}$ is the velocity-matching wavelength.  
$b$ see Eq. (2.11).  
$c\nu_{\text{peak}}$ is the typical frequency of the peak spectral amplitude of terahertz pulses generated through optical rectification of 150 fs laser pulses at the velocity-matching wavelength.

### 2.5 OH1 for the generation and detection of terahertz waves: Experiments

#### 2.5.1 Generation of terahertz pulses using OH1 crystals

We performed terahertz emission experiments using an unpolished 0.365 mm thick $\alpha$-plate of OH1. The pump wavelength was 1460 nm. The electric field of the generated terahertz pulse was measured by electro-optic sampling in a 0.5 mm thick (110)-cut ZnTe crystal using a probe beam with the second-harmonic wavelength (730 nm) [20]. The wavelength was chosen to ensure nearly velocity-matching in the ZnTe crystal. Although this is not the optimum wavelength for OH1, one can see from Fig. 2.4(a) that $l_{\text{optimum}}$ is larger than our crystal length below 2.5 THz. Hence, velocity-mismatch and terahertz absorption do not affect the emitted amplitude significantly. Possible distortions of the measured terahertz transient, which may arise if the peak electric field exceeds the linearity range of the detection, have been corrected using the algorithm from Ref. [36]. The measured signal is plotted in Fig. 2.5. The emission spectrum is continuous and ranges from 0.3 to 3.0 THz with a maximum at 1.3 THz.

For a comparison, the same experiment has been performed with DAST crystals as a source material under identical conditions. DAST has been chosen as a reference material for two reasons. On the one hand, it has been demonstrated to be one of the most efficient terahertz emitter materials so far; on the other hand, it is also very well velocity-matched at 1460 nm [20]. Two $\alpha$-plates of DAST (thicknesses: 0.330 and 0.400 mm, respectively) were used having an average thickness which corresponds to the thickness of the OH1
2.5 OH1 for the generation and detection of terahertz waves: Experiments

![Figure 2.5](image)

**Fig. 2.5.** Terahertz pulse emitted from OH1 exploiting $\chi^{(2)}_{333}$ and detected in ZnTe (red line). (a) Time domain and (b) frequency domain signal. Terahertz pulse emitted from DAST exploiting $\chi^{(2)}_{111}$ under identical conditions for comparison (black line; see text for details).

crystal. The terahertz signals from the two DAST crystals are averaged and plotted in Fig. 2.5.

The peak terahertz amplitude from OH1 exceeds that of DAST in both time- and frequency-domain by 58 percent and 36 percent, respectively. A second advantage, that is relevant mainly for spectroscopic applications, is that the spectrum from OH1 is continuous from 0.3 to 3 THz, in contrast to DAST, where a transverse optical phonon leads to a gap at the resonance frequency of 1.1 THz. This fact is a direct consequence of the non-ionic nature of the OH1 crystal.

2.5.2 OH1 for both generation and detection of terahertz pulses

**Pump energy dependence**

OH1 crystals were also used for the detection of the terahertz pulses. Although standard electro-optic sampling is not possible due to the large intrinsic birefringence of the crystals, we could use a modified detection method based on the spatial phase-modulation of the probe beam induced by the electric field of the terahertz wave through the linear electro-optic effect [13]. The spatial phase-modulation leads to a focusing or defocusing of the probe beam depending on the sign of the terahertz field. A fraction of the probe beam in its center after passing the detection crystal was coupled into a multimode fiber with a core diameter of 62.5 µm and its output was measured with an InGaAs photodiode. The relative modulation $m(E) = (W(E)/W(E = 0)) − 1$ is proportional to the terahertz electric field $E$ for moderate modulations (i.e., $m ≲ 0.5$). As a reference, we used the light that was not coupled into the fiber by measuring its backscattering from a white screen with a second
InGaAs photodiode. This reference was required to correct for the pulse-to-pulse energy fluctuations of the probe beam and thus to enhance the signal-to-noise ratio.

Figure 2.6 shows terahertz pulses generated and detected in two polished OH1 crystals (thicknesses 1.002 and 0.956 mm, respectively) at an optical wavelength of 1300 nm for several values of the pump pulse energy. For this, the pump pulses were attenuated using different neutral density filters. The maximum pump pulse energy of 45 \( \mu J \) leads to a maximum relative modulation \( m(E) \) of 5.0, which is 3.6 times the maximum value reported to date (1.4 in DAST [20]). The maximum observed defocusing of the probe beam reduced the measured diode signal to the noise level. At the highest two pump pulse energies of 45 and 20 \( \mu J \), the maximum defocusing could also be observed in the reference. Thus, the ratio of the signal and the reference at the maximum defocusing is smaller for the pump pulse energy of 20 \( \mu J \) than for 45 \( \mu J \) (see Fig. 2.6).

\[ E = \frac{2\lambda}{n^3_r l \pi} m(E), \quad (2.12) \]

where \( l \) is the length of the detection crystal. We assume a diffraction limited terahertz beam profile within the detection crystal; for the main frequency components near 1 THz, this corresponds to a full width at half maximum \( \rho_0 \) of the terahertz intensity of about 0.6 mm. The terahertz pulse energy can be calculated by integrating the intensity over the beam profile and the spectrum:

\[ W_{\text{THz}} = \frac{\rho_0^2 \pi \varepsilon_0 c}{8 \ln 2} \int \frac{|E(\nu)|^2}{T(\nu)} \, d\nu, \quad (2.13) \]
where the intensity transmission coefficient \( T(\nu) \) at the entrance of the detector crystal is in the limit of zero absorption given by

\[
T(\nu) = \frac{4 n_T(\nu)}{(1 + n_T(\nu))^2}.
\]

Since the relative modulation \( m(E) \) exceeds the linearity range of the detection for the higher pump pulse energies by far, we calculated \( \eta \) for terahertz pulses generated by 3 \( \mu \)J pump pulses. The peak electric field of this terahertz transient of \( E_{\text{peak}} = 8 \) kV/cm is reached at a maximum value of the relative modulation of \( m_{\text{max}} = 0.46 \), i.e., the whole waveform is in the linear regime. Using (2.13)–(2.14), we calculated an energy conversion efficiency of \( \eta = 6 \times 10^{-5} \), which corresponds to a photon conversion efficiency \( \eta_{\text{photon}} = \eta c/(\lambda \nu) \) of 1 percent, where \( \nu = \int |E(\nu)|^2 \nu \, d\nu / \int |E(\nu)|^2 \, d\nu \) is the average generated terahertz frequency. Since the generated terahertz field is proportional to the pump pulse energy, we can extrapolate the terahertz electric field measured for 3 \( \mu \)J to the pump pulse energy of 45 \( \mu \)J. This extrapolation yields a peak electric field of 120 \( \text{kV/cm} \), an energy conversion efficiency of \( \eta = 1 \times 10^{-3} \) and a photon conversion efficiency of 15 percent.

So far, the effect of two-photon absorption of the pump beam has not been taken into account. We measured a two-photon absorption coefficient \( \beta_3 = 0.3 \text{ cm/GW} \) for \( \sigma \)-polarized light with a wavelength of 1300 nm using the method described by Bechtel and Smith [37]. Two-photon absorption of the pump beam is insignificant for the terahertz pulse generated with a pump pulse energy of 3 \( \mu \)J, where the peak intensity was \( I_{\text{pump, max}} = 3 \text{ GW/cm}^2 \). However, it becomes relevant for the 45 \( \mu \)J pump pulse, where \( I_{\text{pump, max}} = 41 \text{ GW/cm}^2 \). To estimate the effect of two-photon absorption on the terahertz conversion efficiency, we averaged the pump pulse energy—which is proportional to the terahertz electric field—over the crystal length, and obtained a reduction of \( \eta \) by a factor of 0.74, resulting in a photon conversion efficiency of 11 percent for the 45 \( \mu \)J pump pulse.

**Pump wavelength dependence**

We investigated the wavelength dependence of the terahertz spectra generated and detected using OH1 crystals in the velocity-matching and transparency range between 1200 and 1460 nm. The intensity of the pump beam has been attenuated to obtain a terahertz signal in the linear detection regime (\( m \leq 0.5 \)). Figure 2.7(a) shows the normalized spectra obtained with a 1.002 mm thick source crystal and a 0.956 mm thick detector crystal. For all these wavelengths, the spectral amplitudes reach their maxima near 1.3 THz. Below 1.4 THz, all spectra normalized to their maximum values are almost identical. The spectral amplitude is reduced around the resonance near 1.5 THz (oscillator 3, see Table 2.1), however it is still large enough for spectroscopic applications. This is in contrast to DAST crystals, for which the absorption at the resonance frequency of 1.1 THz is more than 10
times larger than that of OH1 at 1.5 THz. The position and the amplitude of the second local maximum in the normalized spectra depends on the pump wavelength. A calculation of the spectra according to the theory from [12] leads to the same result [see Fig. 2.7(b)]. The plane-wave approximation has been used in the calculation for both the optical and the terahertz wave. However, the diffraction of the terahertz beam due to the finite pump beam diameter decreases the spectral amplitudes at low frequencies [12]. This explains the discrepancy between the measured and the calculated spectra below about 0.8 THz.

Although all the experiments were carried out in a box purged with dry air, there was some residual humidity. The additional features in the measured spectra compared with the calculated ones stem from this residual water vapor, visible mainly at 1.1, 1.7 and 2.2 THz [1].

![Fig. 2.7. Terahertz spectra generated and detected in 1 mm thick OH1 crystals using different wavelengths, normalized to their maximum values. (a) Measurements; (b) calculation.](image)

### 2.6 Conclusions

The refractive indices $n_2$ and $n_3$ and the absorption coefficients $\alpha_2$ and $\alpha_3$ of the organic crystal OH1 have been measured in the spectral range between 0 and 4 THz using terahertz time-domain spectroscopy. Based on these results, we found that the largest element $\chi^{(2)}_{333}$ of the nonlinear optical susceptibility tensor can be exploited for high efficiency generation and detection of terahertz pulses, thanks to a low absorption $\alpha_3$ for frequencies below 2.5 THz and to velocity-matching with a large range of pump laser wavelengths (1200–1460 nm). The peak spectral amplitude from OH1 was found to be 36 percent larger than that from DAST under identical conditions. For a pump pulse energy of 45 µJ, we
achieved a conversion efficiency of pulse energies of $7 \times 10^{-4}$, corresponding to a photon conversion efficiency of 11 percent.

The results presented in this article are also valid for tunable narrowband terahertz generation through difference frequency generation of two lasers with slightly different wavelengths. Difference frequency generation of frequencies around 1 THz will be especially efficient due to the very low absorption of OH1.

2.7 Supplementary information†

2.7.1 Refractive index $n_1$ and absorption coefficient $\alpha_1$

The refractive index $n_1$ and the absorption coefficient $\alpha_1$ of a 2.564 mm thick $b$-cut OH1 crystal have been measured using TTDS. The dispersion can be described by a Lorentz three-oscillator model [see Eqs. (2.1)–(2.3)]. The parameters of the functions fitted to the data are given in Table 2.4. The measured data and the theoretical dispersion are plotted in Fig. 2.8.

![Graphs showing absorption coefficient and refractive index](image)

Fig. 2.8. (a) Absorption coefficient $\alpha_1$ and (b) refractive index $n_1$ of OH1 for terahertz waves polarized along the $a$-axis. Dots: measured data. Solid lines: best fit to the measured data using a Lorentz three-oscillator model [27] (see Eqs. (2.1)–(2.3) and Table 2.4).

2.7.2 Pump sources for noncritical phase-matching in OH1 crystals

An optical parametric generator and amplifier (OPG/OPA) pumped with an amplified Ti:sapphire laser can deliver sub-picosecond laser pulses with a wavelength in the optimum

†This section is not included in the article [38].
Table 2.4. Parameters for the refractive index $n_1$ and the absorption coefficient $\alpha_1$ of OH1 in the Lorentz-model.$^{a,b}$

<table>
<thead>
<tr>
<th>Oscillator $j$</th>
<th>Resonant frequency $\nu_j = \omega_j/(2\pi)$ (THz)</th>
<th>Damping parameter $\gamma_j$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.701 \pm 0.010$</td>
<td>$0.60 \pm 0.15$</td>
</tr>
<tr>
<td>2</td>
<td>$1.770 \pm 0.011$</td>
<td>$1.32 \pm 0.09$</td>
</tr>
<tr>
<td>3</td>
<td>$2.63 \pm 0.04$</td>
<td>$2.6 \pm 0.4$</td>
</tr>
</tbody>
</table>

$^a$See Eqs. (2.1)–(2.3).

$^b$An additional parameter used in the model calculation is the high frequency refractive index $n_\infty = \sqrt{\varepsilon_\infty} = 1.656 \pm 0.001$.

range (1200–1460 nm) for optical rectification in OH1 crystals. The maximum effective generation length in OH1 crystals is still relatively large at the wavelength of erbium-doped fiber lasers of 1560 nm, i.e., $l_{\text{max}} \approx 0.8 \text{ mm}$ for the frequency of 1 THz [see Fig. 2.4(b)]. However a moderate absorption ($\alpha \approx 0.7 \text{ mm}$ [25]) inhibits the use of a very intense pump beam at this laser wavelength.

A dual-wavelength optical parametric oscillator with two KTiOPO$_4$ (KTP) crystals pumped with a frequency-doubled Nd:YAG laser can provide two idler waves with wavelengths in the optimum range for difference frequency generation in OH1 crystals [39].

### 2.7.3 Critical phase-matching in OH1 crystals

The range of laser wavelengths for collinear type 0 phase-matched terahertz generation and detection in OH1 crystals can be extended by angle-tuning. This is mainly interesting for the use of a femtosecond laser without wavelength conversion in an OPG/OPA, e.g., a Ti:sapphire laser operating at a wavelength near 800 nm or a solid state laser based on a neodymium- or ytterbium-doped gain medium with a central wavelength in the range between 1030 and 1060 nm.

There are two possible schemes for angle-tuning in OH1 crystals: The optical pump and the terahertz beams are polarized in the $ac$- or the $bc$-plane (see Fig. 2.9). The angle-tuning curves for the two phase-matching schemes are shown in the Fig. 2.9 for the generation of 1 THz, because the absorption coefficients are low ($\alpha_j < 1 \text{ mm}^{-1}$) for frequencies near 1 THz for all polarizations $j$ (see Figs. 2.2, 2.3, and 2.8). In the first scheme, phase-matching is fulfilled for the laser wavelengths of 800 and 1060 nm if the optical pump and the terahertz beams propagate at an angle to the $a$-axis of 61° and 44°, respectively [see Fig. 2.9(a)]. In the second scheme, phase-matching is fulfilled for
the laser wavelength 1060 nm if the beams propagate at an angle of 47° to the b-axis [see Fig. 2.9(b)].

The tensor elements of the nonlinear optical susceptibility are increased due to a resonance enhancement at the wavelengths of 800 and 1060 nm compared to their values at the laser wavelength for noncritical phase-matching of 1380 nm [25]. However, the large internal angles for phase-matching at these two wavelengths decrease the effective coefficients and require special cut crystals, which are difficult to fabricate due to cleavage planes. The effective coefficients could not be calculated because the tensor elements \( r_{232} = r_{322} \) and \( r_{131} = r_{311} \) were unknown.

![Diagram](image)

**Fig. 2.9.** Type 0 phase-matching curves for terahertz generation in OH1 crystals: Internal tuning angles \( \theta_{13} \) and \( \theta_{23} \) as functions of the pump laser wavelength \( \lambda \). The orientation of the crystals and the polarizations of the interacting electric fields are depicted above the graphs.
Chapter 3

Velocity-matched terahertz generation by optical rectification in an organic nonlinear optical crystal using a Ti:sapphire laser†

Abstract: Broadband terahertz pulses have been generated in 2-cyclooctylamino-5-nitropyridine (COANP) single crystals by optical rectification of 150fs laser pulses from an amplified Ti:sapphire laser operating at 776nm. Due to better velocity-matching and a higher figure of merit, COANP allows more efficient terahertz generation between 0.2 and 2.4THz than the benchmark electro-optic crystal ZnTe at this laser wavelength. The peak amplitude of the terahertz signal obtained in COANP was 2.5 times larger in the time-domain and 2.1 times larger in the frequency-domain compared to ZnTe. We achieved a 4.3 times higher energy conversion efficiency in COANP than in ZnTe.

3.1 Introduction

A commonly used method for the generation of broadband terahertz pulses is optical rectification of subpicosecond laser pulses in a nonlinear optical crystal (see Ref. [40] for a review). The most important requirements for a high conversion efficiency in this process are a high figure of merit (FoM), velocity-matching between the optical and the terahertz pulses, and a low absorption of the optical and the terahertz waves. For several laser wavelengths, velocity-matched terahertz generation has been demonstrated [9, 12, 38, 41]. At the wavelength of erbium-doped fiber lasers of 1550nm, the organic salt crystal 4-$N,N'$-dimethylamino-$4'$-$N'$-methyl-stilbazolium tosylate (DAST) allows velocity-matched

terahertz generation [12]. The hydrogen-bonded organic crystal 2-[3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene]malononitrile (OH1) was shown to be a very efficient terahertz emitter for laser wavelengths near 1.3 µm [38]. The solid state lasers and fiber amplifiers operating at 1060 nm are often combined with GaP crystals [41], whereas ZnTe is the standard material for terahertz generation using Ti:sapphire lasers operating at a wavelength near 0.8 µm [9]. Due to their higher figures of merit, the organic crystals DAST and OH1 are much more efficient terahertz emitters than the inorganic semiconductors ZnTe and GaP. In this letter, we show that the organic hydrogen-bonded crystal 2-cyclo-octylamino-5-nitropyridine (COANP) is a more efficient source of terahertz radiation than ZnTe at the Ti:sapphire laser wavelength of 776 nm.

3.2 Basic properties of COANP

COANP crystals have the orthorhombic point group symmetry mmm2 [42]. The absorption coefficients $\alpha_2$ and $\alpha_3$ of light polarized along the b- and c-axis are smaller than 0.3 mm$^{-1}$ in the wavelength ranges 500–1500 nm and 1550–1660 nm [42]. The optical group indices $n_{g,1}$, $n_{g,2}$ and $n_{g,3}$ show a relatively small dispersion in the wavelength range 1.0–1.7 µm (see Fig. 3.1). COANP exhibits two tensor elements of the nonlinear optical susceptibility tensor for optical rectification of similar magnitudes, namely $|\chi^{(2)}_{333}| = 55$ pm/V and $|\chi^{(2)}_{322}| = 65$ pm/V at the wavelength $\lambda = 633$ nm and a smaller one $|\chi^{(2)}_{311}| = 13$ pm/V at $\lambda = 633$ nm [43]. The tensor elements $\chi^{(2)}_{ijj}$ have been calculated from the linear electro-optic tensor $r_{jji}$ using Eq. (2.4).

3.3 Terahertz spectroscopic measurements

We have measured the linear optical properties of COANP single crystals at terahertz frequencies using terahertz time-domain spectroscopy (TTDS) for electromagnetic waves polarized along the dielectric axis $x_3$. The experimental setup was described in Ref. [38]. The samples used for the spectroscopy measurements with thicknesses of 0.77 and 1.72 mm were grown from solution [42] and undercooled melts [44], respectively. The results are presented in Fig. 3.1. The dispersion of the refractive index $n_3$ is low for frequencies between 0.5 and 1.6 THz, i.e., $n_3 \in [1.72, 1.75]$ (see Fig. 3.1). In this frequency range, the absorption coefficient $\alpha_3$ is relatively low, i.e., $\alpha_3 < 2$ mm$^{-1}$.

We use a Lorentz two-oscillator model to describe the dispersion of the complex
3.3 Terahertz spectroscopic measurements

Fig. 3.1. Refractive index $n_3$ and absorption coefficient $\alpha_3$ of COANP at terahertz frequencies. Dots: measured data. Solid lines: best fit to the measured data using a Lorentz two-oscillator model (Ref. [27]) [see Eqs. (3.1)–(3.3) and Table 3.1]. In the left panel, the optical group indices $n_{g,1}$ (dotted line), $n_{g,2}$ (dashed line) and $n_{g,3}$ (dash-dotted line) are plotted for comparison as a function of wavelength (upper x scale) (Ref. [45]).

The dielectric function $\epsilon(\omega) = \epsilon'(\omega) + i \epsilon''(\omega)$ whose real and imaginary parts are given by [27]

$$\epsilon'(\omega) = \epsilon_\infty + \sum_{j=1}^{2} \frac{\omega_j^2 f_j (\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2},$$  

(3.1a)

$$\epsilon''(\omega) = \sum_{j=1}^{2} \frac{\omega_j^2 f_j \gamma_j \omega}{(\omega_j^2 - \omega^2)^2 + \gamma_j^2 \omega^2},$$  

(3.1b)

where $\omega$ is the terahertz angular frequency, $\omega_j$ is the resonant angular frequency, $\gamma_j$ is the damping parameter, and $f_j$ is the oscillator strength of the $j$th oscillator. $\epsilon_\infty$ is the high frequency dielectric constant. The refractive index $n(\omega)$ and the intensity absorption coefficient $\alpha(\omega)$ can be obtained from $\epsilon'$ and $\epsilon''$ by

$$n(\omega) = \sqrt{\frac{1}{2} \left[ \sqrt{\epsilon'(\omega)^2 + \epsilon''(\omega)^2} + \epsilon'(\omega) \right]},$$  

(3.2)

$$\alpha(\omega) = \frac{2 \omega c}{\epsilon} \sqrt{\frac{1}{2} \left[ \sqrt{\epsilon'(\omega)^2 + \epsilon''(\omega)^2} - \epsilon'(\omega) \right]},$$  

(3.3)

where $c$ is the speed of light in vacuum. The functions with the oscillator parameters given in Table 3.1 are plotted in Fig. 3.1. They are in excellent agreement with the measured data. Since the parameters of the second resonance could only be determined from measurement data in the low-frequency tail of the resonance, the uncertainties of these parameters may be higher than the standard deviations given in Table 3.1.
Table 3.1. Parameters for the refractive index $n_3$ and the absorption coefficient $\alpha_3$ of COANP in the Lorentz-model [see Eqs. (3.1)–(3.3)]. An additional parameter used in the model calculation is the high frequency refractive index $n_\infty = \sqrt{\epsilon_\infty} = 1.679 \pm 0.003$.

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>Resonant frequency $\nu_j = \omega_j/(2\pi)$ (THz)</th>
<th>Oscillator strength $f_j$ (THz)</th>
<th>Damping parameter $\gamma_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.88 ± 0.01</td>
<td>0.038 ± 0.004</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>2.84 ± 0.06</td>
<td>0.098 ± 0.009</td>
<td>7.0 ± 0.8</td>
</tr>
</tbody>
</table>

**Fig. 3.2.** The coherence lengths $l_c$ are shown for terahertz generation through optical rectification in COANP exploiting $\chi_{333}^{(2)}$ (upper panel) and $\chi_{322}^{(2)}$ (lower panel) as a function of terahertz frequency and laser wavelength.

### 3.4 Generation of terahertz waves: Theory

Each of the three tensor elements of the nonlinear optical susceptibility $\chi_{311}^{(2)}$, $\chi_{322}^{(2)}$, and $\chi_{333}^{(2)}$ can be used for velocity-matched generation of 1 THz radiation. The velocity-matching wavelengths are 750, 1490, and 720 nm for the three different configurations (see Fig. 3.1). Figure 3.2 shows the coherence lengths $l_c$ of optical rectification exploiting $\chi_{333}^{(2)}$ and $\chi_{322}^{(2)}$, respectively, which are given by [9]:

$$l_c = \frac{c}{2\nu|n_T - n_g|}.$$  \hspace{1cm} (3.4)

The terahertz refractive index $n_T = n_3$ has been calculated from the two-oscillator Lorentz model using Eqs. (3.1) and (3.2) with the parameters from Table 3.1. The optical group indices $n_{g,2}$ and $n_{g,3}$ have been calculated from a Sellmeier formula using the parameters
3.4 Generation of terahertz waves: Theory

from Ref. [45]. In a large laser wavelength range, the velocity-mismatch is small for the
generation of frequencies below about 1.5 THz, in particular if the tensor element $\chi^{(2)}_{322}$ is
used (see Fig. 3.2).

3.4.1 Figure of merit for generation of terahertz pulses

In analogy to Ref. [29], we define the FoM for the generation of terahertz pulses through
optical rectification:

$$\text{FoM} = \frac{8|\chi^{(2)}|}{[1 + n_o(\lambda_{vm})]^2 (1 + n_T)},$$  \hspace{1cm} (3.5)

where $\lambda_{vm}$ is the velocity-matching wavelength. In the derivation of Eq. (3.5), the Fresnel
losses of the optical pump and the terahertz beams have been taken into account, and
plane waves and a nondepleted pump beam have been assumed. In the limit of low optical
and terahertz absorption, the spectral amplitude of the generated terahertz electric field
$E$ is given by

$$E(\nu, l) = \pi \mu_0 \nu I_0(\nu) \times \text{FoM} \times \text{sinc}[\pi l/(2l_c)]l,$$  \hspace{1cm} (3.6)

where $l$ is the crystal length, $\mu_0$ is the permeability of vacuum, and $I_0(\nu)$ is the Fourier
transform of the intensity of the laser pulses.

In Table 3.2, the velocity-matching wavelengths and the figures of merit of COANP,
ZnTe and GaP are given for a generated frequency of 1 THz. The terahertz absorption
coefficient is lower than 0.3 mm$^{-1}$ in all the materials for frequencies below 1 THz, hence
(3.6) can be applied to crystals with $l \lesssim 3$ mm. COANP shows the highest FoM.

| Material | $\lambda_{vm}$ (µm)$^a$ | $n_o$ | $n_T$ | $|\chi^{(2)}|$ (pm/V) | FoM (pm/V)$^b$ | References |
|----------|---------------------|------|------|-----------------|---------------|------------|
| COANP ($\chi^{(2)}_{333}$) | 0.72 | 1.63 | 1.73 | 42 | 18 | [43, 45], and this work |
| ZnTe ($\chi^{(2)}_{123}$) | 0.84 | 2.83 | 3.16 | 128 | 17 | [30, 31, 46] |
| GaP ($\chi^{(2)}_{123}$) | 1.00 | 3.12 | 3.34 | 47 | 5 | [47–49] |

$^a$ $\lambda_{vm}$ is the velocity-matching wavelength.

$^b$ see Eq. (3.5).
3.4.2 Coherence length for terahertz generation using a Ti:sapphire laser

In the following, we will discuss terahertz generation in COANP crystals exploiting its coefficient $\chi^{(2)}_{333}$ using the Ti:sapphire laser wavelength of 776 nm. The generation of frequencies below 2.5 THz is nearly velocity-matched at this wavelength in both COANP and ZnTe crystals (see Fig. 3.3). However, the coherence length is larger in COANP than in ZnTe for all frequencies below 2.4 THz. For the calculation of the coherence length in ZnTe, we used the terahertz dispersion from Refs. [31, 46] and the Sellmeier formula from Ref. [30] to calculate the optical group index. We expect a better conversion efficiency in COANP than in ZnTe for all frequencies below 2.4 THz due to its larger coherence length, in particular when using crystals thicker than 1.5 mm.

![Figure 3.3](image.png)

**Fig. 3.3.** The coherence length $l_c$ is shown for terahertz generation through optical rectification in COANP exploiting $\chi^{(2)}_{333}$ using a laser wavelength of 776 nm (solid line). For comparison, the coherence length of ZnTe at the same laser wavelength is plotted as a dotted line.

3.5 Generation of terahertz waves: Experiments

In order to confirm these predictions, we generated terahertz pulses in a 1.72 mm thick COANP crystal through optical rectification of 150 fs pulses with a central wavelength of 776 nm from an amplified Ti:sapphire laser. The pulses were detected through electro-optic sampling in a 0.5 mm thick ZnTe crystal [9]. The measurement is presented in Fig. 3.4. For comparison, the experiment has been repeated under identical conditions using a 2.0 mm thick (110)-cut ZnTe crystal as a source crystal. The polarization of the pump beam in this reference experiment was parallel to the crystallographic direction [111], which is the optimum configuration [50]. The peak terahertz amplitude from COANP exceeds that of ZnTe in both time- and frequency-domain by a factor of 2.5 and 2.1, respectively. We
obtained a 4.3 times higher energy conversion efficiency in COANP than in ZnTe.

Using Eq. (3.6), one may calculate the theoretical ratio of the spectral amplitudes emitted from ZnTe and COANP. This is illustrated in Fig. 3.4 where we calculated the expected spectrum of ZnTe from the theoretical ratio and the measured spectrum of COANP. The expected spectrum is in good agreement with the measured one. Since the relation in Eq. (3.6) does not take absorption into account, the calculated spectrum deviates from the measured one mainly for frequencies near the resonance frequency of 1.88 THz (see Table 3.1).

As one can see from Fig. 3.2, the coherence length $l_c$ of COANP in the $\chi^{(2)}_{333}$ configuration for a wavelength of 1060 nm is larger than 3.5 mm for frequencies below 1.8 THz. At this wavelength, GaP is commonly used for terahertz generation [41]. Due to the more than three times larger FoM, we expect that the conversion efficiency of COANP is significantly higher compared to GaP at this wavelength.

### 3.6 Conclusions

In conclusion, we have measured the refractive index $n_3$ and the absorption coefficient $\alpha_3$ of COANP in the frequency range between 0.5 and 2.5 THz. We have shown that COANP crystals allow more efficient terahertz generation of frequencies below 2.4 THz than ZnTe crystals with the same thickness at the Ti:sapphire laser wavelength of 776 nm.
3.7 Supplementary information†

### 3.7.1 Refractive index $n_2$ and absorption coefficient $\alpha_2$

The samples used for the measurements of the refractive index $n_3$ and the absorption coefficient $\alpha_3$ in Section 3.3 were COANP single crystals with the largest surfaces perpendicular to the $a$-axis. These samples also allowed the determination of the refractive index $n_2$ and the absorption coefficient $\alpha_2$. The measurements of $n_2$ and $\alpha_2$ are presented in Fig. 3.5. A Lorentz two-oscillator model can also be used to describe the dispersion of COANP for waves polarized along the dielectric axis $x_2$ in the frequency range between 0.5 and 3.0 THz. The functions using Eqs. (3.1)–(3.3) with the parameters given in Table 3.3 are plotted in Fig. 3.5.

![Fig. 3.5. Refractive index $n_2$ and absorption coefficient $\alpha_2$ of COANP at terahertz frequencies. Dots: measured data. Solid lines: best fit to the measured data using a Lorentz two-oscillator model (Ref. [27]) [see Eqs. (3.1)–(3.3) and Table 3.3].](image)

<table>
<thead>
<tr>
<th>Oscillator $j$</th>
<th>Resonant frequency $\nu_j = \omega_j/(2\pi)$ (THz)</th>
<th>Oscillator strength $f_j$ (THz)</th>
<th>Damping parameter $\gamma_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.46 \pm 0.02$</td>
<td>$0.168 \pm 0.008$</td>
<td>$3.7 \pm 0.3$</td>
</tr>
<tr>
<td>2</td>
<td>$2.34 \pm 0.03$</td>
<td>$0.097 \pm 0.008$</td>
<td>$4.5 \pm 0.5$</td>
</tr>
</tbody>
</table>

†This section is not included in the article [51].
3.7.2 Critical phase-matching in COANP crystals

There are two possible schemes for type 0 phase-matched terahertz generation in COANP crystals: The optical pump and the terahertz beams are polarized in the ac- or the bc-plane [see Figs. 3.6(a) and (b)]. Only the second scheme is discussed here because the terahertz refractive index $n_1$ was not measured. The birefringence magnitude of the refractive indices $n_2 - n_3 = 0.19$ at the frequency of 1 THz is equal to the one of the optical group indices $n_{g,2} - n_{g,3} = 0.19$ at the laser wavelength for noncritical phase-matching of $\lambda = 720$ nm. Thus, this scheme does not extend the range of laser wavelengths for phase-matching.

For type I phase-matching, the optical pump beam is polarized in the ab-plane [see Fig. 3.6(c)]. The effective coefficient of the nonlinear optical susceptibility for optical rectification $\chi^{(2)}_{\text{eff}}(\lambda)$ is then given by

$$\chi^{(2)}_{\text{eff}}(\lambda) = \sin^2(\theta_{12}) \chi_{311}^{(2)}(\lambda) + \cos^2(\theta_{12}) \chi_{322}^{(2)}(\lambda),$$

where $\theta_{12}$ is the angle between the wave vector of the pump beam and the $a$-axis. The angle-tuning curve and $\chi^{(2)}_{\text{eff}}(\lambda)$ are shown in Fig. 3.7. $\chi_{311}^{(2)}(\lambda)$ and $\chi_{322}^{(2)}(\lambda)$ were calculated from the linear electro-optic tensor elements $r_{113}(\lambda)$ and $r_{223}(\lambda)$ and the refractive indices $n_1(\lambda)$ and $n_2(\lambda)$ reported in the Refs. [43,45] using Eq. (2.4).

![Fig. 3.6. Orientation of the crystals and polarizations of the interacting electric fields for phase-matched terahertz generation of type 0 and type I in COANP crystals.](image-url)
Fig. 3.7. Type I phase-matched terahertz generation in COANP crystals: Internal phase-matching angle $\theta_{12}$ and effective coefficient of the nonlinear optical susceptibility $\chi^{(2)}_{\text{eff}}$ as functions of the pump laser wavelength $\lambda$. The orientation of the crystal and the polarizations of the interacting electric fields are depicted in Fig. 3.6(c).
Chapter 4

Optical properties of several organic electro-optic crystals at terahertz frequencies

4.1 Introduction

In the search for more efficient terahertz emitters, we have investigated the following organic electro-optic crystals:

- 2-[3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene]malononitrile (OH1)
- 2-cyclooctylamino-5-nitropyridine (COANP)
- 4-dimethylaminobenzaldehyde-4-nitrophenylhydrazone (DANPH)
- 4′-nitrobenzylidene-3-acetamino-4-methoxyaniline (MNBA)
- 5-(methylthio)-thiophenecarboxaldehyde-4-nitrophenylhydrazone (MTTNPH)
- 2-(N-prolinol)-5-nitropyridine (PNP)

The results are discussed below in a separate section for each material. Much more detailed investigations of the crystals OH1 and COANP are presented in the Chapters 2 and 3, respectively. The refractive indices and absorption coefficients of all the crystals have been measured through terahertz time-domain spectroscopy (TTDS). The measured dispersion can be described by Lorentz oscillator functions [see Eqs. (2.1)–(2.3)]. The parameters of the functions obtained by the best fit to the measured data are listed in Table 4.1. From these results, their figures of merit and the laser wavelengths for velocity-matched generation of the frequency of 1 THz could be determined for each material (see Table 4.2). Broadband terahertz pulses were generated in all of the investigated crystals through optical rectification of 150 fs laser pulses at the wavelength of 1300 nm.
Table 4.1. Parameters for the refractive index $n_i$ and the absorption coefficient $\alpha_i$ of several organic electro-optic crystals for light polarized along the dielectric axis $x_i$ in the Lorentz-model (see Eqs. (2.1)–(2.3)).

<table>
<thead>
<tr>
<th>Material</th>
<th>Oscillator</th>
<th>Resonant Frequency</th>
<th>Polarization Parameter</th>
<th>Damping</th>
<th>High Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNBA</td>
<td>1.41 ± 0.14</td>
<td>1.018</td>
<td>0.106 ± 0.18</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>2.00 ± 0.5</td>
<td>1.010</td>
<td>0.020 ± 0.40</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.80 ± 0.04</td>
<td>1.009</td>
<td>0.020 ± 0.40</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NMTNP</td>
<td>1.69 ± 0.03</td>
<td>0.119</td>
<td>0.020 ± 0.40</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PNP</td>
<td>1.57 ± 0.02</td>
<td>0.106</td>
<td>0.020 ± 0.40</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NNBPA</td>
<td>1.38 ± 0.12</td>
<td>0.119</td>
<td>0.020 ± 0.40</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

For higher polarized along the dielectric axis $x_i$ in the Lorentz-model [see Eqs. (2.1)–(2.3)].
Table 4.2. Figure of merit (FoM) for the generation of pulses with a central frequency of 1 THz and other relevant parameters of several non-ionic organic electro-optic crystals in comparison with the commonly used inorganic terahertz emitters ZnTe and GaP and the organic salt crystal DAST. Due to the phonon resonance at 1.1 THz of DAST, its parameters are given for the frequency of 2 THz.

| Material | $\lambda_{vm}$ (µm)$^a$ | $n_\omega$ | $n_T$ | $r$ (pm/V) | $|\chi^{(2)}|$ (pm/V)$^c$ | FoM (pm/V)$^d$ | References |
|----------|-----------------|--------|--------|-----|-------------|-------------|------------|
| ZnTe ($\chi^{(2)}_{123}$) | 0.84 | 2.83 | 3.16 | 4 | 130 | 17 | [30,31,46] |
| GaP ($\chi^{(2)}_{123}$) | 1.00 | 3.12 | 3.34 | 1 | 47 | 5 | [47–49] |
| DAST ($\chi^{(2)}_{111}$) | 1.5 | 2.13 | 2.26 | 47 | 480 | 120 | [12,26] |
| OH1 ($\chi^{(2)}_{333}$) | 1.3 | 2.16 | 2.33 | 52 | 560 | 140 | [25,38] |
| COANP ($\chi^{(2)}_{333}$) | 0.72 | 1.63 | 1.73 | 12 | 42 | 18 | [43,45,51] |
| DANPH ($\chi^{(2)}_{111}$) | 1.25 | 2.0 | 2.2 | 32$^b$ | 260 | 71 | [52] |
| MNBA ($\chi^{(2)}_{111}$) | 1.00 | 1.92 | 2.02 | 15 | 100 | 32 | [53] |
| MTTNPH ($\chi^{(2)}_{333}$) | 0.82 | 1.57 | 1.70 | 6$^b$ | 18 | 8 | [54] |
| PNP ($\chi^{(2)}_{211}$) | 1.35 | 1.86 | 1.91 | 8 | 48 | 16 | [43,55] |
| PNP ($\chi^{(2)}_{222}$) | 0.71 | 1.77 | 1.91 | 11 | 53 | 19 | [43,55] |

$^a\lambda_{vm}$ is the velocity-matching wavelength.

$^b$ calculated using Eq. (4.1).

$^c$ see Eq. (2.4).

$^d$ see Eq. (3.5).

The electro-optic tensor elements $r_{ij}$ of DANPH and MTTNPH, which are required for the calculation of the nonlinear susceptibility tensor elements $\chi^{(2)}_{jii}$ for optical rectification and the figures of merit for terahertz generation (see Eq. (2.4) and (3.5), respectively), have not yet been reported in the literature to the best of our knowledge. However, the electronic contribution to the electro-optic tensor elements, which is the dominant contribution for organic crystals [56], can be calculated by using the following equation derived from a quantum-mechanical two-level model for the dispersion of the microscopic nonlinearities and the oriented-gas model for the relation between the microscopic and macroscopic nonlinearities [56]:

$$r_{iiij}(\nu_o) = \frac{\left[ f_i(\nu_o) \right]^2 f_j(\nu_T)}{n_i(\nu_o)^4 \left[ f_j(2\nu') \right] f_i(\nu'_o)} \frac{(3\nu'^2 - \nu^2_\omega)(\nu^2_\omega - \nu'^2_\omega)(\nu^2_\omega - 4\nu'^2_\omega)}{3(\nu^2_\omega - \nu'^2_\omega)^2 \nu_\omega^2} d_{jii}(-2\nu'; \nu'_o, \nu'_o),$$

(4.1)

where $n_i(\nu)$ is the refractive index at the frequency $\nu$ for light polarized along the dielectric axis $x_i$, $f_i(\nu) = (n_i(\nu)^2 + 2)/3$ is the local field correction in the Lorentz approximation, $\nu_o = c/\lambda$ is the frequency of the optical wave, $\nu_T$ is the frequency of the terahertz wave,
\( \nu_{eg} = E_{eg}/h \) is the resonance frequency, \( E_{eg} \) is the energy difference of the two-level model and \( d_{jii} \) are the nonlinear optical coefficients for second-harmonic generation.

## 4.2 DANPH

4-dimethylaminobenzaldehyde-4-nitrophenylhydrazone (DANPH) crystallizes in three different structures, one of which is favorable for applications in nonlinear optics due to its large nonlinear optical coefficients \( d_{111} = 200 \text{ pm/V} \) and \( d_{122} = 270 \text{ pm/V} \) at the laser wavelength \( \lambda = 1542 \text{ nm} \) [52]. It belongs to the monoclinic point group symmetry \( m \). The crystals grow as plates perpendicular to the \( b \)-axis [52]. The absorption coefficient for light polarized along the dielectric axis \( x_1 \) is smaller than 0.12 mm\(^{-1} \) in the wavelength range between 0.7 and 2 \( \mu \)m [52].

Preliminary TTDS measurements were performed on a 0.100 mm thick DANPH single crystal of a high quality. The lateral size of the sample of approximately 1 mm was only of the order of the terahertz beam waist. A significant fraction of the terahertz wave passed outside the sample, which prevented a precise determination of the optical properties of DANPH. However, the sample could be used for a terahertz emission experiment. Figure 4.1 shows terahertz pulses emitted from the DANPH crystal and detected in a 1.0 mm thick OH1 crystal. Note that higher frequencies might have been generated in DANPH than the upper detection limit of 3 THz of this experiment. Also shown in Fig. 4.1 is a terahertz transient generated in a 0.365 mm thick OH1 crystal. The maximum terahertz signal normalized with the crystal length and the pump pulse energy was of a comparable magnitude for the two materials. From these preliminary results, we conclude that DANPH is a candidate for a high conversion efficiency comparable to the one demonstrated in OH1,

![Fig. 4.1. Terahertz pulses generated in a 0.100 mm thick DANPH crystal and detected in a 1.0 mm thick OH1 crystal using a laser wavelength of 1300 nm. Terahertz transients generated in a 0.365 mm thick OH1 crystal are shown for a comparison. The curves are normalized to their maximum amplitude.](image-url)
and it has a potentially wider gap-free terahertz spectrum than OH1.

From this emission experiment and from the preliminary TTDS measurements, a refractive index of approximately 2.2 was determined and the existence of strong resonances in the spectral range between 0.5 and 2.5 THz could be excluded. The coherence length is larger than 0.25 mm for terahertz frequencies up to 3 THz using a laser wavelength in range between 1 and 1.5 µm. The figure of merit for terahertz generation of DANPH is exceptionally high, and its value may be considerably underestimated since it was calculated using only the electronic contribution to the electro-optic tensor element $r_{111}$. In DAST, the calculated value of $r_{111}^e$ is about 75 percent of the measured low-frequency electro-optic coefficient [56].

### 4.3 MNBA

4′-nitrobenzylidene-3-acetamino-4-methoxyaniline (MNBA) crystallizes in the monoclinic point group symmetry $m$ [53]. Since the crystals grow as plates perpendicular to the $b$-axis, the largest tensor element of the nonlinear optical susceptibility $\chi^{(2)}_{111}$ can be exploited for optical rectification. The absorption coefficient for light polarized along the dielectric axis $x_1$ is smaller than $0.2 \text{ mm}^{-1}$ in the wavelength range between 0.6 and 1.6 µm [53].

The refractive index $n_1$ and absorption coefficient $\alpha_1$ of MNBA measured through TTDS in the range between 0.5 and 3.0 THz are presented in Fig. 4.2. The crystal shows four resonances in this spectral range. The generation of frequencies near 1 THz is ideally velocity-matched for femtosecond lasers with a wavelength near 1 µm. MNBA has a more

![Fig. 4.2. Refractive index $n_1$ and absorption coefficient $\alpha_1$ of MNBA at terahertz frequencies. Dots: measured data. Solid lines: best fit to the measured data using a Lorentz four-oscillator model (Ref. [27]) [see Eqs. (2.1)–(2.3) and Table 4.1]. In the left panel, the optical group index $n_{g,1}$ (dashed line) is plotted for comparison as a function of wavelength (upper x scale) (Ref. [53]).](image-url)
than six times larger figure of merit for terahertz generation than GaP, which has similar velocity-matching properties (see Table 4.2).

A similarly broadband gap-free spectrum as in OH1 could be generated in a 1.0 mm thick MNBA crystal (see Fig. 4.3). However, the spectral amplitude of the terahertz pulses generated in the MNBA crystal is decreased due to terahertz absorption near the resonance frequency of 1.9 THz.

### 4.4 MTTNPH

5-(methylthio)-thiophenecarboxaldehyde-4-nitrophenylhydrazone (MTTNPH) crystals belong to the orthorhombic point group mm2 [54]. We calculated the electronic contribution to the electro-optic coefficients $r_{113}^e = 1.7 \text{ pm/V}$, $r_{223}^e = 3.6 \text{ pm/V}$, and $r_{333}^e = 3.5 \text{ pm/V}$ at the wavelength $\lambda = 1542 \text{ nm}$ using Eq. (2.4) and the refractive indices and nonlinear optical coefficients reported in Ref. [54].

The refractive index and absorption spectra of MTTNPH for terahertz waves polarized along the dielectric axis $x_3$ are shown in Fig. 4.4. Two phonon resonances are observed with the resonance frequencies of 0.7 THz and about 2.5 THz, respectively. Only the tensor element $\chi^{(2)}_{333}$ of the nonlinear optical susceptibility can be exploited for velocity-matched generation of the frequency of 1 THz. The velocity-matching wavelength of 0.82 µm lies within the tuning range of Ti:sapphire lasers. However, the figure of merit for terahertz generation of MTTNPH is lower than the one of ZnTe (see Table 4.2).

Figure 4.5 shows terahertz pulses generated in a 1.0 mm thick MTTNPH crystal and detected in a 1.0 mm thick OH1 crystal. Terahertz absorption due to the two phonon resonances of the MTTNPH crystal decrease the bandwidth of the generated terahertz spectrum significantly.
4.5 PNP

2-(N-prolinol)-5-nitropyridine (PNP) crystals belong to the monoclinic point group 2 [55]. TTDS measurements have been performed for waves polarized along the dielectric axis $x_2$. One weak and two strong resonances are observed in the frequency range between 0.5 and 2.7 THz (see Fig. 4.6). The tensor element $\chi^{(2)}_{211}$ allows velocity-matched generation of the frequency of 1 THz for the laser wavelength of 1.35 µm. Terahertz generation exploiting $\chi^{(2)}_{222}$ is ideally velocity-matched for the wavelength of 0.71 µm and nearly ideally velocity-matched for wavelengths of Ti:sapphire femtosecond lasers. Figure 4.7 shows terahertz pulses generated in a 0.6 mm thick PNP crystal exploiting $\chi^{(2)}_{222}$ and detected in
a 1.0 mm thick OH1 crystal. The spectral amplitude of the generated terahertz pulses is strongly decreased near the resonance frequencies at 1.3 and 2.1 THz, respectively.

![Graph showing optical properties of organic crystals at terahertz frequencies](image1)

**Fig. 4.6.** Refractive index $n_2$ and absorption coefficient $\alpha_2$ of PNP at terahertz frequencies. Dots: measured data. Solid lines: best fit to the measured data using a Lorentz three-oscillator model (Ref. [27]) [see Eqs. (2.1)–(2.3) and Table 4.1]. In the left panel, the optical group indices $n_{g,1}$ (dotted line) and $n_{g,2}$ (dashed line) are plotted for comparison as a function of wavelength (upper x scale) (Ref. [55]).

![Graph showing terahertz pulses](image2)

**Fig. 4.7.** Terahertz pulses generated in a 0.6 mm thick PNP crystal exploiting its tensor elements of the nonlinear optical susceptibility $\chi^{(2)}_{222}$ and detected in a 1.0 mm thick OH1 crystal using a laser wavelength of 1300 nm.
Chapter 5

Determination of the refractive index over a wide wavelength range through time-delay measurements of femtosecond pulses†

Abstract: We present a simple method to measure the refractive index dispersion over a broad wavelength range (0.6–1.6 µm). In a first step, the optical group indices are obtained by measuring the time-retardation of tunable 150 fs laser pulses within a sample relative to air. The refractive index dispersion is then calculated using a Sellmeier equation that describes the measured group index dispersion. We show that our experimental data agree with previously published results to within $2 \times 10^{-4}$ for a 3 mm thick sample of fused silica and to within $3 \times 10^{-3}$ for the index $n_1$ of a 2 mm thick crystal of the highly dispersive and anisotropic organic crystal 4-\(N,N\)-dimethylamino-4'\(-N'\)-methyl-stilbazolium tosylate (DAST).

5.1 Introduction

The dispersion of a dielectric material, i.e., the dependence of the refractive index $n$ on the optical wavelength $\lambda$, is a key parameter for all kinds of photonic applications. One important example are nonlinear optical processes such as second harmonic generation (SHG) and optical parametric amplification (OPA). From momentum conservation it follows that a sufficient conversion efficiency may only be obtained if the processes are phase-matched, a condition that strongly depends on the refractive indices at all involved wavelengths [57].

When developing novel nonlinear optical materials, it is thus of primary importance to measure the dispersion at a very early stage, when one typically disposes of only one crystal. Several methods exist for the measurement of $n(\lambda)$ of bulk solid state materials, out of which the minimum deviation method is most commonly used to yield accurate results [58]. However, this technique requires that the sample is cut as a wedge that is of limited use for other applications; additionally, such wedges are often difficult to prepare in novel crystalline materials that possess certain growth or cleavage planes. Other methods are either surface sensitive (e.g., ellipsometric measurements) or the sample has to be rotated (e.g., Michelson interferometry) which complicates the measurements in birefringent materials since one measures combinations of different indices rather than the main indices alone.

In order to get the refractive index over a wide range of the wavelength $\lambda$, one may use a set of sources (e.g., lasers or atomic vapor lamps) emitting at different wavelengths; however, changing sources is laborious and will leave gaps in the measured spectrum. Alternatively, one may use broadband sources, either in combination with a monochromator, or for spectral interferometry [59,60].

In this article, we discuss how the index dispersion of transparent media can be obtained from a measurement of the time-retardation $\tau(\lambda)$ that laser pulses undergo while passing a sample with coplanar surfaces. The pulses in our experiment are tunable continuously over a wide wavelength range ($\lambda = 580–1600\,\text{nm}$) with a single source, namely an optical parametric generator/amplifier (OPG/OPA) pumped by an amplified Ti:Sapphire femtosecond laser. The refractive index $n(\lambda)$ is calculated from a Sellmeier function fitted to the group index data $n_g(\lambda)$ that are directly derived from $\tau(\lambda)$. A similar experiment was used by Delbarre et al. [61] to determine some dispersion characteristics of AgGaS$_2$. However, the wavelength range used in their experiment ($\lambda = 500–700\,\text{nm}$) was not sufficient to determine $n(\lambda)$ unambiguously without any additional measurement, in contrast to the measurements presented here.

### 5.2 Theory

The refractive index $n(\lambda)$ is a measure of the linear response of a given material to an electromagnetic wave with a vacuum wavelength $\lambda$ and is related to the microscopic polarizability of the constituent atoms or molecules. Assuming that these constituents behave like a system of harmonic oscillators with discrete resonance frequencies $\nu_k$, one may describe the refractive index dispersion by the well-known Sellmeier function [62]. In this article, we use the following form:

$$n(\lambda) = \left(n_0^2 + \frac{q \lambda_0^2}{\lambda^2 - \lambda_0^2} - B \lambda^2\right)^{1/2}$$  \hspace{1cm} (5.1)
This equation describes the dispersion within the transparency range in the visible and near-infrared of most dielectrics reasonably well. The main contribution to $n(\lambda)$ is assumed to stem from one single oscillator with a frequency $\nu_0 = c/\lambda_0$ and with an oscillator strength $q$, where $\lambda_0$ typically lies in the ultraviolet or blue-green part of the spectrum. $n_0$ accounts for oscillators with $\lambda_k \ll \lambda$, and the $B\lambda^2$ term summarizes all contributions from resonances in the mid- and far-infrared with $\lambda_k \gg \lambda$.

The effect of the refractive index on a monochromatic lightwave is a reduction of its phase velocity $v_p(\lambda) = c/n(\lambda)$ compared to the vacuum velocity $c$. A laser pulse with a center wavelength $\lambda$ however will generally not propagate with $v_p(\lambda)$, but rather with the group velocity $v_g(\lambda) = c/n_g(\lambda)$, where the group index $n_g(\lambda)$ is given by \[ n_g(\lambda) = n(\lambda) - \lambda \frac{\partial n}{\partial \lambda} \quad (5.2) \]

The time $T$ required for this pulse to pass a homogeneous layer of thickness $d$ is thus

\[ T(d, \lambda) = \frac{n_g(\lambda)}{c} d \quad (5.3) \]

The retardation $\tau(d, \lambda) = T_{\text{sample}}(d, \lambda) - T_{\text{air}}(d, \lambda)$ of the pulse within the sample relative to air is hence proportional to the difference of the respective group indices:

\[ n_g(\lambda) - n_{g, \text{air}}(\lambda) = \frac{c \tau(d, \lambda)}{d} \quad (5.4) \]

The index dispersion of air and consequently its group index are known from the literature with high precision [63]. Of course the retardation may also be measured relative to vacuum, where $n = n_g \equiv 1$ independent of wavelength.

Using Eq. (5.4), one can calculate the material’s group index $n_g$ from a measurement of the time-retardation $\tau$ caused by a sample of known thickness $d$. The Sellmeier parameters and hence the refractive index dispersion may then be obtained by fitting the theoretical group index function $n_g(\lambda)$, that is calculated using Eqs. (6.3) and (5.2), to a set of measured values of $n_g$ for several wavelengths.

### 5.3 Experimental

In a typical experiment, $\tau$ is in the order of a few picoseconds which cannot be directly resolved with electronic detectors. This problem can be overcome by measuring the correlation of the pulse from the sample with a second sub-picosecond probe pulse, typically from the same source as the sample pulse. The experimental setup for such an experiment is described in Fig. 5.1.

The laser source in our experiment was an amplified Ti:sapphire laser providing 160 fs pulses at a center wavelength of 0.776 µm and a repetition rate of 1 kHz. By means of an optical parametric generator and amplifier (OPG/OPA), we were able to generate pulses
Determination of the refractive index over a wide wavelength range

**Fig. 5.1.** Setup for the measurement of the time-retardation \( \tau(\lambda) \). The tunable laser pulse from the OPG/OPA is split into two parts that later coincide again in the correlation setup that is described in Fig. 5.2. The optical path length of one pulse can be varied by a computer controlled delay line; the maximum correlation signal indicates that the pulses arrive simultaneously. Such a correlation measurement is performed twice, once with the sample in one arm, and once without a sample (reference measurement). The difference of the arrival times is equal to the time-retardation that is discussed in Section 5.2.

**Fig. 5.2.** Principle of the correlation measurement using non-collinear second-harmonic generation (NCSHG). The two laser pulses incide on a crystal with a finite nonlinear optical susceptibility \( d \). Two photons, one from each pulse, can mix inside the crystal to generate a NCSHG photon with the double frequency (energy conservation) and a propagation in the direction of the bisector (momentum conservation). The probability for this process is highest if both pulses arrive simultaneously, hence a measurement of the NCSHG energy yields information on the temporal overlap of the two pulses (correlation).

that were tunable from 1.1 to 1.6 \( \mu m \) (parametric signal wave) \[57\]. The wavelength was controlled by an internal grating of the OPG/OPA, such that no external wavelength measurement was necessary. The range could be extended by frequency-doubling of the parametric idler wave (0.75–1.1 \( \mu m \)) or signal wave, respectively (0.55–0.8 \( \mu m \)).

Due to the superposition principle, the correlation between the sample pulse and the probe pulse cannot be detected using linear optics, such that one has to choose a nonlinear technique. Delbarre et al. \[61\] used non-collinear second-harmonic generation (NCSHG). Here the pulses mix within a second-order nonlinear optical crystal and generate a third
pulse with the wavelength $\lambda/2$ in the direction of the bisector, whose energy serves as the correlation signal (see Fig. 5.2). Figure 5.3 shows one example of a correlation experiment using NCSHG. Alternatively, one may use two-photon absorption (TPA) in a material that absorbs photons below a cut-off wavelength $\lambda_{co}$, typically in a semiconductor with a bandgap energy $E_g = \frac{hc}{\lambda_{co}}$. For $\lambda_{co} < \lambda < 2\lambda_{co}$, the fraction of the energy being absorbed depends on the total intensity, i.e., it is highest if both pulses are present simultaneously. The correlation is then given by the TPA-induced decrease in the transmitted probe pulse energy. An even simpler way to make use of TPA is to direct both sample and probe pulses onto a semiconductor photo diode, whose signal is proportional to the total number of absorbed photons and therefore reflects the correlation.

An advantage of NCSHG over TPA is that the signals are background free which results in less noise and a higher precision in the determination of the retardation $\tau(\lambda)$. However, it is limited to wavelengths $\lambda$ that are at least twice the wavelength of the absorption edge of the nonlinear crystal. Moreover, one generally has to ensure that the SHG process is phase matched for each individual wavelength in order to obtain a detectable signal, which may be difficult to achieve with one single nonlinear crystal. The nonlinear crystals used for the NCSHG were $\beta$-barium borate (BBO) (all wavelengths), and for $\lambda > 1200$ nm also in a crystal of the organic salt DAST ($4-N,N$-dimethylamino-$4'N'$-methyl-stilbazolium tosylate) [12,26]. Due to its large nonlinear optical susceptibility $d_{111} = 1010$ pm/V [64], DAST provides a reasonably strong NCSHG signal even if it is not phase matched, which greatly facilitates the measurements. In BBO, phase matching was achieved by angle tuning.

Fig. 5.3. Normalized correlation signal at a wavelength $\lambda = 980$ nm. Filled diamonds, reference measurement, i.e., no sample. Open diamonds, measurement with a sample of fused silica ($d = 3.04$ mm). The line is the sum of two Gaussian functions fitted to the data.
5.4 Results

We measured the group index dispersion of two different samples, a \((3.040 \pm 0.001)\) mm thick plate of fused silica and a \((1.970 \pm 0.001)\) mm thick crystal of DAST with parallel faces polished to optical quality. The retardation \(\tau(\lambda)\) was determined by fitting Gaussian functions through the measured correlation signals (see Fig. 5.3). The group index was then calculated using (5.4) with a correction for the group index of air \([63]\).

The measured group indices of fused silica and DAST (for light polarized along its dielectric 1-axis) are presented in Figs. 5.4 and 5.5, respectively. The plotted Sellmeier functions for \(n_g(\lambda)\) were calculated analytically from (6.3) using (5.2), with their parameters fitted to the data. The index dispersion \(n(\lambda)\) of fused silica, derived from \(n_g(\lambda)\), differs from the literature values \([65]\) by less than \(3 \times 10^{-4}\) over the whole measured wavelength range. The effects of varying material quality from different suppliers or a sample temperature varying between 20°C and 25°C were shown to be at least one order of magnitude smaller \([65]\). Since the resonance that gives the main contribution to \(n(\lambda)\) lies in the ultraviolet and thus far away from the wavelength range of our measurement, the dispersion is very low \((n_{\text{max}} - n_{\text{min}} = 0.02)\), and the infrared contribution—the parameter \(B\) in (6.3)—manifests itself as an increase of \(n_g(\lambda)\) above 1.2 µm. In DAST however, the resonance lies in the green spectral region \([66]\), and the dispersion is much stronger. Therefore the contribution of infrared resonances is negligible, and the function plotted in Fig. 5.5 was fitted only with the three parameters \(n_0\), \(q\), and \(\lambda_0\), keeping \(B = 0\) fixed. Even with this simplification, it reproduces the measured data well, and the calculated function \(n_1(\lambda)\) is again in very good agreement with literature values \([26]\), with a maximum deviation of less than \(3 \times 10^{-3}\). The wavelength range for which we measured the group index in DAST is smaller than that for fused silica. Below 750 nm, higher order dispersion effects become so

![Index dispersion of fused silica](image.png)

**Fig. 5.4.** Index dispersion of fused silica. Filled circles, measured group indices. Dotted line, Sellmeier function for group indices, fitted to the data. Solid line, refractive index calculated from the Sellmeier function. Open squares, literature values for the refractive index \([65]\).
5.5 Discussion

The accuracy of these measurements is determined by several factors. First to mention is the uncertainty in the thickness $d$ which is 1 μm for our samples. From (5.4) one sees that the relative error of $n_g - n_{\text{air}}$ is the same as that of $d$. This corresponds to systematic errors in the group index of $1.5 \times 10^{-4}$ for fused silica and of about $1 \times 10^{-3}$ for DAST. The accuracy of the correlation measurement is affected by the temporal shape of the pulses. For those pulses that were achieved by frequency-doubling ($\lambda < 1.1 \mu m$), this shape was closer to a Gaussian than for the parametric signal wave. Therefore the data points below 1.1 μm exhibit a smaller error than those above in Figs. 5.4 and 5.5. A different source of error is due to the intrinsic bandwidth of the 150 fs laser pulses which lies between 7 nm for $\lambda = 600$ nm and 50 nm for $\lambda = 1600$ nm (full width at half maximum). It is therefore difficult to precisely determine the center wavelength of the pulse at which the group index is measured. We attribute the apparent discontinuity of the data points at 1.1 μm for the measurement in DAST (Fig. 5.5) to a deviation of the actual center wavelength from the set wavelength. This uncertainty in $\lambda$ is however largely compensated if the fitting procedure includes a sufficient number of data points.

An important precondition for precise retardation measurements is that the samples possess parallel end faces. Even a small wedge angle will, besides the uncertainty in the beam path length within the sample, lengthen the path between the sample and

![Index dispersion $n_1(\lambda)$ of DAST. Filled circles, measured group indices. Dotted line, Sellmeier function for group indices, fitted to the data. Solid line, refractive index calculated from the Sellmeier function. Open squares, literature values for the refractive index [26].](image)

strong that the shape of the sample pulse gets distorted and the error in the correlation measurement becomes too large. Note also that the absorption cut-off for DAST lies at 700 nm [67].
the place of the correlation measurement and alter the spatial overlap with the probe pulse. This may be circumvented by inserting a focusing lens in a 4f-configuration which will ensure the pulse overlap for the correlation. According to Fermat’s principle, the optical path length—the refractive index integrated over the geometrical path—is the same independent of where the beam passes the lens. However, the time-retardation cannot be exactly corrected for since Fermat’s principle does not hold for the group index.

The agreement of the fitted Sellmeier function with the literature values is improved with increasing width of the wavelength range for which the group indices $n_g(\lambda)$ have been measured. This may be explained by the fact that the various parameters of the Sellmeier function have their most visible impact on different parts of the spectrum. The index variation $dn/d\lambda$ is largest for shorter wavelengths and depends primarily on the values $q$ and $\lambda_0$ that are related to the principle oscillator [see Eq. (6.3)]. On the other hand, for longer wavelengths, where $dn/d\lambda$ is small, the $n_0$ and $B$ terms are more important. In order to get the correct set of parameters, the wavelength range used for the fit has to include both regimes. We found empirically that reliable results for $n(\lambda)$ are obtained if the wavelength $\lambda$ is varied over about an octave.

The method presented in this article may be complemented by a direct measurement of the refractive index at a certain wavelength $\lambda_a$ with a different method. The value $n(\lambda_a)$ may then be used as an anchor point of the Sellmeier function, for which the number of fit parameters is reduced by one. A similar procedure was proposed by Delbarre et al. [61].

### 5.6 Conclusions

In conclusion, we have demonstrated that the refractive index dispersion of a transparent sample can be determined from a Sellmeier function fitted to the group index dispersion over a sufficiently large wavelength range. The group index data were obtained by measuring the time retardation of femtosecond laser pulses through a sample of known thickness. The accuracy of the measurement depends on the sample thickness $d$ and on the index variation $\partial n/\partial \lambda$ and is on the order of $10^{-4}$ to several times $10^{-3}$ for $d \sim 2$ mm. This accuracy is sufficient for predicting the usefulness of new materials for different applications, e.g., the wavelengths and configurations for phase matching in nonlinear optical processes, or the mode propagation in optical waveguides. For the increasing number of research groups that have a tunable femtosecond laser system at their disposal, the described method offers a very convenient way to measure the index dispersion rapidly and over a wide wavelength range without technical complexity.
Chapter 6

Linear and nonlinear optical properties of the organic crystal DSTMS†

Abstract: We report on the linear and nonlinear optical properties of the novel organic crystal 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS). The principal refractive indices $n_1$, $n_2$, and $n_3$ have been determined by a direct measurement of the group index dispersion over a broad wavelength range from 0.6 to 1.6 µm. The linear absorption coefficients for light polarized along the dielectric axes have been measured in the transparency range from 600 to 2000 nm. DSTMS crystals show a large birefringence of $\Delta n = 0.5$ and low absorption $\alpha < 0.7 \text{cm}^{-1}$ in the telecommunication wavelength range at 1.55 µm. Furthermore, the nonlinear optical tensor elements $d_{111}$, $d_{122}$, and $d_{212}$ have been determined by the Maker-fringe technique at the fundamental wavelength of 1.9 µm. DSTMS crystals exhibit a very large nonlinear activity with a nonlinear optical coefficient $d_{111} = 214 \pm 20 \text{pm/V}$. Phase-matching curves determined from our optical data showed that parametric oscillation can be achieved in the wavelength range from 1 to 2.2 µm with effective nonlinear optical coefficients larger than 25 pm/V.

6.1 Introduction

Organic non-centrosymmetric materials are of great interest for applications in nonlinear optics, such as parametric light generation, frequency conversion, terahertz (THz) wave generation, and electro-optic light modulation [68]. These materials offer vast design possibilities to tailor the linear and nonlinear properties, and very high optical nonlinearities

can be achieved. Owing to the almost completely electronic origin of the nonlinearity, they are well suited for future high-speed devices. Compared with more widely studied poled electro-optic polymers [69], organic nonlinear optical crystals exhibit superior orientational (thermal) stability and photostability, which are the most critical parameters for implementing organic materials into real devices. Waveguide structuring for integrated optics with organic crystals by photobleaching [66,70], femtosecond ablation [71], and ion implantation [72], as well as electro-optic modulation in thin organic single crystalline films [73] and channel waveguides produced by a graphoepitaxial melt growth [74] have been demonstrated. Besides these applications, organic crystals have recently attracted much attention as very efficient THz emitters by exploiting the process of optical rectification. The requirements for efficient THz generation are a high second-order nonlinear optical susceptibility and the possibility for velocity matching that is achievable in organic materials owing to relatively low dielectric constants [12]. The organic crystal 4-\(N,N\)-dimethylamino-4′-\(N′\)-methyl-stilbazolium tosylate (DAST) is at present the only commercial available material showing very high second order nonlinear activity with \(d_{111} = 210 \text{ pm/V} \) at 1.9\( \mu \text{m} \) [64] combined with a low dielectric constant \(\epsilon_1 = 5.2\), and is therefore a very efficient source of THz radiation [12]. The growth of high optical quality DAST single crystals is still a challenge, and therefore optimization of the growth techniques [75–77] and the development of new molecules for crystal growth [78–81] are subjects of present research.

We have recently developed a new promising stilbazolium salt 4-\(N,N\)-dimethylamino-4′-\(N′\)-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS) with very favorable crystal growth characteristics [82]. Owing to the high solubility in methanol—more than two times the one of DAST at room temperature [67,82]—we were able to obtain very-large-area bulk single crystals of more than \(3 \times 3 \times 0.2 \text{ cm}^3\) with high optical quality. In our work we report on the linear and nonlinear optical properties of DSTMS and present the phase-matching conditions for generation of light by optical parametric processes. We prove that DSTMS has superior properties as compared with DAST, since DSTMS shows excellent optical quality and the growth of large and high optical quality crystals is faster and more reproducible.

### 6.2 Crystal properties

DSTMS consists of a positively charged nonlinear optical chromophore stilbazolium and a negatively charged 2,4,6-trimethylbenzenesulfonate anion as shown in Fig. 6.1(a). The counter ion is used to override the preferred antiparallel crystallization of the chromophores. The single crystals used in our experiments were all grown in our laboratory from super-saturated methanol solution by the temperature-lowering method [82]. The samples used
6.3 Refractive indices of DSTMS

The refractive indices of DSTMS were determined with the previously reported group-index dispersion method [83] that can be summarized as follows. In a first step the group index $n_g$ is obtained by measuring the time retardation $\Delta T$ of a femtosecond pulse within a sample relative to air. By acquiring group-index data over a broad wavelength range and analyzing the data set with the Sellmeier equation, the refractive index dispersion $n(\lambda)$ can be calculated. We applied this simple method because it is well suited for measuring the refractive indices of coplanar crystal plates.
The time retardation $\Delta T$ of the pulse within the sample relative to air is determined at each wavelength by two correlation measurements with the experimental setup shown in Fig. 6.2. In a first measurement the correlation between a probe pulse traveling in a delay line and the pulse propagating through the sample is measured. For the second measurement the sample is removed. In our experimental configuration the correlation was determined by non-collinear phase-matched second-harmonic generation in a nonlinear optical $\beta$-BaB$_2$O$_4$ crystal. Thus, a signal is detected with the photodiode only when a spatial and temporal overlap between the probe pulse and the second pulse, which propagates through the sample or air in the reference measurement, is achieved. The time retardation $\Delta T$ is given by

$$\Delta T(d, \lambda) = \frac{d}{c} \left[ n_g(\lambda) - n_{g, \text{air}}(\lambda) \right], \quad (6.1)$$

where $d$ is the thickness of the sample and $c$ the speed of light in vacuum. For the group index in air we used $n_{g, \text{air}} = 1$. The group index $n_g$ is defined as

$$n_g(\lambda) = n(\lambda) - \lambda \frac{\partial n(\lambda)}{\partial \lambda}. \quad (6.2)$$

For our measurements we used an optical parametric generator/amplifier (OPG/OPA) (Quantronix, TOPAS) pumped with a Ti:sapphire laser providing 160fs pulses at a center wavelength of 776nm with a repetition rate of 1kHz. Thus we were able to measure the group refractive index in a broad wavelength range from 570 to 1600nm for light polarized along the principle dielectric axes. Figure 6.3 shows the measured group indices.
6.3 Refractive indices of DSTMS

Fig. 6.3. Group indices \( n_{g,1} \) (circles), \( n_{g,2} \) (diamonds), and \( n_{g,3} \) (triangles) of DSTMS as a function of the wavelength \( \lambda \). The dashed curves are according to Eqs. (6.2) and (6.3) and correspond best to the experimental data, obtained by least-squares theoretical analysis. The solid curves are the corresponding dispersion relations of the refractive indices \( n_1 \), \( n_2 \), and \( n_3 \), respectively.

Table 6.1. Sellmeier parameters for the refractive index dispersion of Eq. (6.3) that correspond best to the experimental data shown in Fig. 6.3.

<table>
<thead>
<tr>
<th></th>
<th>( n_1 )</th>
<th>( n_2 )</th>
<th>( n_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q )</td>
<td>1.45 ± 0.05</td>
<td>0.36 ± 0.04</td>
<td>0.11 ± 0.07</td>
</tr>
<tr>
<td>( n_0 )</td>
<td>2.026 ± 0.006</td>
<td>1.627 ± 0.004</td>
<td>1.579 ± 0.005</td>
</tr>
<tr>
<td>( \lambda_0 ) (nm)</td>
<td>532 ± 5</td>
<td>502 ± 11</td>
<td>360 ± 100</td>
</tr>
</tbody>
</table>

\( n_{g,1} \) (circles), \( n_{g,2} \) (diamonds), and \( n_{g,3} \) (triangles) for light polarized along the dielectric \( x_1 \), \( x_2 \), and \( x_3 \) axes, respectively. To analyze the measured group-index dispersion we used a theoretical Sellmeier formula for \( n(\lambda) \) considering one main oscillator given by

\[
n^2(\lambda) = n_0^2 + \frac{q\lambda_0^2}{\lambda^2 - \lambda_0^2}.
\]

where \( \nu_0 = c/\lambda_0 \) is the resonance frequency of the main oscillator and \( q \) is the oscillator strength. \( n_0 \) summarizes contributions from all other oscillators. The dashed curve in Fig. 6.3 corresponds best to the experimental data obtained by a least-square theoretical analysis. The resulting parameters are listed in Table 6.1. The solid lines in Fig. 6.3 are the calculated refractive-index dispersion curves for \( n_1 \), \( n_2 \), and \( n_3 \) obtained with the parameters of Table 6.1. Because of the weak dispersion of the refractive index \( n_3 \), the resonance wavelength \( \lambda_0 \) and the oscillator strength \( q \) along this axis could be determined with limited precision only.

DSTMS is highly anisotropic exhibiting a refractive index difference \( \Delta n = 0.5 \) between...
the refractive indices \( n_1 \) and \( n_2 \) at 1.5\( \mu m \), which can be explained by the preferential alignment of the nonlinear optical chromophores along the \( x_1 \) axis, as depicted in Fig. 6.1.

### 6.4 Absorption coefficients of DSTMS

The transmission was measured for light polarized along the dielectric axes in the wavelength range from 400 to 2000 nm. The absorption coefficients were calculated from the measured transmission curves, taking into account Fresnel losses due to multiple reflections at the crystal surfaces. As shown in Fig. 6.4, the absorption at telecommunication wavelengths is below 0.7 cm\(^{-1}\) for all polarizations. In the near infrared wavelength range weak absorption bands at about 1.15, 1.4 and 1.7\( \mu m \) are present, corresponding to overtones of the C–H stretching vibration at 3.3\( \mu m \). The cutoff wavelength, which we defined for an absorption of 12 cm\(^{-1}\), is at 685 nm for \( \alpha_1 \), 655 nm for \( \alpha_2 \), and 575 nm for \( \alpha_3 \). The relatively large shift can be explained by the orientation of the nonlinear optical chromophores.

![Absorption coefficients of DSTMS](image)

**Fig. 6.4.** Absorption coefficients \( \alpha_1 \) (solid curve), \( \alpha_2 \) (dashed curve) and \( \alpha_3 \) (dotted curve) of DSTMS as a function of the wavelength \( \lambda \).

### 6.5 Nonlinear optical properties

Since DSTMS belongs to the point-group symmetry \( m \), the nonzero tensor elements \( d_{ijk} = \frac{1}{2} \chi^{(2)}_{ijk} \) of the nonlinear optical susceptibility tensor elements are consequently \( d_{111}, d_{122}, d_{133}, d_{131} = d_{113}, d_{232} = d_{223}, d_{212} = d_{221}, d_{311}, d_{322}, d_{333} \) and \( d_{313} = d_{331} \), resulting in an induced nonlinear optical polarization at the second-harmonic frequency \( P^{2\omega} \) with the components of

\[
P_1^{2\omega} = \epsilon_0 \left( d_{111} E_1^2 + d_{122} E_2^2 + d_{133} E_3^2 + 2d_{113} E_1 E_3 \right),
\]

(6.4)

\[
P_2^{2\omega} = \epsilon_0 \left( 2d_{223} E_2 E_3 + 2d_{212} E_1 E_2 \right),
\]

(6.5)

\[
P_3^{2\omega} = \epsilon_0 \left( d_{311} E_1^2 + d_{322} E_2^2 + d_{333} E_3^2 + 2d_{313} E_1 E_3 \right),
\]

(6.6)
where $E_i$ are the components of the incident electric field $E^\omega$ at the fundamental frequency $\omega$ and $\epsilon_0$ is the electric permittivity of free space.

The nonlinear optical tensor elements were measured by the standard Maker-fringe technique generalized for anisotropic absorbing materials [84]. As fundamental wavelength, the first Stokes line at $\lambda = 1907$ nm of a high-pressure Raman cell filled with $H_2$ was used, pumped by a $Q$-switched Nd:YAG laser operating at 1064 nm. A typical Maker-fringe curve obtained by measuring the $d_{111}$ element of DSTMS is shown in Fig. 6.5.

![Fig. 6.5. Maker-fringe curve obtained by rotating a c plate DSTMS crystal around the dielectric $x_1$ axis. The impinged fundamental beam at 1.9 $\mu$m as well as the generated second-harmonic light at 0.95 $\mu$m were s polarized.](image)

With $c$ plates of DSTMS the nonlinear optical susceptibility elements $d_{111}$, $d_{212}$, and $d_{122}$ could be measured by selecting the appropriate polarization of the fundamental and of the second-harmonic waves. All measurements were referenced to quartz with $d_{111} = 0.277$ pm/V at 1.9 $\mu$m [64]. The obtained tensor elements and the corresponding coherence lengths $l_c$ are summarized in Table 6.2.

DSTMS has a high second-order nonlinear optical activity. As expected, the nonlinear optical tensor element $d_{111}$ is the largest owing to the preferential alignment of the chromophores along the $x_1$ axis of the crystal. The measured values are comparable to the ones of DAST with $d_{111} = 210 \pm 55$ pm/V, $d_{122} = 32 \pm 4$ pm/V, and $d_{212} = 25 \pm 3$ pm/V [64].

With the obtained results on the nonlinear optical susceptibilities and the dispersion of the refractive indices the electronic contribution to the electro-optic effect can be determined. In organic materials the electronic contribution to the electro-optic effect is dominant, in DAST it is about 75% of the low-frequency electro-optic coefficient $r^T$ [56]. The electronic contribution to the electro-optic effect $r^e$ at frequency $\omega$ can be estimated by using the quantum-mechanical two-level model for the dispersion of the microscopic nonlinearities [68] and the oriented-gas model for the relation between the microscopic and macroscopic nonlinearities [56]. This model is related to the nonlinear optical tensor
components $d_{ijk}$ by

$$r_{ij}^e(\omega) = \frac{-4}{n_{\omega,i}^2 n_{\omega,j}^2 f_k^{2\omega} f_j^{2\omega} f_i^{2\omega}} \frac{f_i^{\omega} f_j^{\omega} f_k^{0}}{3(\omega_{eg}-\omega^2)^2 \omega_{eg}^2} \left(3\omega_{eg}^2 - \omega^2\right) \left(\omega_{eg}^2 - \omega'^2\right) \times d_{kij}(-2\omega', \omega', \omega'),$$

(6.7)

where $f_i^\omega = (n_{\omega,i}^2 + 2)/3$ is the local field correction at frequency $\omega$ for light polarized along the dielectric $x_i$ axis in the Lorentz approximation and $\omega_{eg} = 2\pi \nu_0$. Using the obtained values we get $r_{111}^e = 37 \pm 3$ pm/V. For DAST the same evaluation yields $r_{111}^e = 31 \pm 8$ pm/V at 1.9 $\mu$m. Therefore, the electro-optic figure of merit $n_3^3 r_{111}^e$ of DSTMS, which is the important quantity concerning electro-optic modulation, is about 10% higher compared with the one of DAST.

### Table 6.2. Nonlinear optical coefficients $d_{ijk}$, $^a$ coherence lengths $l_c$, $^a$ electronic contribution to the electro-optic coefficient $r_{111}^e$, $b$ and the corresponding electro-optic figure of merit $^b$ at 1.9 $\mu$m of DSTMS (this work) and DAST [64].

<table>
<thead>
<tr>
<th></th>
<th>DSTMS</th>
<th>DAST</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{111}$ (pm/V)</td>
<td>214±20</td>
<td>210±55</td>
</tr>
<tr>
<td>$l_{111}^c$ (\mu m)</td>
<td>3.6 ± 0.3</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>$d_{122}$ (pm/V)</td>
<td>31±4</td>
<td>32±4</td>
</tr>
<tr>
<td>$l_{122}^c$ (\mu m)</td>
<td>0.87 ± 0.03</td>
<td>0.67 ± 0.03</td>
</tr>
<tr>
<td>$d_{212}$ (pm/V)</td>
<td>35±4</td>
<td>25±3</td>
</tr>
<tr>
<td>$l_{212}^c$ (\mu m)</td>
<td>2.7 ± 0.3</td>
<td>2.1 ± 0.2</td>
</tr>
<tr>
<td>$r_{111}^e$ (pm/V)</td>
<td>37±3</td>
<td>31±8</td>
</tr>
<tr>
<td>$n_3^3 r_{111}^e$ (pm/V)</td>
<td>320±30</td>
<td>290±75</td>
</tr>
</tbody>
</table>

$^a$ Determined in a Maker-fringe experimental configuration at the fundamental wavelength of 1.9 $\mu$m.

$^b$ Calculated using Eq. (6.7) and measured data.

### 6.6 Phase-matched parametric interaction

The favorable dispersion of DSTMS with $n_1 > n_2 > n_3$ and the relatively large off-diagonal elements $d_{122}$ and $d_{212}$ make efficient parametric generation of type I and II possible. The conditions that have to be fulfilled for efficient nonlinear interactions are energy conservation and momentum conservation (phase-matching): $\omega_3 = \omega_1 + \omega_2$ and $\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2$, respectively, where $\mathbf{k}_i$ denotes the wave vector at frequency $\omega_i$. For
6.6 Phase-matched parametric interaction

collinear interactions, for which all wave vectors are parallel to another, the phase-matching condition is

\[ n(\omega_3) \omega_3 = n(\omega_1) \omega_1 + n(\omega_2) \omega_2. \]  \hfill (6.8)

The nonlinear optical polarization \( P^{\omega_3} \) for sum-frequency generation from the fundamental waves \( E^{\omega_1,2} \) is described by

\[ P^{\omega_3}_i = \epsilon_0 \sum_{ijk} d^{(-\omega_3,\omega_1,\omega_2)}_{ijk} E^{\omega_1}_j E^{\omega_2}_k, \]  \hfill (6.9)

where \( d_{ijk} \) are the corresponding nonlinear optical tensor elements. For general directions of the wave vector and the polarizations in the crystal, the projection of the induced polarization at frequency \( \omega_3 \) along the direction of the electric field of the generated wave at \( \omega_3 \) can be written as

\[ |P^{\omega_3}| = 2\epsilon_0 d_{\text{eff}} |E^{\omega_1}| |E^{\omega_2}|, \]  \hfill (6.10)

with

\[ d_{\text{eff}} = \sum_{ijk} d^{(-\omega_3,\omega_1,\omega_2)}_{ijk} \cos(\alpha_i^{\omega_3}) \cos(\alpha_j^{\omega_1}) \cos(\alpha_k^{\omega_2}), \]  \hfill (6.11)

where \( \alpha_i^{\omega} \) is the angle between the electric field vector at frequency \( \omega \) and the axis \( i \) of the Cartesian coordinate system, in which \( d_{ijk} \) is given [85]. Since the electric field vectors are not perpendicular to the wave vectors \( \mathbf{k} \) in birefringent materials, the walk-off angles between the Poynting vectors and the wave vectors were taken into account for the calculation of the angles \( \alpha_i \).

In Fig. 6.6(a1) and (b1) the calculated phase-matching curves for parametric light generation of type I (the generated photons at \( \lambda_1 \) and \( \lambda_2 \) are of the same linear polarization) and II (the generated photons are of orthogonal linear polarization) as functions of the internal angle \( \theta \) are shown. The solid curve corresponds to a pumping wavelength of \( \lambda_3 = 750 \text{ nm} \), the dashed curve to 800 nm, the dotted curve to 960 nm, and the dashed-dotted curve to a wavelength of 1064 nm, which are all emission lines of available high-power solid-state laser and diode sources. We can see that these sources are all well suited as pump wavelengths for parametric generation of light in DSTMS. The corresponding effective nonlinear optical coefficients \( d_{\text{eff}} \) were calculated with Eq. (6.11), taking into account the dispersion of the nonlinear optical coefficient by applying the quantum-mechanical two-level model [68]. Light in the wavelength range from 1 to 2.2 \( \mu \text{m} \) can be generated with type I phase-matching by tuning the angle \( \theta \) in a narrow range from 68° to 70.5°. Above 2.2 \( \mu \text{m} \) material absorption hinders an efficient generation of light. Type II phase-matching offers the advantage of higher effective nonlinear optical coefficients, ranging from more than 10–40 pm/V compared with type I phase-matching with 6–10 pm/V, whereas tuning of the angle \( \theta \) in a broader range is required to access the whole wavelength range from 1 to 2.2 \( \mu \text{m} \).
Fig. 6.6. Phase-matching curves for parametric light generation of type I (a1) and II (b1) as functions of the internal tuning angle $\theta$ for pumping wavelength of 750 nm (solid curve), 800 nm (dashed curve), 960 nm (dotted curve) and 1064 nm (dashed-dotted curve). The corresponding effective nonlinear optical coefficients $d_{\text{eff}}$ are depicted in (a2) and (b2). The orientation of the samples and the polarizations of the interacting electric fields are depicted above the graphs.
Compared with inorganic crystals LiNbO$_3$ with a nonlinear optical figure of merit of $\text{FM} = d_{\text{eff}}^2/n_{\text{eff}}^3 \approx 3 \text{ pm}^2/\text{V}^2$ and BBO with $\text{FM} < 1 \text{ pm}^2/\text{V}^2$, which are often used for parametric light generation, DSTMS shows a 2 orders of magnitude higher figure of merit $\text{FM} \approx 160 \text{ pm}^2/\text{V}^2$ for the generation of $\lambda_1 = 1.5 \mu$m by type II phase-matching pumped with $\lambda_3 = 750 \text{ nm}$.

**6.7 Conclusions**

We have determined the principal refractive indices of the recently developed organic nonlinear optical salt DSTMS in the wavelength range from 0.6 to 1.6 $\mu$m. A large anisotropy of the refractive index was measured, in agreement with the crystallographic packing of the nonlinear optical chromophores. The absorption coefficients have been determined in the wavelength range from 600 to 2000 nm. DSTMS shows very low absorption $\alpha < 0.7 \text{ cm}^{-1}$ at telecommunication wavelengths combined with a high electronic contribution to electro-optic coefficient $r_{111}^e = 37 \text{ pm/V}$ and is therefore very interesting for high-speed photonic devices.

Furthermore, we have measured the nonlinear optical coefficients $d_{111}$, $d_{122}$, and $d_{212}$. DSTMS has a very high second-order susceptibility $d_{111} = 214 \pm 20 \text{ pm/V}$, comparable with that of the well-investigated DAST. Therefore and because of the easier and faster growth compared with DAST it is very promising for nonlinear optical applications including THz generation and detection. We have determined the phase-matching conditions for parametric light generation and have shown that DSTMS is well suited for optical parametric oscillation in the wavelength range from 1 to 2.2 $\mu$m because of large $d_{\text{eff}}$ coefficients.
Chapter 7

A terahertz time-domain spectrometer for simultaneous transmission and reflection measurements at normal incidence†

Abstract: We present a versatile terahertz time-domain spectrometer that allows reflection measurements at normal incidence and double pass transmission measurements in a single experimental setup. Two different modes for transmission measurements are demonstrated for precise measurements of transparent high or low refractive index materials, respectively. The refractive indices and absorption coefficients of cesium iodide, potassium bromide, sodium chloride, polytetrafluoroethylene (PTFE, Teflon), and silicon have been measured in the frequency range between 1.4 and 4.7 THz. The parameters of the Lorentz oscillator functions describing the phonon-polariton dispersions of CsI and KBr have been determined.

7.1 Introduction

The terahertz frequency range of the electromagnetic spectrum is typically defined to be between 0.1 and 10 THz. Today, terahertz waves are used for imaging and spectroscopy in many fields of science and technology (see [40] for a review). Terahertz time-domain spectroscopy (TTDS) is a phase-sensitive technique for the determination of the refractive index and the absorption coefficient at terahertz frequencies. TTDS experiments are most often performed in transmission setups, because transmission spectrometers are easier to implement and give more accurate results than reflection spectrometers. However, strongly

†By Fabian D. J. Brunner, Arno Schneider, and Peter Günter. Article published in Optics Express 17, 20684–20693 (2009).
absorbing samples can only be measured in reflection.

The majority of the reflection spectra reported in the literature have been measured at a non-normal angle of incidence [86–89]. However, the geometry of normal incidence is favorable for both terahertz spectroscopy and imaging. In reflection spectroscopy, the refractive index and the absorption coefficient can be calculated from the reflected terahertz signals by exact analytical formulas that are more simple for normal incidence. In terahertz time-of-flight tomography, the terahertz beam experiences a lateral offset if it is reflected from different layers of a sample at non-normal incidence, which limits the maximum accessible depth of the three-dimensional image [90]. Due to the lateral offset of the terahertz beam at non-normal incidence, also the positioning of the sample is more critical. For reflection at 45°, the tolerance of the distance between the sample and the terahertz emitter and detector is less than the diameter of the terahertz beam. A much larger tolerance is obtained by the use of normal incidence, which is crucial for remote sensing applications such as standoff detection of explosives. An experimental setup with normal incidence of the terahertz beam onto the sample can be implemented by introducing a beamsplitter into the terahertz beam path at the expense of reducing the detected terahertz signal in amplitude [7,91].

In this article, we present a spectrometer in a transceiver configuration in which the terahertz pulses are generated and detected in a single electro-optic crystal. This geometry allows reflection measurements at normal incidence without the drawback of a reduced terahertz signal caused by a beamsplitter. The concept of a terahertz transceiver has been discussed in the literature for both photoconductive antennas and electro-optic crystals with the zinc blende structure [50,92,93]. However, the configuration using ZnTe presented in Ref. [50] has several limitations. On the one hand, the optimum crystal orientation for terahertz generation is different than for detection, leading to a significantly decreased overall efficiency of the transceiver compared to a setup with two separate crystals for generation and detection. More importantly, the experiment in Ref. [50] uses a quadratic detection scheme (crossed polarizers, zero optical bias), i.e., it is not the electric field \( E(t) \) that is detected, but rather its square \( E(t)^2 \). This is sufficient for time-of-flight imaging, but impractical for terahertz time-domain spectroscopy, where the undistorted waveform \( E(t) \) is essential. It is possible to correct the distortions of terahertz waveforms, but only with a non-zero optical bias [36]. However, the introduction of an optical bias in the setup of Ref. [50] would drastically increase the noise level. The transceiver configuration presented in this article does not suffer from any of these limitations. For the birefringent organic crystal 4-\( N,N \)-dimethylamino-4′-\( N′ \)-methyl-stilbazolium tosylate (DAST), the optimum orientation is the same for terahertz generation and detection, and the detection scheme of terahertz-induced lensing does not require crossed polarizers and is intrinsically distortion-free. The terahertz generation does not influence the terahertz detection, if these two processes take place in one DAST crystal, because they are separated in time.
by 2\,\text{ns} in our setup. To our knowledge, there is no excitation with such a long lifetime taking place in the DAST crystal. Possible thermal effects can also be excluded since the crystal is well transparent for the pump beam, and the power of the absorbed terahertz radiation is negligibly small. Thus, the dynamic range and bandwidth of our transceiver type spectrometer are the same as for the setup using two separate DAST crystals for terahertz generation and detection [12].

Apart from a more compact experimental setup and a more simple data analysis in reflection spectroscopy, the transceiver configuration has further intrinsic advantages. We demonstrate that our spectrometer can also be used for double pass transmission measurements without any modification of the experimental setup between the reflection and the transmission experiments. Thus, we can precisely measure the refractive index and the absorption coefficient of both transparent and strongly absorbing materials in a single experimental setup.

### 7.2 Experimental setup

#### 7.2.1 Reflection measurements

The experimental setup is schematically shown in Fig. 7.1. The laser used for this work is an erbium-doped fiber laser delivering 70\,fs pulses with an energy of 1.8\,nJ at a repetition rate of 100\, MHz and a central wavelength of 1560\,nm. The laser beam is split into a pump and a probe beam. Terahertz pulses are generated through optical rectification of the pump pulses in a 0.630\,mm thick DAST crystal exploiting its largest nonlinear optical susceptibility tensor element $\chi^{(2)}_{111} = 480\,\text{pm/V}$ [12, 26]. The terahertz beam is reflected from a glass plate coated with indium tin oxide (ITO) [94]. The reflection of the pump beam from the ITO coated glass plate is blocked by a germanium crystal. The terahertz beam is focused onto the sample using an off-axis elliptical mirror. The terahertz beam reflected back from the surface of the sample is refocused onto the same DAST crystal by the elliptical mirror. The probe beam is transmitted through the ITO coated glass plate and propagates collinear with the terahertz beam though the DAST crystal. The electric field of the terahertz pulse is measured by electro-optic sampling in the DAST crystal [13].

Due to the small pulse energy of the laser, the relatively weak detected terahertz signal needs to be measured using lock-in amplification. This technique requires a modulation of the terahertz signal, which is achieved by mechanically chopping the terahertz beam. The experiments are conducted in a dry air atmosphere to avoid absorption of the terahertz wave due to ambient water vapor.

As a reference measurement, the terahertz signal reflected from a gold coated planar mirror is recorded. Taking into account that the refractive index of air is $n \approx 1$ and gold is a nearly perfect reflector at terahertz frequencies [17], the ratio of the sample and the
reference spectra is given by

$$\frac{|E_{\text{sample}}(\nu)|}{|E_{\text{ref.}}(\nu)|} \exp(i[\phi_{\text{sample}}(\nu) - \phi_{\text{ref.}}(\nu)]) \equiv r(\nu) \exp[i\phi(\nu)] = \frac{n(\nu) + i\kappa(\nu) - 1}{n(\nu) + i\kappa(\nu) + 1},$$

(7.1)

where $\nu$ is the terahertz frequency, $r$ is the amplitude ratio, $\phi$ is the phase difference, and $n$ and $\kappa$ are the real and the imaginary part of the complex refractive index $\tilde{n}$, respectively. Equation (7.1) can be solved analytically, and we find the following expressions for the refractive index $n(\nu)$ and the power absorption coefficient $\alpha(\nu) = \kappa(\nu) 4\pi \nu / c$:

$$n(\nu) = \frac{1 - r(\nu)^2}{1 + r(\nu)^2 - 2r(\nu) \cos \phi(\nu)},$$

(7.2)

$$\alpha(\nu) = \frac{4\pi \nu}{c} \frac{2r(\nu) \sin \phi(\nu)}{1 + r(\nu)^2 - 2r(\nu) \cos \phi(\nu)},$$

(7.3)
The precise placement of the reference mirror with respect to the surface of the sample is crucial, since a minor displacement $\delta x$ in the longitudinal direction leads to a phase error $\delta \phi = 4 \pi \nu \delta x / c$, which may result in large errors of the calculated refractive index and absorption coefficient. In order to minimize $\delta x$, we have designed a special sample holder. Both the sample and the reference mirror are pressed from behind to an aluminum frame that can be moved perpendicular to the terahertz beam using a motorized translation stage (see Fig. 7.1).

In the measurements of the optical properties of the ionic crystals CsI, KBr, and NaCl presented later in this article, we could correct the phase error $\delta \phi$ as follows. If the displacement $\delta x$ is introduced as an additional parameter into the theoretical functions which describe the dispersion of the crystals given by Eqs. (7.8)–(7.10), $\delta x$ can be obtained along with other parameters of the functions by a fitting procedure (see Subsection 7.3.1 for details). The same procedure can also be used to correct the phase error for other material classes whose dispersion is described by different theoretical functions, e.g., by the Drude theory for the dispersion of free carriers in doped semiconductors [86].

### 7.2.2 Double pass transmission measurements

The experimental setup shown in Fig. 7.1 can also be used for double pass transmission measurements without any readjustment of the optical components. In these measurements, the terahertz pulse propagates through the sample, is then reflected back and propagates a second time through the sample, now in the opposite direction. There are two different configurations for such a measurement: Either the terahertz pulse is back-reflected from a spherical mirror with its focus at the sample position (see Fig. 7.1). Alternatively, the terahertz pulse reflected from the rear surface of the sample $E_{\text{rear surface}}$ is recorded. For simplicity, we restrict the following discussion on optically thick samples, where the reflections of the terahertz pulses from the front and the rear surface of the sample are well separated in time. The data analysis for optically thin samples can easily be derived for the first configuration in analogy to the data analysis in standard transmission measurements of optically thin samples [15, 16].

For the measurement of the reference signal in the first configuration, the sample is moved out of the terahertz beam (position 3 of the sample holder, see Fig. 7.1). The measurement and the reference measurement are denoted by $E_{\text{sample}}^{\text{double pass}}$ and $E_{\text{ref}}^{\text{double pass}}$, respectively. For a weakly absorbing material ($\kappa(\nu) \ll 1$), the imaginary part of the Fresnel transmission and reflection coefficients can be neglected. The refractive index $n$ and the absorption coefficient $\alpha$ can then be calculated from the phases $\phi$ and the amplitudes $|E|$
of the two measurements using the following relations:

\[ n(\nu) = \frac{c \left( \phi_{\text{sample}}^{\text{double pass}}(\nu) - \phi_{\text{ref.}}^{\text{double pass}}(\nu) \right)}{4\pi \nu l} + 1, \]  

(7.4a)

\[ \alpha(\nu) = -\frac{1}{l} \ln \left( \frac{|E_{\text{sample}}^{\text{double pass}}(\nu)|}{|E_{\text{ref.}}^{\text{double pass}}(\nu)|} \frac{(n + 1)^4}{4(n)^2} \right). \]  

(7.4b)

The second configuration where the terahertz pulse is reflected from the rear surface of the sample is preferable for materials with a high refractive index, since the Fresnel reflection losses increase with the refractive index. For a material with a refractive index \( n \) larger than 4.2, the measured spectral amplitude \( |E_{\text{sample}}^{\text{rear surface}}(\nu)| \) is larger than \( |E_{\text{sample}}^{\text{double pass}}(\nu)| \) and thus has a better signal-to-noise ratio. Many materials have a refractive index larger than 4.2 in the terahertz frequency range, e.g., \( \text{LiNbO}_3 \ (n_o \geq 6.7, n_e \geq 5.1) \), \( \text{LiTaO}_3 \ (n_o > 6.4, n_e > 6.3) \), or rutile \([46,95]\). For this configuration, the pulse reflected from the planar mirror \( E_{\text{ref.}} \) can be used as a reference. The refractive index \( n \) and the absorption coefficient \( \alpha \) can be calculated using the following equations:

\[ n(\nu) = \frac{c \left( \phi_{\text{sample}}^{\text{rear surface}}(\nu) - \phi_{\text{ref.}}(\nu) - \pi \right)}{4\pi \nu l}, \]  

(7.5a)

\[ \alpha(\nu) = -\frac{1}{l} \ln \left( \frac{|E_{\text{sample}}^{\text{rear surface}}(\nu)|}{|E_{\text{ref.}}(\nu)|} \frac{(n + 1)^3}{4n(n - 1)} \right). \]  

(7.5b)

Note that the phase difference \( \phi_{\text{sample}}^{\text{rear surface}}(\nu) - \phi_{\text{ref.}}(\nu) \) in Eq. (7.5a) is affected by the same phase error as in reflection spectroscopy. However, the phase error is much less critical for the determination of \( n \) and \( \alpha \) in transmission spectroscopy. The displacement \( \delta x \) and the error in the determination of the thickness of the sample \( \delta l \) are typically of the same order of magnitude (1–30 \( \mu \text{m} \)). They lead to a systematic error of the refractive index given by:

\[ \delta n = \frac{n}{l} \sqrt{\delta l^2 + \delta x^2}. \]  

(7.6)

To circumvent the phase problem in the second configuration, one can use the pulse reflected from the front surface of the sample \( E_{\text{sample}} \) as a reference. The refractive index \( n \) and the absorption coefficient \( \alpha \) are then given by:

\[ n(\nu) = \frac{c \left( \phi_{\text{sample}}^{\text{rear surface}}(\nu) - \phi_{\text{sample}}(\nu) - \pi \right)}{4\pi \nu l}, \]  

(7.7a)

\[ \alpha(\nu) = -\frac{1}{l} \ln \left( \frac{|E_{\text{sample}}^{\text{rear surface}}(\nu)|}{|E_{\text{sample}}(\nu)|} \frac{(n + 1)^2}{4n} \right). \]  

(7.7b)

### 7.3 Measurements

#### 7.3.1 Phonon-polariton dispersion of CsI, KBr, and NaCl

The performance of the spectrometer in the reflection mode has been tested by measuring the phonon-polariton dispersion of the salt crystals CsI, KBr, and NaCl. The samples
Table 7.1. Parameters for the dielectric dispersion of the alkali halide crystals CsI, KBr, and NaCl in the harmonic approximation.\(^a\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Ref.</th>
<th>(\nu_{\text{TO}}) (THz)</th>
<th>(\nu_{\text{LO}}) (THz)</th>
<th>(\gamma) (GHz)</th>
<th>(\epsilon_\infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsI</td>
<td>this work</td>
<td>1.84 ± 0.01</td>
<td>2.65 ± 0.02</td>
<td>45 ± 3</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>[96]</td>
<td>1.84 ± 0.01</td>
<td>2.45 ± 0.01</td>
<td>69</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>[97]</td>
<td>1.86</td>
<td>2.74</td>
<td>45</td>
<td>± 3</td>
</tr>
<tr>
<td>KBr</td>
<td>this work</td>
<td>3.44 ± 0.01</td>
<td>4.65 ± 0.03</td>
<td>120 ± 6</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>[98]</td>
<td>3.39</td>
<td>4.74</td>
<td>150</td>
<td>2.43</td>
</tr>
<tr>
<td>NaCl</td>
<td>[3]</td>
<td>4.92</td>
<td>7.86</td>
<td>270</td>
<td>2.31</td>
</tr>
</tbody>
</table>

\(^a\) See Eq. (7.8).

were polished crystal windows purchased from Sigma-Aldrich. The real and imaginary parts of the dielectric function \(\epsilon(\nu) = \epsilon'(\nu) + i \epsilon''(\nu)\) of the alkali halide crystals can be described in the harmonic approximation by [3]

\[
\epsilon'(\nu) = \epsilon_\infty \frac{(\nu_{\text{LO}}^2 - \nu^2)(\nu_{\text{TO}}^2 - \nu^2) + \gamma^2 \nu^2}{(\nu_{\text{TO}}^2 - \nu^2)^2 + \gamma^2 \nu^2}, \quad (7.8a)
\]

\[
\epsilon''(\nu) = \epsilon_\infty \frac{(\nu_{\text{LO}}^2 - \nu_{\text{TO}}^2) \gamma \nu}{(\nu_{\text{TO}}^2 - \nu^2)^2 + \gamma^2 \nu^2}, \quad (7.8b)
\]

where \(\nu_{\text{TO}}\) is the transversal optical phonon frequency, \(\nu_{\text{LO}}\) is the longitudinal optical phonon frequency, \(\gamma\) is the damping parameter, and \(\epsilon_\infty\) is the high frequency dielectric constant. The refractive index \(n(\nu)\) and the absorption coefficient \(\alpha(\nu)\) can be obtained from \(\epsilon'(\nu)\) and \(\epsilon''(\nu)\) by

\[
n(\nu) = \sqrt{\frac{1}{2} \left[ \epsilon'(\nu)^2 + \epsilon''(\nu)^2 + \epsilon'(\nu) \right]}, \quad (7.9)
\]

\[
\alpha(\nu) = \frac{4\pi \nu}{c} \sqrt{\frac{1}{2} \left[ \epsilon'(\nu)^2 + \epsilon''(\nu)^2 - \epsilon'(\nu) \right]} \quad (7.10)
\]

Theoretical functions for the amplitude ratio \(r(\nu)\) and the phase difference \(\phi(\nu)\) are calculated from \(n(\nu)\) and \(\kappa(\nu) = \alpha(\nu) c/(4\pi \nu)\) using Eq. (7.1). The phase error is included into the theoretical phase difference by adding \(4\pi \nu \delta x/c\). The theoretical functions for \(r\) and \(\phi\) are fitted to the measured data. The parameters of the functions determined for CsI and KBr are listed in Table 7.1. They are in reasonable agreement with the literature values which are also given in Table 7.1 for a comparison. Since the spectral amplitude measured with our system is relatively low for frequencies above \(\approx 4.3\) THz, we could not precisely determine the parameters for NaCl. However, the phase-error of the measurement could be corrected by a fitting procedure using the parameters reported in Ref. [3].

For a comparison, the displacement \(\delta x\) was measured independently, and a reasonable agreement with the value determined by the fitting procedure was found. The terahertz
Fig. 7.2. Refractive index and absorption coefficient of CsI measured by terahertz time-domain spectroscopy in reflection at normal incidence. Dots: measured data; solid lines: best fit to the measured data using a Lorentz oscillator function (see Eqs. (7.8)–(7.10) and Table 7.1).

The pulse reflected from the front surface of a silicon crystal mounted in the sample holder was shifted in time by 153 fs compared to the terahertz pulse reflected from the reference mirror, which corresponds to a displacement of $\delta x = 23.0 \, \mu m$. Note that the very small absorption of silicon does not give rise to a significant phase change of the reflected terahertz wave. In a subsequent spectroscopy measurement of CsI, a displacement of $\delta x = 21.5 \, \mu m$ was determined using the fitting procedure. The difference of these two values of $\delta x$ of 1.5 $\mu m$ lies within the mechanical reproducibility of mounting a sample in the sample holder.

The measured refractive index and absorption coefficient of CsI and the theoretical functions calculated from Eqs. (7.8)–(7.10) using the parameters from Table 7.1 are plotted in Fig. 7.2. The measured spectra are in very good agreement with the theoretical functions and with the TTDS measurements previously presented in Ref. [99]. The features in the spectra at 3 THz shown in Fig. 7.2 can be explained by the increased error due to a phonon resonance in the DAST transceiver crystal [12]. All the measurement data in this article are presented for frequencies $\nu \geq 1.4 \, \text{THz}$ due to the strong absorption in the DAST crystal near the resonance frequency of 1.1 THz [12].

The measured data and the theoretical curves for KBr are shown in Fig. 7.3. The measured dispersion is in very good agreement with the theoretical one calculated from the Lorentz oscillator functions.

The results for NaCl are shown in Fig. 7.4. The theoretical curves plotted in Fig. 7.4 are calculated from Eqs. (7.8)–(7.10) using the parameters from Ref. [3]. There is also a good agreement between the measurement data and the theoretical functions in consideration of the fact that the errors in this measurement are large for frequencies above 4.3 THz.
7.3 Measurements

### Fig. 7.3.
Refraction index and absorption coefficient of KBr measured by terahertz time-domain spectroscopy in reflection at normal incidence. Dots: measured data; solid lines: best fit to the measured data using a Lorentz oscillator function (see Eqs. (7.8)–(7.10) and Table 7.1).

### Fig. 7.4.
Refraction index and absorption coefficient of NaCl measured by terahertz time-domain spectroscopy in reflection at normal incidence. Dots: measured data; solid lines: theoretical dispersion calculated from Eqs. (7.8)–(7.10) using the parameters from Ref. [3].

#### 7.3.2 Double pass transmission measurements on PTFE and Si

The effectiveness of the double pass transmission measurement technique has been demonstrated using polytetrafluoroethylene (PTFE, Teflon) and silicon whose terahertz spectra are well known from the literature [6,34]. The PTFE sample was a 10 mm thick plate. Due to the low refractive index of PTFE, the first measurement mode was used where the terahertz beam is back-reflected from an external spherical mirror (see Fig. 7.1). The measured refractive index and absorption coefficient of PTFE are plotted in Fig. 7.5.

Both measurement modes have been performed on a 2.137 mm thick polished silicon crystal purchased from Sigma-Aldrich. In the second measurement mode, the terahertz beam is back-reflected from the rear surface of the sample. The results are shown in
7 A terahertz time-domain spectrometer for reflection measurements

Fig. 7.5. Refractive index and absorption coefficient of PTFE measured by terahertz time-domain spectroscopy in a double pass transmission configuration where the terahertz pulse is back-reflected from an external spherical mirror (see text for details).

Fig. 7.6. Refractive index and absorption coefficient of silicon measured by terahertz time-domain spectroscopy in two different double pass transmission configurations (see text for details). Solid lines: the terahertz pulse is back-reflected from the rear surface of the sample. Dashed lines: the terahertz pulse is back-reflected from an external spherical mirror.

Fig. 7.6. The absorption coefficient of Si is lower than the detection limit in these experiments ($\alpha < 0.2 \text{mm}^{-1}$). The features at 3 THz in the spectra of Si measured by the second mode can be explained by the large error due to a phonon resonance in the DAST transceiver crystal [12]. All the spectra are in good agreement with the ones published in the Refs. [6,34].

7.4 Conclusions

A versatile terahertz time-domain spectrometer for simultaneous transmission and reflection measurements at normal incidence is presented. The use of normal incidence
not only facilitates the data analysis in reflection spectroscopy, but it is also ideal for terahertz reflection tomography. Without any modifications of the experimental setup, we can measure the refractive indices and absorption coefficients of transparent samples in transmission or of absorbing samples in reflection. Thus, we can also determine the optical properties of one material in its transparency and its non-transparency range of the terahertz spectrum in a single experiment.

The refractive index and absorption spectra of the materials CsI, KBr, NaCl, PTFE, and Si obtained with this spectrometer are in good agreement with the literature data. The measured phonon-polariton dispersion of the salt crystals CsI, KBr, and NaCl can be well described by a harmonic approximation. The parameters of the Lorentz oscillator functions have been determined for CsI and KBr.

The experimental setup presented here can also be used with different combinations of an electro-optic crystal and a femtosecond laser, e.g., 4-N,N-dimethylamino-4'-N'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS) in combination with an erbium-doped fiber laser, 2-cyclooctylamino-5-nitropyridine (COANP) pumped with a Ti:sapphire laser, or 2-[3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene]malononitrile (OH1) combined with a laser operating at a wavelength near 1300 nm, in order to make use of the optimum phase-matching properties [22,38,51]. COANP and OH1 crystals were proven to be very efficient emitters of a gap-free terahertz spectrum ranging from 0.3 to 3.0 THz [38,51].
Chapter 8

Conclusions and outlook

8.1 Organic electro-optic crystals for terahertz generation and detection

In this thesis, the potential of the organic electro-optic crystals OH1, COANP, DANPH, MTTNPH, and PNP as terahertz emitter and detector crystals was investigated. The refractive indices and absorption coefficients were measured using terahertz time-domain spectroscopy and the phase-matching properties were discussed for each material.

The crystal OH1 was found to be more efficient than the benchmark terahertz emitter crystal DAST. For spectroscopic applications, OH1 has the additional advantage that its emission spectrum is continuous, in contrast to that of DAST, where a transverse optical phonon leads to a gap at the resonance frequency of 1.1 THz. The OH1 crystal shows a low terahertz absorption coefficient $\alpha_3$ and allows phase-matched generation and detection of terahertz frequencies in the whole range between 0.3 and 2.5 THz for a pump laser wavelength range from 1200 to 1460 nm. For a pump pulse energy of 45 $\mu$J, we achieved a peak terahertz electric field of 100 kV/cm and a conversion efficiency of $7 \times 10^{-4}$, corresponding to a photon conversion efficiency of 11 percent.

The standard electro-optic crystal for terahertz time-domain systems using a Ti:sapphire laser is the inorganic semiconductor ZnTe. We could demonstrate that COANP allows more efficient terahertz generation between 0.2 and 2.4 THz than ZnTe at the laser wavelength of 776 nm due to better phase-matching and a higher figure of merit. The peak amplitude of the terahertz signal obtained in a 1.72 mm thick COANP crystal was 2.5 times larger in the time-domain and 2.1 times larger in the frequency-domain compared to the one obtained in a 2.0 mm thick ZnTe crystal. We achieved a 4.3 times higher energy conversion efficiency in COANP than in ZnTe.

The ideal electro-optic crystal for an ultra-broadband terahertz time-domain spectrometer—if it exists—is not yet found. This crystal would combine all the advantages of the existing emitter crystals: It would allow a highly efficient generation of a broadband
Conclusions and outlook

and gap-free spectrum ranging from 0.1 to 10 THz at a wavelength of a femtosecond laser, i.e., at 0.8, 1.0 or 1.5 µm, respectively. Thus, the quest for better terahertz emitter crystals continues. Some of the existing organic electro-optic crystals have not yet been investigated, but also novel promising organic crystals are currently being developed.

8.2 Optical measurement methods

A simple method for the measurement of the optical group index and refractive index dispersion was developed. Its typical accuracy of a few times $10^{-3}$ for 2 mm thick samples is sufficient for phase-matching calculations of nonlinear optical processes in novel crystals. The method was applied on the organic ionic crystal DSTMS, which is an excellent terahertz emitter with similar properties as DAST. The nonlinear optical properties of DSTMS were also measured.

A terahertz transceiver for birefringent electro-optic crystals is described. It can be used for terahertz time-domain spectroscopy in transmission and reflection at normal incidence. The optical properties of a material can be measured in its transparency and its non-transparency range of the terahertz spectrum in a single experiment using this spectrometer. The transceiver geometry is advantageous for several applications, e.g., for remote sensing or imaging. If the terahertz beam is collimated using a parabolic mirror, the distance between the transceiver and the target is uncritical. In this geometry, also a very thick transparent sample can be investigated using terahertz time-of-flight tomography.
Appendix A

Error analysis in terahertz time-domain spectroscopy

In this appendix, the main sources of error in terahertz time-domain spectroscopy are briefly discussed. The propagation of the experimental errors into the calculated refractive index $n$ and absorption coefficient $\alpha$ is shown. The procedures presented here were used throughout the thesis. The errors of $n$ and $\alpha$ were required for the calculation of the uncertainties of the parameters of the Lorentz oscillator functions describing the dispersion of most materials investigated in this thesis.

The most important systematic error in transmission spectroscopy is the error of the determination of the thickness of the sample $\delta l$. The relative errors of $n - 1$ and $\alpha$ are equal to the relative error of $l$ [see Eqs. (A.8) and (A.9)].

In reflection spectroscopy, the displacement of the reference mirror with respect to the surface of the sample $\delta x$ in the longitudinal direction leads to a systematic error of the phase difference $\delta \phi = 4\pi \nu \delta x/c$, which may result in large errors of the calculated refractive index $n$ and absorption coefficient $\alpha$ [see Eqs. (7.2) and (7.3)].

The noise in the time-domain signal stems primarily from the fluctuations in the pulse energy and the pointing instability of the laser. In the following, it will be shown how this noise propagates into the frequency-domain.

A.1 Error propagation in the Fourier transform

In terahertz time-domain spectroscopy, the electric field $E(t)$ of a terahertz wave is measured at $N$ equally spaced points in time $t_j = t_0 + \Delta t j, j = 0, 1, 2, \ldots, N - 1$. In order to avoid aliasing effects, the time interval $\Delta t$ must be smaller than $1/(2\nu_{\text{max}})$, where $\nu_{\text{max}}$ is the highest frequency contained in the signal. Each data point $E(t_j)$ is an average over $M$ samples $E(t_j)_s$:

$$E(t_j) = \frac{1}{M} \sum_{s=1}^{M} E(t_j)_s. \quad (A.1)$$
The standard deviation of an individual data point \( \sigma_{E(t_j)} \) can be estimated by the following equation:

\[
\sigma_{E(t_j)} = \sqrt{\frac{1}{M - 1} \sum_{s=1}^{M} (E(t_j)_s - E(t_j))^2}.
\]  
(A.2)

The frequency-domain signal \( E(\nu_k) \) at the frequencies \( \nu_k = \Delta \nu k, k = 0, 1, 2, \ldots, N - 1 \) with the frequency spacing \( \Delta \nu = 1/(\Delta t N) \) is obtained by the discrete Fourier transform:

\[
E(\nu_k) = E_R(\nu_k) + i E_I(\nu_k) = \sum_{j=0}^{N-1} \exp(-i 2\pi \nu_k t_j) E(t_j) \Delta t,
\]  
(A.3)

where \( E_R(\nu_k) \) and \( E_I(\nu_k) \) are the real and the imaginary parts of \( E(\nu_k) \). Note that \( E(\nu_k) = E^*(\nu_{N-k}) \).

Since the electric field \( E(t_j) \) measured at the different times \( t_j \) can be assumed to be statistically independent, one can calculate the standard deviations of the spectral amplitude \( |E(\nu_k)| = \sqrt{E_R(\nu_k)^2 + E_I(\nu_k)^2} \) and the phase \( \phi(\nu_k) = \tan^{-1}[E_I(\nu_k)/E_R(\nu_k)] \) using the following equations [100]:

\[
\sigma_{|E(\nu_k)|} = \frac{1}{|E(\nu_k)|} \sqrt{E_R(\nu_k)^2 \sigma_{E_R(\nu_k)}^2 + E_I(\nu_k)^2 \sigma_{E_I(\nu_k)}^2 + 2 E_R(\nu_k) E_I(\nu_k) \sigma_{E_R(\nu_k) E_I(\nu_k)}^2},
\]  
(A.4)

\[
\sigma_{\phi(\nu_k)} = \frac{1}{|E(\nu_k)|^2} \sqrt{E_I(\nu_k)^2 \sigma_{E_R(\nu_k)}^2 + E_R(\nu_k)^2 \sigma_{E_I(\nu_k)}^2 - 2 E_R(\nu_k) E_I(\nu_k) \sigma_{E_R(\nu_k) E_I(\nu_k)}^2},
\]  
(A.5)

where the variances and the covariance of \( E_R(\nu_k) \) and \( E_I(\nu_k) \) are given by:

\[
\sigma_{E_R(\nu_k)}^2 = \sum_{j=0}^{N-1} [\Delta t \cos(2\pi \nu_k t_j)]^2 \sigma_{E(t_j)}^2;
\]  
(A.6a)

\[
\sigma_{E_I(\nu_k)}^2 = \sum_{j=0}^{N-1} [\Delta t \sin(2\pi \nu_k t_j)]^2 \sigma_{E(t_j)}^2;
\]  
(A.6b)

\[
\sigma_{E_R(\nu_k) E_I(\nu_k)} = -\frac{1}{2} \sum_{j=0}^{N-1} (\Delta t)^2 \sin(4\pi \nu_k t_j) \sigma_{E(t_j)}^2.
\]  
(A.6c)

For the error analysis of a spectroscopic measurement, we need to calculate the variances of the phase difference \( \phi(\nu_k) \) and the ratio of the spectral amplitudes \( r(\nu_k) \):

\[
\sigma_{\phi(\nu_k)}^2 = \sigma_{\phi_{\text{sample}}(\nu_k)}^2 + \sigma_{\phi_{\text{ref.}}(\nu_k)}^2,
\]  
(A.7a)

\[
\sigma_{r(\nu_k)}^2 = r(\nu_k)^2 \left( \frac{\sigma_{|E_{\text{sample}}(\nu_k)|}^2}{|E_{\text{sample}}(\nu_k)|^2} + \frac{\sigma_{|E_{\text{ref.}}(\nu_k)|}^2}{|E_{\text{ref.}}(\nu_k)|^2} \right),
\]  
(A.7b)
A.1 Error propagation in the Fourier transform

A.1.1 Error calculation in transmission spectroscopy

If \( n(\nu_k) \) and \( \alpha(\nu_k) \) have been calculated from Eqs. (1.15) and (1.16), respectively, their errors due to the laser noise and the uncertainty in the determination of \( l \) are given by:

\[
\sigma_{n(\nu_k)} = \sqrt{\left( \frac{c}{2 \pi \nu_k l} \sigma_{\phi(\nu_k)}^2 + (n(\nu_k) - 1)^2 \left( \frac{\delta l}{l} \right)^2 \right)},
\]

\[
\sigma_{\alpha(\nu_k)} = \sqrt{\left( \frac{2}{l} \frac{1}{r(\nu_k)} \right)^2 \sigma_{r(\nu_k)}^2 + \left( \frac{2}{l} \frac{1 - n(\nu_k)}{n(\nu_k) [n(\nu_k) + 1]} \right)^2 \sigma_{n(\nu_k)}^2 + \alpha(\nu_k)^2 \left( \frac{\delta l}{l} \right)^2}.
\]

The first term on the right hand side of Eq. (A.9) becomes predominant for a high absorption.

A.1.2 Error calculation in reflection spectroscopy

The linear approximations made in the derivations of the following formulas are only valid for very small displacements, i.e., \( \delta x \ll c/(4\pi \nu_k) \).

\[
\sigma_{n(\nu_k)}^2 = \frac{4}{[1 + r(\nu_k)^2 - 2r(\nu_k) \cos \phi(\nu_k)]^4} \left\{ \left[ (r(\nu_k)^2 + 1) \cos \phi(\nu_k) - 2r(\nu_k) \right]^2 \sigma_{r(\nu_k)}^2 \right. \\
\left. + \left[ r(\nu_k)^3 - r(\nu_k) \right]^2 \sin^2 \phi(\nu_k) \left[ \sigma_{\phi(\nu_k)}^2 + \left( \frac{4\pi \nu_k}{c} \right)^2 \delta x^2 \right] \right\},
\]

\[
\sigma_{\alpha(\nu_k)}^2 = \frac{(8\pi \nu)^2}{c^2 [1 + r(\nu_k)^2 - 2r(\nu_k) \cos \phi(\nu_k)]^4} \left\{ \left[ r(\nu_k)^2 - 1 \right]^2 \sin^2 \phi(\nu_k) \sigma_{r(\nu_k)}^2 \\
+ \left[ (r(\nu_k)^2 + 1) \cos \phi(\nu_k) - 2r(\nu_k) \right]^2 r(\nu_k)^2 \left[ \sigma_{\phi(\nu_k)}^2 + \left( \frac{4\pi \nu_k}{c} \right)^2 \delta x^2 \right] \right\}.
\]
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List of publications

Journal articles


Presentations


- “Hydrogen-bonded organic electro-optic crystals for high-efficiency generation of terahertz waves,” invited talk at Ajou University, Suwon, South Korea, September 28, 2009.


- “Direct measurement of the optical group index dispersion,” talk at the Annual Meeting of the Swiss Physical Society, University of Zurich, February 20–21, 2007.
Acknowledgements

I would like to thank all those people who contributed to the successful completion of this thesis:

• Prof. Peter Günter for giving me the opportunity to work in his group.

• Prof. Bertram Batlogg for being the examiner for this thesis.

• Arno Schneider for being an excellent teacher and supervisor at every stage of my doctoral studies.

• O-Pil Kwon, Seong-Ji Kwon, and Mojca Jazbinšek for the synthesis and growth of OH1 crystals.

• Jaroslav Hajfler for his expert sample preparation.

• Marcel Stillhart for sharing his experience with terahertz time-domain systems based on compact femtosecond lasers with me.

• Christian Herzog and Paolo Losio for building up a professional IT infrastructure.

• Frederik (Pepino) Sulser for maintaining the group’s file server in my absence.

• Marcel Sturzenegger and Steffen Reidt for technical assistance.

• Tobias Bach for sharing the office and all the coffee breaks in the bistro with me.

• Everybody from the nonlinear optics group for the relaxing lunch and coffee breaks and interesting discussions.

• My father for his support during my studies.
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