Ultra-broadband Terahertz spectroscopy with Terahertz air photonics

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3 Self-Referenced Ultra-Broadband TRTS

3.1 Introduction

Many reports exist to date on THz generation using dual-color laser-induced air plasma, and on THz detection using air-biased coherent-detection (ABCD) [43, 49, 51, 54, 55, 64, 119]. Yet, the implementation of THz air-photonics in accurate ultra-broadband THz spectroscopy of materials has remained challenging, and only a limited number of reports exist on that subject [36, 96, 98, 103, 108]. While THz air-photonics offers unique possibilities such as direct access to the entire THz spectral range in a single measurement and very high (e.g. sub-50 fs) temporal resolution in transient THz spectroscopy, at the same time it poses new challenges, directly stemming from the ultra-wide THz bandwidth available.

As discussed in Chap. 2, most THz spectrometers traditionally operate in transmission configuration, where the THz pulses interact with the volume of the material of interest. However, in many practical cases, such as for arbitrary-thick samples, the transmission geometry cannot be implemented in a straightforward manner in the case of ultra-broadband THz spectroscopy. The reason is that most materials are often opaque in some spectral region contained in the broadband range (ca. 2–15 THz) due to the presence of optically active lattice vibrations (phonons, see e.g. Chap. 2.3.2). Since most of the THz radiation is absorbed in the material, the interaction of the THz field with the material cannot be quantified, and the advantage of the ultra-broad bandwidth of the air-photonics THz pulse is thus lost. In turn, the reflection geometry becomes a natural choice, as it allows one to utilize the full bandwidth of the THz pulse in the spectroscopy experiment. Yet the reflection geometry has been used very rarely, to date [36, 99–103], as such a configuration poses additional challenges as described in [120]. The purpose of this chapter is to provide explicit guidelines for ultra-broadband transient THz spectroscopy with THz air-photonics in reflection geometry.
In Sec. 3.3 a self-referenced technique for transient THz spectroscopy and specifically tailored for ultra-broadband THz air-photonics is presented. This self-referenced data acquisition method takes direct advantage of the very nature of ABCD detection and it minimizes the phase error naturally affecting the high-frequency components of the THz pulse (Sec. 3.2). In Sec. 3.4 we demonstrate that commonly used approximations in THz data analysis, such as that of a homogeneously excited film, are not appropriate for the correct retrieval of the optical properties from the reflectance spectra in ultra-broadband THz spectroscopy. We explore the limitations of these popular approximations. For the weak signal limit, we derive an analytical expression for conversion of the measured transient THz reflectance into the complex-valued THz conductivity spectrum of the sample which is the quantity of interest. Our theoretical findings are experimentally tested and verified by performing ultra-broadband TRTS of a thick semi-insulating GaAs wafer which exhibits a strong phonon absorption band around 8 THz [121] (Sec. 3.6). Additionally, the sensitivity to experimental errors is discussed (Sec. 3.5).

3.2 Phase Error

Unlike transmission THz spectroscopy (Chap. 2), in reflection THz spectroscopy the interaction between the THz pulse and the sample takes place mainly on the surface of the sample, therefore, the interaction strength is inherently low. As a consequence, both changes in amplitude and phase of the reflected THz pulse are small, and the retrieval of optical properties from reflection experiments is very sensitive to accurate measurements of the reflectivity phase, as pointed

![Figure 3.1. Basic principle of a TRTS in reflection geometry. The reflected THz pulses are acquired when the sample is not photo-excited (left) and when the sample is photo-excited (right).](image-url)
out already long time ago for steady-state measurements [99,101,122,123]; special precautions must be therefore taken to eliminate possible sources of phase errors [122].

In THz-TDS phase errors originate primarily from the displacement of the sample relative to the reference material when one is physically replaced by the other in the THz spectrometer. In transient THz spectroscopy (Fig. 3.1), i.e. in a pump-probe experiment, the data from the reference and the sample are acquired, respectively, from the THz reflected from the unexcited and the excited sample. When the sample is not replaced by any other reference material as in time-resolved THz spectroscopy (TRTS), the main source of phase error affecting is mostly related to a possible long-term drift or jitter of the time-offset between the THz and gating optical branches. If the photo-induced change in reflectance is small relative to the steady-state reflectance, the relative change in reflectance can be related to the transient conductivity in a straightforward

![Figure 3.2](image-url)

**Figure 3.2.** Illustration of the influence of the phase error on the conductivity retrieved from transient reflectance. Black lines: model conductivity used to calculate transient reflectance spectra. Red lines: conductivity retrieved from the transient reflectance containing an artificial phase shift corresponding to ±1 µm change in the optical path length between the THz reflected from the excited and unexcited sample. The minor micron-sized drift in the optical path can easily lead to wrong assignment of the conductivity mechanisms: the originally dispersion-free conductivity appears as a Drude response when a positive phase shift is artificially introduced, or it exhibits a signature of localization (negative imaginary part) when a negative phase shift is artificially introduced.
manner. The latter can be directly measured by using a lock-in amplifier which allows for the measurement of small transient reflectance signals (< 1%) given by the difference between the THz reflected from the excited and unexcited sample. The reference and the differential THz signals (difference between the THz interacting with the unexcited and excited sample) are typically acquired in two distinct scans that can be separated by several minutes or even hours.

We note that a time offset $\tau$ as small as 3 fs (which corresponds to only 1 $\mu$m change in the optical path length) can significantly influence the inferred material response already for the frequencies around 1 THz [122]. Since the corresponding phase shift $\phi = 2\pi \nu \tau$ is proportional to the probing frequency $\nu$, the determination of the optical properties from reflection measurements at frequencies $\geq 10$ THz critically requires the elimination of any possible source of the displacement between the THz and gating optical branches in the experiment. Figure 3.2 shows the difference between the real and inferred conductivity responses for $\pm 1 \mu$m change in the optical path length between the THz reflected respectively from the unexcited and from the excited sample. We note that similar effects also apply to the acquisition of transmission spectra of thin samples for which the sensitivity to the phase error may be comparable [124].

3.3 Self-Referenced THz Spectroscopy with ABCD

In order to improve the phase stability in transient THz spectroscopy, and to suppress artifacts due to long-term changes in the THz signal such as, for instance, drifts of the relative delay between THz and gating pulses in optical pump-THz probe measurements (OPTP), Iwaszczuk et al. [125] proposed a self-referenced data acquisition scheme based on the double-modulation of both the optical pump and the THz probe using a dual-blade optical chopper. This experimental procedure ensures that both the reference and the differential signals are acquired simultaneously in one single scan, instead of comparing two consecutive acquisitions separated by minutes or even hours.

As changes of the optical paths due to thermal-mechanical instabilities or laser power and pulse shape drifts occur on a time scale of several minutes or hours in lab time, the effects of these instabilities are drastically reduced if the differential and reference THz signals are acquired in one single scan. This method was specifically conceived for electro-optic sampling [13, 126] which directly detects a signal linear in the THz electric field. This scheme, how-
Figure 3.3. Experimental setup for ultra-broadband self-referenced THz reflection spectroscopy based on THz air-photonics.

However, cannot be straightforwardly applied to the THz air-photonics detection using ABCD [51], since obtaining a signal proportional to the THz field from ABCD would require an additional modulation step in the detection path. The methodology of our self-referenced THz spectroscopy is also based on the double-modulation approach. The first modulation channel at the frequency of $f/3$ is provided by an optical chopper transmitting every third pump pulse (Fig. 3.3). The second modulation channel is provided by the ABCD detection unit itself: the modulation is achieved by switching the high voltage bias in the ABCD detector unit, which is supplied by a square wave oscillating between $V = \pm 1.6\, \text{kV}$, at the frequency of $f/2$. In the presence of the electric field (bias plus THz electric field), a second-harmonic (SH) component of the near-infrared gating pulse is generated and measured using a photo-multiplier tube (Fig. 3.3). A dual-harmonic lock-in amplifier (AMETEK 7270) permits the simultaneous acquisition of the photo-multiplier tube (PMT) output signal at two harmonic frequencies: at the frequency of $f/6$, which becomes the fundamental modulation frequency in this measurement as explained below, and at its third harmonic $f/2$. We show below that these two modulation steps are sufficient to extract a signal that is linear in the THz field, although the SH generation is a $\chi^{(3)}$ process which is quadratic in the total applied field [51]. We note that this detection method is intrinsically different from the more conventional electro-optic sampling, which directly provides a signal linear in the THz field [126]. Under the experimental conditions shown in Fig. 3.4a-b, the intensities of the second harmonic can be written as:
Figure 3.4. Self-referenced acquisition scheme for ABCD detection. a) THz and pump pulses impinging on the sample. b) From the top to the bottom: High-voltage electric bias; THz pulse reflected from the excited (red) and unexcited (black) sample; incident gating pulses (red); second harmonic pulses (blue) in the ABCD detection. Couples of twin-signals (dashed/solid lines of the same color) are circled in red and green for the THz pulse reflected from the excited and unexcited sample respectively. c) Signals detected in the lock-in amplifier when the reference frequencies are respectively $f/6$ and $f/2$. Twin-signals (dashed/solid lines of the same color) are 180° out of phase and their vector sum is linearly proportional to the THz field (Eq. 3.2).

\[
I_{0,e}^{\pm} \propto \left| \chi^{(3)} I_{\omega} (E_{0,e} \pm E_{bias}) \right|^2 \tag{3.1}
\]

where $\chi^{(3)}$ is the third-order non-linear susceptibility of air and $I_{\omega}$ is the near infrared gating pulse intensity (cf. Sec. 1.3.2).

The subscripts and superscripts in Eq. (3.1) are used to describe the four possible SH intensities which are marked with the distinct colored circles in Fig. 3.4b. During one period of the fundamental frequency $f/6$ we encounter four different signals ($I_{0}^{+}, I_{e}^{+}, I_{0}^{-}, I_{e}^{-}$): the THz pulse probes either the unexcited sample $E_0$ (green) or the excited sample $E_e$ (red); and this is combined with
either of the two high voltage bias polarities at ABCD unit, a positive $+E_{bias}$ (dashed red/green) or negative polarity (solid red/green). In the following we refer to the signals generated from the same THz field but under opposite ABCD bias, as twin-signals. Namely, $(I_0^+, I_0^-)$ and $(I_e^+, I_e^-)$ are the two pairs of twin-signals, which can be recognized in Fig. 3.4b by the pairs of circles with the same color but different line styles.

A quick inspection of Eq. (3.1) reveals that the SH intensities contain not only the heterodyne signal (simply proportional to the THz field) but also an offset and a term quadratic in the THz field. The two latter spurious components can be eliminated using appropriate lock-in detection, which is the core of our self-referenced acquisition scheme (Fig. 3.4b-c). The input signal of the dual harmonic lock-in amplifier is formed by the vectorial sum of six phase-shifted components repeated with the fundamental frequency of $f/6$ (Fig. 3.4c). From simple algebraic considerations we find that the heterodyne detection signals corresponding to the THz fields can be obtained by summing the twin-signals in the mutual phase opposition:

$$E_{0,e} \propto (I_{0,e}^+ - I_{0,e}^-).$$  \hspace{1cm} (3.2)

When the lock-in reference is set to $f/6$, the input signal can be decomposed into three couples of twin-signals satisfying Eq. (3.2) where each couple contributes by one-third to the overall signal. This relation is illustrated in Fig. 3.4c by the pairs of opposite vectors colored with two different shades of red and green, respectively, for the THz pulse reflected from the unexcited and excited sample. The couple in red gives rise to the heterodyne signal proportional to $E_e$ and the sum of those in green is proportional to $E_0$. The overall signal at $f/6$ is proportional to the differential THz waveform:

$$S_{f/6} = k \left[ (I_0^+ - I_e^-) - 0.5 (I_0^+ - I_0^-) - 0.5 (I_0^+ - I_0^-) \right] \propto (E_e - E_0).$$  \hspace{1cm} (3.3)

where $k$ is a factor determined by the PMT and the lock-in amplifier instruments. To achieve self-referenced detection, the pure reference signal must be also acquired from an independent linear combination of $E_0$ and $E_e$. The latter can be obtained by demodulating the signal at $f/2$. As shown in Fig. 3.4c the input signal at $f/2$ can be decomposed into three couples of in-phase twin signals yielding:

$$S_{f/2} = k \left[ 2 (I_0^+ - I_0^-) + (I_e^+ - I_e^-) \right] \propto (2E_0 + E_e).$$  \hspace{1cm} (3.4)

The reference THz signal $E_0$ can be then easily reconstructed from Eqs. (3.3) and (3.4). The noise of the THz signal from the unexcited sample and that of
the THz signal from the excited sample are partially correlated because of their simultaneous acquisition. As a result, the noise affecting the differential signal $S_{f/6}$ is lower relative to that in the signals originating from separate acquisitions $E_0$ and $E_e$.

To provide an experimental proof of our self-referenced spectroscopy method, we have characterized an undoped 0.33 mm thick GaAs wafer photo-excited at 800 nm at room temperature. GaAs is an archetypical ionic semiconductor, widely used in electronics, with a direct bandgap of 1.4 eV and a Drude-like photoconductivity response [127–129]. To illustrate the operation of our demodulation method, we performed a 1D-pump scan with the THz delay line fixed at the peak value of the THz probe signal, and the optical pump being time-delayed (Fig. 3.5). For negative pump-probe delays, the average differential signal $S_{f/6}$ is zero since there is no photo-induced change in the response function of the sample. Immediately after photo-excitation, the reconstructed THz peak amplitude reflected from the excited sample $E_e$ rapidly rises to its maximum value, as the GaAs reflectivity increases in amplitude due to the presence of free carriers (the GaAs becomes slight more metallic), and then

\[ \frac{3S_{f/6}}{S_{f/2} - S_{f/6}}. \]

**Figure 3.5.** Self-referenced acquisition of a 1D pump-probe scan at the peak of the THz field for a GaAs wafer excited at 800 nm with a pump fluence of 0.35 mJ cm$^{-2}$. Lines in black and red are the simultaneously acquired signals $S_{f/6}$ and $S_{f/2}$ respectively. Lines in blue and magenta are respectively the reconstructed THz signals from the unexcited and excited sample obtained by using Eqs. (3.3) and (3.4). The quantity of interest is the relative differential reflectance (cf. next section) given by $3S_{f/6}/(S_{f/2} - S_{f/6})$. 
it slowly returns to the equilibrium level as the differential signal approaches zero. At the same time, the reconstructed reference signal $E_0$, corresponding to the THz pulse reflected from the unexcited sample, does not change upon photo-excitation for all pump-probe delays, in perfect agreement with the expectations.

As a result, the demonstrated double-modulation technique, using a simple chopper for optical pump modulation and a natural bias-switching sequence in the ABCD unit for THz detection modulation, allows one to simultaneously acquire the THz signals reflected from the unexcited and the photo-excited samples.

### 3.4 Analysis of Transient Reflectance Spectra

In this section we concentrate on the analysis of transient reflectance spectrum in the frequency domain. We assume a thick bulk sample, such that all multiple internal reflections of a probing THz pulse can be simply separated by the temporal windowing. One face of the sample is optically excited and all the pump pulse energy is absorbed within the sample (i.e. excitation density at the sample output face vanishes). Note that in our analysis we do not impose the approximation that the photoexcited layer is thin compared to the THz wavelength. In reflection geometry the principal measurable quantity is the complex transient reflectance spectrum:

$$\frac{\Delta r}{r_0} \equiv \frac{E_e - E_0}{E_0},$$  \hspace{1cm} (3.5)$$

where $r_0 = (1 - n_0)/(1 + n_0)$ is the sample reflectivity without photo-excitation and $n_0$ is the complex refractive index of the unexcited sample, at THz frequencies.

In order to calculate $\Delta r$ induced by the photo-excitation, one should solve the wave equation with a prescribed depth profile of the transient conductivity $\Delta \sigma(z)$. This can be done analytically in the limit of the small signal ($\Delta r \ll r_0$). This calculation yields a general expression valid for any sample thickness and any conductivity profile $\Delta \sigma(z)$ as shown by P. Kužel in the appendix of Ref. [120]. In this thesis, that calculus is also reported in the Appendix. In the case of a bulk sample, where multiple internal reflections can be removed, the
general expression (Eq. (A.8)) can be simplified to:

$$\frac{\Delta r}{r_0} \approx \frac{2Z_0}{n_0^2 - 1} \cdot \int_0^L \Delta \sigma(z) \exp \left[ \frac{2i\omega n_0 z}{c} \right] dz,$$

(3.6)

where $Z_0$ is the wave impedance of vacuum, $L$ is the sample thickness, and $c$ is the speed of light in vacuum. It should be noted that in an analogous formula for the transmission geometry [130], the exponential term in Eq. (3.6) is absent in the argument of the integral. In other words, in the limit of small signal the measured differential transmittance $\Delta t/t_0$ is simply proportional to the transient sheet conductivity $\Delta \Sigma$, independently of the particular depth profile of the excitation density:

$$\frac{\Delta t}{t_0} \propto \Delta \Sigma = \int_0^L \Delta \sigma(z) dz.$$

(3.7)

The difference between Eqs. (3.6) and (3.7) is very important and, consequently, the analysis of transient transmission and reflection signals must be also different. In the transmission geometry, all the charges contribute to the differential signal \textit{in phase}, which means that their spatial distribution in the $z$ direction does not play any role if their response to the THz field is linear. By contrast, in the reflection geometry the contributions to the total reflectance given by the transient conductivity of each infinitesimal layer in the photoexcited region are mutually \textit{dephased} (Eq. (3.6)). This represents an intrinsic complication: inappropriate analysis of the data may generate an additional phase error. The reflectance is strongly sensitive to the particular profile of the excitation density.

The profile of the excitation density may acquire various forms; the most common case (that of e.g. photoexcited homogeneous semiconductors) is an exponential excitation profile given by the Lambert-Beer absorption law (Fig. 3.6a):

$$\Delta \sigma(z) = \Delta \sigma_s \exp[-\alpha z].$$

(3.8)

In this case Eq. (3.6) yields:

$$\frac{\Delta r}{r_0} = \frac{2Z_0}{n_0^2 - 1} \cdot \frac{\Delta \sigma_s}{\alpha} \cdot \frac{1}{1 - \frac{2i\omega n_0}{\alpha c}},$$

(3.9)

where $\alpha$ is the linear optical absorption coefficient ($\alpha L \gg 1$) and $\Delta \sigma_s$ is the photoconductivity at the surface of the slab. It should be noted that the transient reflectance expressed by Eq. (3.6) assumes an analogous form to Eq. (3.7)
3.4 Self-Referenced Ultra-Broadband TRTS

only when the thickness \(d = 1/\alpha\) of the photoexcited part of the sample is much smaller than the shortest wavelength of the broadband THz radiation \((2\omega n_0 d/c \ll 1)\), in the so-called thin-film approximation (TFA), as shown in Fig. 3.6b:

\[
\frac{\Delta r}{r_0} \approx \frac{2Z_0}{n_0^2 - 1} \cdot \Delta \Sigma,
\]

(3.10)

where \(\Delta \Sigma = \Delta \sigma_s/\alpha\) in the case of the exponential excitation profile (Eq. (3.9)).

In many theoretical models, a step-like excitation approximation (SEA) is also used (Fig. 3.6c). In this approximation, the spatial dependence of the photoexcited layer is neglected and a homogeneous conductive layer with thickness \(1/\alpha\) is considered. The transient reflectance in Eq. (3.6) then reads:

\[
\frac{\Delta r}{r_0} \approx \frac{2Z_0}{n_0^2 - 1} \cdot \frac{\Delta \sigma_s}{\alpha} \cdot \exp \frac{2i\omega n_0}{\alpha c} \left[ \frac{2i\omega n_0}{\alpha c} \right] - 1.
\]

(3.11)

In a truly thin-film excitation limit both Eq. (3.9) and Eq. (3.11) reduce to the same form (Eq. (3.10)). For thicker excited layers, Eq. (3.10) loses its validity and Eq. (3.11) does not properly account for the profile of the excitation density. We illustrate these results on a calculation of a differential reflectance of a photoexcited GaAs wafer under normal incidence.

We consider an exponential excitation profile given by \(\alpha = 1.3\ \mu m^{-1}\) which corresponds to the linear absorption in GaAs at 800 nm [121, 127] and the dispersion of the unexcited GaAs including the strong phonon mode at \(\nu_{TO} = 8.04\) THz, in formula: \(n_0 = \sqrt{\varepsilon}\), with \(\varepsilon\) being the complex-valued dielectric function, \(\varepsilon = \varepsilon_\infty + \nu_{TO}^2(\varepsilon_0 - \varepsilon_\infty)/(\nu_{TO}^2 - \nu^2 + i\gamma\nu)\) where \(\varepsilon_0\) is the static

![Figure 3.6](image-url)

**Figure 3.6.** Photoconductive layer in the a) exponential depth-profile approximation (Eq. (3.9)), b) thin-film approximation (Eq. (3.10)) or c) step-like excitation approximation (Eq. (3.11))
permittivity value, $\varepsilon_\infty$ is the electronic contribution to the permittivity of GaAs, and $\gamma$ is the damping constant of the lattice oscillation [121]. The response of the photoexcited carriers is modeled by a Drude term: $\Delta \sigma_s = \Delta \sigma_{dc} / (1 - i 2 \pi f \tau_s)$ with $\tau_s = 250$ fs [101, 128, 129] and $\Delta \sigma_{dc} = 1 \text{ S m}^{-1}$. The photoconductivity is chosen such that $\Delta r / r_0 < 1\%$. First, we calculated the reflectance of an excited sample by numerical solution of Maxwell’s equations in a medium inhomogeneous along $z$; for this, we used the method described in [131] which transforms the problem to the solution of an ordinary differential equation. From that we deduced the differential reflectance spectra $\Delta r / r_0$. Next, we inverted equations (3.9), (3.10), and (3.11) to retrieve the photoconductivities within these approximations. The results are summarized in Fig. 3.7.

The thin film approximation (TFA), Eq. (3.10), is found to result in considerable deviations from the correct result, already at frequencies just above 1 THz (for the optical penetration depth of $1/\alpha = 0.7 \mu\text{m}$). The results obtained

![Figure 3.7. Real (solid, a) and imaginary (dashed, b) parts of the photoconductivity of a GaAs wafer retrieved within various approximations. Blue curves: input Drude-like conductivity used to calculate the transient reflectivity. Red and green curves are erroneous conductivities calculated respectively using TFA (3.10) and SEA (3.11). The conductivity retrieved using (3.9) exactly matches the blue curve in the plot. Inset: zoom of the real and imaginary parts of the calculated photoconductivities.](image)
by SEA using (3.11) are marginally better, but the agreement with the correct curve is still relatively poor. Finally, Eq. (3.9) correctly retrieves the properties of photoexcited GaAs and it proves that the knowledge of the excitation profile is crucial for the accurate analysis of the transient reflectance spectra. Note that an inappropriate use of TFA or SEA may lead to unphysical results, such as a negative-valued real conductivity in absorbing media (inset of Fig. 3.7). We also observe that the conductivity spectrum retrieved using inappropriate approximations is strongly distorted in the vicinity of the TO and LO phonon modes where it shows a clear artifact (inset of Fig. 3.7). Indeed, the equilibrium reflectance \( r_0 \) is quite high in this spectral range and this indicates that these transient data are highly sensitive to experimental errors.

It should be noted that penetration depths up to \( \sim 0.1 \mu m \) are short enough to enable the application of the TFA in the range of a few THz. The use of higher energy pump photons usually leads to shorter penetration depths. However, we have to keep in mind that such a shorter penetration depth can be considered in the evaluation of the spectra only if the photocarrier diffusion is negligible (this is the case for short pump-probe delays and/or low-mobility materials). If the carrier diffusion is important, Eq. (3.6) should be used with the appropriate depth profile of carrier concentration [128,129]. In the following part, we illustrate the sensitivity of the retrieved transient conductivity to experimental errors on a particular case of the finite time-domain scan length.

3.5 Sensitivity to Experimental Errors

The frequency resolution in the time-domain spectroscopy is \( 1/(2T) \) where \( T \) is the length of the acquisition time window; in other words, the frequency cannot be determined with an accuracy better than \( 1/(2T) \). The error in the conductivity \( \delta(\Delta \sigma) \) due to an uncertainty of the frequency \( \delta \nu \) reads:

\[
\delta(\Delta \sigma) = \frac{\partial (\Delta \sigma)}{\partial (\Delta r/r_0)} \cdot \frac{\partial (\Delta r/r_0)}{\partial \nu} \cdot \delta \nu.
\]  

(3.12)

An example of this error is shown in Fig. 3.8.

Close to a sharp TO phonon-mode and in the reststrahlen band between TO and LO modes the amplitude of the differential reflectance is strongly reduced since \( r_0 \) is simply saturated and the plasma oscillations of photocarriers cannot couple directly to the transverse mode of the lattice. As a consequence, the first term of the product at the right-hand-side of Eq. (3.12) diverges and any minor error of the transient signal \( \delta (\Delta r/r_0) \) is thus strongly amplified when
Figure 3.8. Error in the transient conductivity $\delta(\Delta \sigma)$ due to a frequency uncertainty $\delta \nu$ of 0.05 THz corresponding to the frequency resolution of a 10 ps time window. Around the reststrahlen band, the transient reflectance, therefore, the calculated transient conductivity is extremely sensitive to small variations in frequency.

the transient conductivity is calculated. As the LO phonon frequency $f_{LO}$ is approached, a sharp peak appears in the measured differential reflectivity as a sign of the interaction between the free carrier oscillations and the LO vibration of the lattice. As a result, the second term at the right-hand-side of Eq. (3.12) diverges, leading to a large error in the conductivity retrieved around the LO phonon mode.

It should be noted that the frequency and its uncertainty appearing in Eq. (3.12) can be replaced by any other relevant physical quantity and its corresponding uncertainty, such as, for instance, the refractive index of the unexcited sample $n_0$ and its uncertainty $\delta n_0$. Thus, even if the uncertainty of the conductivity is largely dominated by the standard error of the measured differential reflectance, the uncertainty of the refractive index is strongly magnified in the spectral region around the reststrahlen band and it might also be no longer negligible. This is indeed a good additional reason to exclude the frequencies around the reststrahlen band from the reliable spectral window.
3.6 Experimental Demonstration on GaAs

Let us turn back to the time-resolved reflectance experiments with an undoped 0.33 mm thick GaAs wafer photo-excited at 800 nm, and apply the analysis approaches described above to measured data. The THz reflectance spectrum was acquired at 3.5 ps after photo-excitation, using the double-modulation self-referenced technique as described in Sec. 3.3. The resulting transient conductivities retrieved using the three analysis approaches: general analysis approach using the spatially-distributed excitation profile Eq. (3.9), TFA Eq. (3.10), and SEA Eq. (3.11), are shown in Fig. 3.9.

The data points around the reststrahlen band have been discarded because of larger relative error as illustrated in Fig. 3.8. The conductivity retrieved by the general approach (Eq. (3.9), blue points in Fig. 3.9) was successfully fitted
Figure 3.10. Points: real (open) and imaginary (solid) parts of the transient conductivity of the same GaAs sample but measured at low THz frequencies in a conventional THz spectrometer. The spectrum was acquired under the same excitation conditions of Fig. 3.9 and the Drude fit (black curves) returns a scattering time ($\tau = 0.11$ ps) consistent with that one inferred from the measurements performed using the THz air-photonics setup.

using a Drude model. The Drude fitting parameters provide values of the carrier relaxation time of $0.09(1)$ ps and of the carrier density $6(1) \times 10^{16}$ cm$^{-3}$. The Drude carrier concentration is in reasonable agreement with the density of absorbed photons ($\sim 9 \times 10^{16}$ cm$^{-3}$). The inferred scattering time is consistent with of the value of $0.10(1)$ ps obtained using conventional transmission THz spectroscopy in the frequency range $0.2-2.5$ THz under the same excitation conditions (Fig. 3.10). As mentioned before in this section, when the low signal limit is not satisfied Eq. (3.9) cannot be applied. The experimental test about the validity range of (3.9) is shown in Fig. 3.11. The THz conductivities were calculated from several differential reflectance signals acquired at different excitation power conditions by using Eq. (3.9) (blue points) or by numerically solving the wave equation (black points). Only when the differential signal was below 1% Eq. (3.9) lead to the correct result.

Finally, it should be noted that broadband THz spectroscopy is more sensitive to conductivity contributions characterized by shorter carrier momentum scattering times. It can be thus highly suitable for the investigation of low-mobility semiconductors such as CdS or ZnO. For the case of high-mobility semiconductors such as GaAs, it may be possible to distinguish further contributions on top of the main Drude response, which may indicate e.g. the presence of a distribution of scattering times [128]. In this sense, ultra-broadband THz spectroscopy paves the way towards a much better understanding of fine details.
3.7 **Self-Referenced Ultra-Broadband TRTS**

![Figure 3.11](image_url)  

**Figure 3.11.** Points: real (open) and imaginary (solid) parts of the THz transient conductivity of GaAs calculated by using Eq. (3.9) (blue) and by numerically solving the wave equation (black). The spectra are taken at different pump excitation fluences respectively a) $42 \mu\text{J cm}^{-2}$, b) $10 \mu\text{J cm}^{-2}$, c) $3 \mu\text{J cm}^{-2}$. Equation (3.9) retrieves the correct values of the photoconductivity, only when the relative differential reflectance $\lesssim 1\%$ which corresponds to an excitation fluence of $3 \mu\text{J cm}^{-2}$.

of charge transport in electronic materials.

### 3.7 **Conclusions**

In this chapter we have provided general guidelines for ultra-broadband transient THz spectroscopy with THz air-photonics. We described a novel double-modulation technique specifically tailored towards using with air-based coherent detection (ABCD), which allows for self-referenced transient spectroscopy with minimal phase error over the entire ultra-broad bandwidth of the air-photonics THz signals. Additionally, we have provided an accurate conductivity retrieval
approach, which requires the knowledge of the spatial distribution of the photocarriers within the sample. This has an important implication especially for experiments carried out at long pump-probe delays where the initially exponential profile may substantially expand and change its shape due to the diffusion of the free carriers in the photoexcited sample.

In the limit of small signals, a convenient analytical expression linking the THz photo-reflectivity and THz photoconductivity was developed. At the same time, we have demonstrated that the use of popular approximations, such as TFA or SEA, is likely to result in false (and also unphysical) features in the recovered photoconductivity spectra. The applicability criteria of these approximations were discussed. Finally, we have provided an estimate of the relative error in the measured photoconductivity, caused by the spectrally sharp features in the background dielectric function of the material and the finite acquisition time of the THz scan. Our experimental protocol and the developed data analysis approach was successfully verified using the transient THz spectroscopy on GaAs, an archetypal material for this class of experiments.