



Ultra-Broadband Terahertz Spectroscopy with Terahertz Air Photonics

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# SUMMARY

The subject of this thesis is terahertz (THz) spectroscopy based on air photonics. THz spectroscopy is a well-established technique which allows for measuring the steady-state or transient dielectric properties of the materials in the THz range. As THz photons have a very low energy, typically below interband excitations, they are, for instance, ideal probes of intraband transitions and low-energy vibrational modes. Further, THz spectroscopy employs time-domain detection which provides access to the amplitude and phase spectral information of the THz pulse. As a result, the real and imaginary part of the complex-valued dielectric function of the material of interest can be directly inferred from the THz measurements.

The typical bandwidth covered by conventional THz spectrometers is often limited to the low THz frequencies ( $\lesssim 3$  THz) because of phase-matching limitations imposed by the materials employed by conventional THz transmitters and receivers. In the last decades, air-based THz sources and detectors have emerged as an efficient alternative for generating and detecting ultra-broadband THz pulses. As air is virtually non-dispersive, the optical-THz phase matching condition is automatically met. As a result, single-cycle sub-100 fs THz transients with peak field strengths up to several hundreds of kilovolt per centimeter have been generated using air-plasma sources. These ultrashort THz pulses contain a very broad spectrum extending over the entire traditional THz spectral range (0.1–30 THz) without any gaps. The exceptional performances in terms of time-resolution, bandwidth, and field strength granted by THz air photonics naturally offer unique opportunities for THz spectroscopy. In this thesis we have sampled the capabilities of THz air photonics by performing steady-state ultra-broadband THz spectroscopy of some common polymers, and transient ultra-broadband THz spectroscopy of, respectively, solution processed methylammonium lead iodide ( $\text{MAPbI}_3$ ) perovskite films and undoped gallium arsenide (GaAs). In addition, we have presented explicit guidelines for ultra-broadband transient THz spectroscopy with air-photonics, including a novel method for self-referenced signal acquisition minimizing the phase error, and a numerically-accurate approach to the transient reflectance data analysis.

In chapter 1 we have discussed the principles of THz air photonics. We have introduced the asymmetric transient current model which explains how ultrashort THz pulses can be generated in a two-color laser induced air plasma and discussed the air biased coherent detection (ABCD) which ensures heterodyne ultra-broadband detection of the THz waveforms in air. Then, we have described in detail our THz air photonics spectrometer and characterized the THz pulse. In the last part of the first chapter, we have given a first demonstration

of capabilities of our THz air photonics spectrometer in which  $\text{MAPbI}_3$  perovskites films have been measured using the THz spectroscopy in transmission and reflection geometry.

In chapter 2 we have shown the results of steady-state ultra-broadband THz spectroscopy of common polymers. Time-domain ultra-broadband THz spectroscopy is particularly useful in polymer science as many vibrational modes in polymers occur across the entire THz spectral region. Further, many polymers are often employed as materials for THz-photonics components such as THz windows, lenses, waveguides and dielectric mirrors. However, these materials are usually well characterized only at low THz frequencies while the 3–15 THz range has been rarely explored since neither conventional THz spectrometers nor Fourier transform infrared spectroscopy can often guarantee adequate performances in that spectral range. The complex-valued refractive index of low-density polyethylene (LDPE), cyclic olefin/ethylene copolymer (TOPAS<sup>®</sup>), polytetrafluoroethylene (PTFE or Teflon<sup>®</sup>), and polyamide-6 (PA6) have been measured in the 2–15 THz range using THz air photonics. LDPE and TOPAS<sup>®</sup> are very suitable as ultra-broadband THz photonics materials since both polymers have shown a spectrally-flat refractive index and negligible absorption in the entire spectral window. By contrast, resonant high-frequency vibrational modes have been observed and assigned to their molecular origin in PTFE and PA6. Additionally, their complex-valued dielectric functions have been theoretically reproduced in the entire spectral window using a multiple-Lorentzian model.

In chapter 3 we have presented the explicit guidelines for ultra-broadband transient THz spectroscopy with air-photonics. Many critical challenges inherent to this technique have been treated and resolved. As the high-frequency components of the ultra-broadband THz pulse are particularly sensitive to phase instabilities, special care must be taken to minimize the phase error. Self-referenced THz spectroscopy, as described in chapter 3, ensures the acquisition of the reference and differential THz waveforms in one single scan instead of two distinct acquisitions separated by several minutes or hours. Thus, the effects of long-term changes in the THz signals, such as drifts of the relative delay between the THz and optical branches, are drastically reduced. As most materials are often opaque in the broad spectral range of the THz air photonics spectrometer, the transmission geometry cannot be always successfully applied, especially for arbitrary-thick samples. For example, our 0.33 mm-thick GaAs sample shows a resonant absorption mode at ca. 8 THz which reduces most of the transmitted THz signal to the noise level. The advantage of the ultra-broad bandwidth of the air-photonics THz pulse is thus lost. However, thinner samples also have some drawbacks. For example, even if the sample is sufficiently thin, thus sufficiently transparent as, for instance, our 300 nm-thick films of  $\text{MAPbI}_3$ , the choice of the sample substrate is very narrow since most of the materials are not transparent in the ultra-broadband THz range.

The reflection geometry naturally comes across as the only possible way for ultra-broadband THz spectroscopy in many practical cases. However, the analysis of the transient reflectance spectra presents an intrinsic complication relative to the geometry. Indeed, in the transmission geometry, all the photo-generated

charges contribute to the differential transmittance *in phase*, which means that their spatial distribution along the direction of the THz beam does not play any role if their response is linear in the THz field. As a result, the transient transmittance is directly proportional to the sheet conductivity in the small signal approximation. By contrast, the contributions to the total reflectance given by the transient conductivity of each layer in the photoexcited region are mutually *dephased*. Thus, the spatial distribution of the charges must be also taken into account when the reflection geometry is employed and a more general expression relating the transient reflectance to the conductivity must be used. In the end of chapter 3, our theoretical findings have been experimentally tested and verified by performing ultra-broadband THz spectroscopy in reflection geometry of a thick semi-insulating GaAs wafer.

In chapter 4 we have discussed the plasmon-phonon coupling and the sub-picosecond dynamics of photocarriers in undoped GaAs. This subject has a particular scientific and technological relevance as GaAs is an archetypal semiconductor, ubiquitously used in electronics. The THz air photonics spectrometer has been employed to monitor the ultra-broadband THz photoconductivity of GaAs on a time scale smaller than the carrier-lattice interaction. Whereas the rise of the photoconductivity is instantaneous after the photoexcitation, the establishment of a screened coulomb potential takes a finite time to be set up. In a polar semiconductor such as GaAs, the longitudinal optical (LO) phonons can couple to the carrier plasma oscillations via the Fröhlich interaction thus, the plasmon dynamics is correlated to that of the phonon. The 50 fs time resolution of the air photonics THz pulse has allowed us to observe the dynamics of the photo-carriers before the many-body correlations have been established within the lattice-carrier system. Only after the constitution of the coupled plasmon-phonon modes after ca. 240 fs, the free carrier dynamics starts to be dominated by the plasmon damping. Drude fits of the photoconductivity spectra have provided estimates of the scattering time and of the plasma frequency for each pump-THz delay. However good agreement with the Drude model has been found only at pump-THz delays longer than 320 fs. In the time range from 240 to 400 fs, we have observed an increase of the scattering time from ca. 60 to 140 fs. Subsequently, the scattering time settles to the latter value at least until ca. 700 fs after photo-excitation. The plasma frequency remains largely constant over the time range 240–700 fs, as changes in the carrier density and effective mass of the photo-carriers are negligible respect to the change in the scattering time. These observations are in fair agreement with previous reports.

In summary, we have introduced a broadband, air-based THz setup, and have demonstrated its capabilities in different (transmission and reflection) geometries. The setup has been used for both steady-state spectroscopy of polymers, and time-resolved spectroscopy of photo-excited semiconductors, and has allowed for new insights into lattice vibrations and carrier dynamics in these systems.