MCGILL UNIVERSITY

DOCTORAL THESIS

Transient Multi-THz Spectroscopy of Hybrid Organometallic Perovskites

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"It is in the admission of ignorance and the admission of uncertainty that there is a hope for the continuous motion of human beings in some direction that doesn't get confined, permanently blocked, as it has so many times before in various periods in the history of man."

Richard P. Feynman

Abstract

The present thesis focus on the implementation of an air based time resolved terahertz (THz) spectrometer and its application to the study of different systems. Air plasma THz generation is ultrabroadband in nature, and is extremely useful to probe ultrafast carrier dynamics within the bandwidth of the pulse, giving important insights of the fundamental physical processes which occurs just after photoexcitation. "THz gap" as it was referred on early times, given the lack of enough sensitive detection and generation methods, nowadays has become a more investigated energy range given the important advances in the development of efficient THz emitters and detectors, however THz sources are still scarce. This thesis contributes to a small extent to fill the THz gap by reporting a new THz radiation source, showing how the widely used β -barium borate nonlinear crystal presents a strong phase stable narrowband emission at 10.6 THz with a power and crystal angular dependence consistent with an optical rectification process, owing the THz narrow emission character to efficient phase matching over a small frequency range.

THz spectroscopy measures the changes in phase and amplitude of the THz pulse field as it interacts with the sample, having access to valuable information which is encoded in the electric field changes, this allows the extraction of the optical properties of the sample. By means of multi-THz spectroscopy photoconductivity measurements were performed on a single crystal $Pb_2P_2Se_6$, a prospective material for γ -ray detectors. Clear phonon signatures were found within the bandwidth of the pulse, the temporal dynamics of the photoexcited carriers were investigated presenting a power law decay consistent with dispersive transport, finally an estimation of the mobility yielded a value of $\sim 10 \text{ cm}^2 \text{ (Vs)}^{-1}$.

The air based THz spectrometer was used to study the photoexcited carrier dynamics in large single crystal $CH_3NH_3PbI_3$ perovskite in the 4 - 125 meV energy range in order to understand its intrinsic properties. Perovskites have been widely investigated all around the world given their fascinating properties however their fundamental photophysics properties related to the free charge generation and their dynamics is not yet well understood. The work presented in this thesis, shows the measurement of the dark state dielectric function in the 25 - 100 meV range. Time resolved studies gives ultrafast dynamics of the free charges generation as well as an extremely high charge carrier mobility (500-800 cm² (Vs)⁻¹), unprecedented for a solution processed material. Signature of an exciton orbital transition was found, allowing the estimation of the exciton binding energy on the order of ~17 meV at room temperature.

Abrégé

La thèse présentée ici traite de l'implémentation d'un spectromètre térahertz (THz) résolu en temps employant l'air comme médium ainsi que son application à l'étude de différents systèmes. La génération THz à l'aide d'un filament de plasma dans l'air possède une bande spectrale ultra-large et est extrèmement utile pour sonder les dynamiques ultrarapides des porteurs de charge dans sa bande spectrale. Celle-ci donne d'importantes informations sur les procédés physiques fondamentaux se déroulant suite à une photoexcitation. Le « gap THz », terme référant au manque de méthodes de détection et de génération souvent employé durant les débuts du champ de recherche, est aujourd'hui devenu une région du spectre électromagnétique plus étudiée. C'est grâce aux avancées faites en développement des sources d'émission efficaces de radiation THz et de détection que le « gap » se referme, bien que les sources restent rares. Cette thèse contribue à remplir le « gap » en démontrant une nouvelle source de radiation THz, démontrant que le cristal de β -borate de barium, largement répandu, présente une forte émission à 10.6 THz. La dépendance angulaire cristalline de l'intensité de l'émission est consistante avec un procédé de redressement optique devant sa bande d'émission étroite à un accord de phase sur une mince bande spectrale.

Les mesures de spectroscopie THz modifient la phase et l'amplitude du pulse incident lorsque celui-ci interagit avec l'échantillon. Ceci donne accès, via l'information encodée dans le changement du champ électrique, aux propriétés optiques de l'échantillon. La photoconductivité d'un échantillon de $Pb_2P_2Se_6$ cristallin, un candidat potentiel pour les détecteurs de rayons γ , est mesurée par spectroscopie multi-sonde THz. Des signatures claires de phonons sont observées dans la bande spectrale du pulse, les dynamiques temporelles des porteurs de charge photoexcités sont étudiées, présentant une décroissance suivant une loi de puissance cohérente avec celle du transport dispersif. Finalement, une estimation de la mobilité de cet échantillon est faite à ~10 cm² $(Vs)^{-1}$.

Le spectromètre THz est employé afin d'étudier les dynamiques de porteurs de charges photo-injectés dans le pérovskite cristallin $CH_3NH_3PbI_3$ dans la gamme d'énergies de 4 à 125 meV afin de mieux comprendre ses propriétés intrinsèques. Les pérovskites ont été largement étudiés partout dans le monde dû à leur propriétés fascinantes. Toutefois, leur propriétés photo-physiques fondamentales liées à la génération de porteurs de charges libres ainsi qu'à leurs dynamiques ne sont toujours pas bien comprises. Le travail présenté dans cette thèse présente les mesures de la fonction diélectrique dans l'état sombre entre 25 et 100 meV. Une étude résolue en temps des dynamiques ultrarapides de la génération des porteurs de charge libres démontre une mobilité extrêmement haute ($500-800 \text{ cm}^2 \text{ (Vs)}^{-1}$), du jamais vu pour un matériau traité en solution. La signature d'une transition excitonique orbitale est observée, permettant l'estimation de son énergie de liaison, soit ~17 meV à température ambiante.

To my parents Carlos Eduardo and Margarita

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Multi-Cycle Terahertz Emission from β-Barium Borate

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Chapter 3 is based on this published manuscript. The author of this thesis performed the experiments, data analysis and manuscript preparation. D. Cooke supervised the experiment and assisted in data analysis as well as in preparing the manuscript.

Charge Transport Mechanisms in a Pb₂P₂Se₆ Semiconductor

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Contents

Al	Abstract iii					
Ac	Acknowledgements ix					
Co	ontrik	outions		xi		
1	Intr	oductio	n	1		
	1.1	THz R	adiation	3		
	1.2	Terahe	ertz Spectroscopy	6		
	1.3	Narro	wband THz Emission from β -Barium Borate	8		
	1.4	THz S	tudy of Gamma Ray Detector Material	9		
	1.5	Hybri	d Metal Halide Perovskites	10		
		1.5.1	Charge Carrier Mobility	11		
		1.5.2	Exciton Binding Energy	12		
		1.5.3	Multi-THz time resolved spectroscopy	14		
2	Exp	erimen	tal Methods	15		
	2.1	THz C	Generation and Detection Mechanisms	16		
		2.1.1	Photoconductive Antenna	17		
		2.1.2	Optical Rectification	18		

		2.1.3	Air Plasma THz Generation	23
		2.1.4	Air Plasma THz Detection - ABCD	28
	2.2	Time-	Domain THz Spectroscopy	31
		2.2.1	Fresnel Equations	31
	2.3	Time-	Resolved THz Spectroscopy	36
		2.3.1	1-Dimensional Scan	36
		2.3.2	2-Dimensional Scan	37
		2.3.3	Time-Resolved THz Spectrometer - Delay Lines	39
		2.3.4	Thin Film Approximation	41
		2.3.5	Drude Model	43
		2.3.6	Lorentz Model	47
	n for Multi-Transient THz Spectroscopy -			
		Techn	ical Description	50
		2.4.1	Ultrafast Ti:Sapphire Amplifier	50
		2.4.2	Time-Domain THz Spectrometer	51
		2.4.3	Time-Resolved THz Spectrometer in Transmission	52
		2.4.4	Artifacts that can Arise - Group Delay	54
		2.4.5	Time-Resolved THz Spectrometer in Reflection	56
		2.4.6	Technical Details	57
3	Nar	rowbar	nd THz Emission from β -Barium Borate	65
	3.1	Abstra	act	66
	3.2	Introd	luction	66
	3.3	Exper	imental	68
	3.4	Result	ts and Discussion	70

xiv

	3.5	Conclusion	77			
4	Cha	Charge Transport Mechanisms in a New Gamma Ray Detector Material				
	4.1	Introduction	80			
	4.2	Optical Pump – THz Probe in Reflection	81			
	4.3	Non-Drude Conductivity	84			
	4.4	Mobility Estimation	89			
5	Hyb	orid Metal Halide Perovskites	91			
	5.1	Abstract	92			
	5.2	Introduction	92			
	5.3	Methods	95			
		5.3.1 Sample preparation	95			
		5.3.2 THz spectroscopy	95			
	5.4	Results	97			
	5.5	Conclusions	109			
6	Con	clusions	111			
Bi	Bibliography 11					

List of Figures

1.1	Electromagnetic Spectrum - THz Gap	3
1.2	Air Plasma THz Emission vs ZnTe	5
2.1	Schematic of Photoconductive Antenna	18
2.2	Schematic of Optical Rectification	19
2.3	Schematic of Free Space Electro-Optic Detection	22
2.4	Two Color Air Plasma THz Generation Schematic	24
2.5	Laser Field Asymmetry	26
2.6	Electron Drift Velocity	27
2.7	ABCD THz Detection Schematic	30
2.8	Transmission and Reflection of Light at an Interface	32
2.9	Incident, Transmitted and Reflected Fields in Sample of Thickness d	33
2.10	THz Pulse Propagated in Air and Through 500 μ m Silicon $\ldots \ldots \ldots$	34
2.11	Extracted refractive index of a 500 µm Silicon sample	35
2.12	Time Resolved THz Spectroscopy - 1D Scan	37
2.13	Time Resolved THz Spectroscopy - 2D Map	38
2.14	Schematic of Pulses used in a TRTS Experiment	39
2.15	Drude Model Conductivity	45
2.16	Silicon Optical Conductivity	46

xviii

2.17	Lorentz Model Conductivity	49
2.18	Laser System Schematic	50
2.19	Setup TDS Transmission	52
2.20	Setup TRTS Transmission	53
2.21	THz Propagation through GaAs	54
2.22	Group Delay Transmission	55
2.23	Setup TRTS Transmission vs Reflection geometries	56
2.24	THz water vapor absorption	57
2.25	Schematic of THz Plasma Phase Difference	59
2.26	ABCD Linearity	61
3.1	BBO THz Generation Schematic	68
3.2	BBO THz Generation Setup	69
3.3	Time Domain Electric Field	70
3.4	Fourier Power Spectrum	71
3.5	THz Electric Field Dependence on the Pump Energy	72
3.6	Multi-THz Transmission Through β-BBO	73
3.7	Refractive Index of β-BBO	74
3.8	Coherence Length	75
3.9	2D Angular Dependence	76
3.10	Angular Dependence Polar Plot	77
4.1	Picture of γ -ray material Pb ₂ P ₂ Se ₆	81
4.2	Reflected multi-THz pulse from $Pb_2P_2Se_6$	83
4.3	Amplitude and Phase of Δr	84

4.4	Fluence Dependence of Δr	85
4.5	Fluence Dependence of Δr - Log-Log Plot	86
4.6	Power Law Fits	87
4.7	THz Transmission Through $Pb_2P_2Se_6$	88
5.1	Schematic of Time-Resolved multi-THz Spectroscopy	96
5.2	Multi-THz Pulses after Interaction with Single Crystal $CH_3NH_3PbI_3$	97
5.3	Fourier Amplitude Spectra of multi-THz pulses	98
5.4	Dark State Dielectric Function of Single Crystal $CH_3NH_3PbI_3$	99
5.5	Reflected multi-THz Transient from $CH_3NH_3PbI_3$	100
5.6	Amplitude and Phase of $\Delta \tilde{r}$	101
5.7	Model of the Complex Refractive Index	102
5.8	Complex Conductivity Spectrum	104
5.9	Charge Carrier Generation Efficiency	105
5.10	Charge Carrier Mobility	106
5.11	Exciton 2-D Δr and Vertical Cuts	107

List of Abbreviations

ABCD	Air Biased Coherent Detection
APD	Avalanche Photo Diode
β-ΒΒΟ	beta-Barium BOrate
FFT	Fast Fourier Transform
FWHM	Full Width at Half Maximum
FWM	Four Wave Mixing
IR	Infra Red
MAPI	MethylAmonium Lead Iodide
OPA	Optical Parametric Aamplifier
OPTP	Optical Pump Terahertz Probe
PMT	Photo Multiplier Tube
SHG	Second Harmonic Generation
TDS	Time Domain Spectroscopy
TFISH	Terahertz Field Induced Second Harmonic
THz	Tera Hertz
TRTS	Time Resolved Terahertz Spectroscopy

Physical Constants

Speed of Light	$c = 2.997\ 924\ 58 imes 10\ ^8\ [m/s]$
Planck constant	$h = 6.626\ 0.69\ 934 \times 10^{-34}\ [J{\cdot}s]$
Charge of electrons	$e = 1.602 \ 176 \ 620 \times 10^{-19} \ [C]$
Mass of electrons	$m_e = 9.109\ 383\ 56\ \times\ 10^{\text{-}31}\ [kg]$
Boltzmann constant	$k_B = 1.380\;648\;52\times10^{\text{-}23}\;[J/K]$
Permittivity of free space	$\epsilon_0 = 8.854\ 187\ 817 imes 10^{-12}\ [F/m]$
Permeability of free space	$\mu_0=4\pi\times10^{\text{-7}}[H/m]$
Free space impedance	$Z_0 = 376.730\ 313\ 461\ [\Omega]$

List of Symbols

Е	Electric Field	[V/m]
Р	Polarization	$[C/m^2]$
J	Current Density	$[A/m^2]$
χ	Electric Susceptibility	
$ au_p$	Pump Probe Time	[s]
$\widetilde{\mathbf{T}}$	Complex Transmission Function	
Т	Amplitude Transmission Function	
φ	Phase Transmission Function	
$\widetilde{\mathbf{n}}$	Complex Refractive Index	
n	Real Refractive Index	
к	Imaginary Refractive Index	
α	Absorption Coefficient	[cm] ⁻¹
$\widetilde{\epsilon}$	Complex Relative Permittivity	
ϵ_1	Real Relative Permittivity	
ε_2	Imaginary Relative Permittivity	
σ_{dc}	DC conductivity	[S]
$\widetilde{\sigma}$	Complex Conductivity	[Ω·cm] ⁻¹
σ_1	Real Conductivity	[Ω·cm] ⁻¹

σ_2	Imaginary Conductivity	[Ω·cm] ⁻¹
ω_{p}	Plasma Frequency	[s] ⁻¹
n _d	Charge Carrier Density	[cm ⁻³]
τ	Charge Carrier Scattering Time	[s]
μ	Charge Carrier Mobility	[cm ² /s]
ω	Angular Frequency	[s] ⁻¹
d	Penetration Depth	[m]
m*	Effective Mass	[kg]
E_b	Exciton binding energy	[eV]
F	Fluence	[J/cm ²]
R	Reflection Coefficient	

Chapter 1

Introduction

Since ancient times, scientists have been captivated by the interaction of light with matter. The desire to understand this interaction has pushed the development of new radiation sources and several advanced linear and nonlinear spectroscopic techniques. The historically difficult to access frequency window between infrared and microwaves (0.3 - 30 THz) defined as Terahertz (THz) radiation is both of fundamental importance to understanding low energy, meV scale excitations in materials, as well as technologically important parameters such as conductivities, lifetimes and mobilities. Although not visible for the human eye, its range of energy is ideal to probe a variety of low energy physical processes including intraband transitions [1], lattice and molecular vibrations [2–5], excitons [6] and free charge carrier dynamics [7, 8].

Prior to 1989, the lack of efficient emitters and sensitive detectors operating in the THz frequency range lead to researchers referring to this region as the "THz gap" [9]. Nowadays, THz technology has made significant progress driven primarily by the advances in femtosecond laser science and photoconductive or nonlinear optical techniques to generate and detect few cycle, phase-stable pulses of THz light (THz pulses) with dynamic ranges exceeding 10⁶ (in power) [10]. These pulses are ideal for

spectroscopic investigations of materials across the entire THz spectral region. By coherently detecting the THz pulse electric field and comparing transmitted or reflected pulses interacting with a sample and a reference (usually vacuum), the amplitude and phase changes of the THz pulses allow direct extraction of the sample's complex optical properties (dielectric function, conductivity or index of refraction, equivalently). Moreover, the short pulse character of THz pulses and the perfect synchronization to a femtosecond optical pulse train enables an optical pump - THz probe scheme called time-resolved THz spectroscopy where time-energy maps can be measured with few fs and sub-meV precision. This has enabled several fundamental studies into the ultrafast properties and dynamics of low energy excitations in matter that cannot be probed through any other technique [11].

This chapter introduces the reader to THz radiation, optical techniques to access this region and spectroscopic applications of time-resolved THz spectroscopy (TRTS) and time-domain THz spectroscopy (TDTS) to different systems. In this thesis, an air plasma-based THz setup capable of generating pulses covering the entire THz gap was constructed and baseline tests on standard, well understood materials were conducted. This setup was the main experimental tool for this thesis. Numerical code was developed to better understand and interpret the spectroscopic time-energy maps, and account for several artifacts that arise due to mixing of temporal and energetic information from dispersion. This setup was used to measure for the first time narrowband THz emission from the most commonly used nonlinear optical crystal in femtosecond laser labs: β BBO crystal. In the chalcophosphate compound Pb₂P₂Se₆, a next generation gamma ray detector material, TRTS is used to measure picosecond photoconductivity dynamics of photoexcited carriers, critical for device performance. Finally,



FIGURE 1.1: Electromagnetic spectrum showing the THz region.

we have applied our multi-THz spectrometer to elucidate several fundamental optoelectronic properties of the recent rediscovered and intensely studied single crystal hybrid organometallic perovskite CH₃NH₃PbI₃. Our findings answer several important fundamental questions that define the limitations of this material which is of increasing importance for next generation optoelectronic devices including photovoltaics and lasers.

1.1 THz Radiation

The THz region of the electromagnetic spectrum is located between the infrared and microwave region and is depicted in Fig. 1.1, loosely defined as between 0.1 THz and 30 THz [12]. In understanding THz light-matter interactions, the energy scale is important to place relative to the rest of the spectrum: 1 THz corresponds to 10^{12} Hz, has a period of 1 ps, a wavelength of 300 μ m, a photon energy of 4.14 meV, and corresponds to around 1/6 of the thermal energy available at room temperature:

$$1 \text{ THz} = 10^{12} \text{ Hz} = 1 \text{ ps} = 300 \text{ }\mu\text{m} = 48 \text{ K} = 4.14 \text{ meV}$$

The microwave and infrared region have numerous efficient sources and detectors, however historically this has not been the case for the THz region as there are no quantum detectors for THz and the thermal background is high for incoherent detection. For many years THz sources and detectors were scarce given that we are surrounded by sources of incoherent light (room temperature is around 25.6 meV, or 6 THz).

The development of femtosecond lasers over the last decades led to the growth of THz generation, detection and spectroscopy techniques, photoconductive antennas and optical rectification became the common way to generate and detect broadband THz pulses [10]. Free-space broadband THz pulses were first generated and detected by means of photoconductive antennas [9], where an above band gap short laser pulse is used to generate free carriers in a semiconductor under an applied electric field and the carriers will be accelerated generating the electromagnetic pulse. Although this method can be used at high frequencies, the intensity is low and the bandwidth is ultimately limited by the material response [7].

Due to its simplicity, optical rectification of femtosecond pulses became a common method to generate broadband THz pulses [13–15]. In this method, a χ^2 nonlinear medium is used for the emission of a THz pulse in a co-linear, phase matched geometry, making it easy to align. However a phase matching condition needs to be satisfied, the THz phase index and the optical pulse group index are required to be similar for efficient THz generation. Mismatch in this quantities will ultimately limit the bandwidth of the emitted THz pulse as they walk off one another in time and space during propagation through the crystal. Optical phonon dispersion present in the material will strongly limit the emitted field as well as reabsorb the emitted THz field. An example of optical rectification is shown by the red dotted line in Fig. 1.2, where a 0.5 mm ZnTe



FIGURE 1.2: (a) Example of an Air Plasma THz emission (blue line) compared with a emission from ZnTe (red dotted line) and (b) their corresponding Fourier amplitude spectra.

crystal is used to generate a THz pulse. Its corresponding Fourier components mainly die at around 3 THz due to an optically active phonon located a 5.3 THz [16]. Above this phonon, some frequency components are still present however they are very weak.

Some of the restrictions present in the optical rectification process can be avoided by changing the nonlinear medium to a gas [17]. Although a different physical process, it has been shown that the nonlinear interaction of a two-color femtosecond laser pulses, within an induced plasma generates an ultra short, single-cycle THz pulse [18] as the one shown by the blue line in Fig. 1.2. The THz pulses generated by this method are limited only by the bandwidth of the femtosecond laser pulse since no phase matching constraints are present nor phonons need to be taken into consideration. In addition, simple homonuclear gases such as nitrogen do not have rotational transitions in the THz range. For these reasons an ultrabroadband bandwidth is contained within the pulse and can cover the full THz gap, spanning frequencies from 0.1 up to 40 THz

[19]. These type of ultrabroadband pulses are also called multi-THz pulse, and allows the realization of THz spectroscopy over an extremely wide energy range unavailable until recent years.

1.2 Terahertz Spectroscopy

Early studies on the far infrared spectral region were performed through the Fourier transform infrared (FTIR) spectroscopy where Fourier transformation of an interferogram was done to determine a spectrum [20]. Here, the dielectric function and optical conductivity are determined from reflectivity spectrum by Kramers-Kronig analysis. With the advent of ultrashort laser pulses it has been possible to achieve time resolved far infrared studies with a subpicosecond temporal resolution. The great advantage of Terahertz spectroscopy is the measurement of the THz electric field pulse itself rather than its intensity. Given that, the amplitude and phase are directly related to the index of refraction and the absorption coefficient of the sample, the complex valued conductivity $\tilde{\sigma}(\omega)$, is directly extracted without the use of the Kramer-Kroning relations.

Ultrabroadband THz pulses, allow the characterization of the optical properties of a material in that frequency range. The simplest method to perform THz spectroscopy is called THz time-domain spectroscopy (THz-TDS), where the THz pulse electric field is time-sampled coherently, that is, the amplitude and phase are obtained. This technique allows the study of the interaction between the THz electromagnetic field and the sample probing its equilibrium properties. Some of the first THz-TDS studies in 1989 mapped THz absorption by water vapour [21], and were later applied to dielectrics and semiconductors [22]. Time-resolved THz spectroscopy (TRTS) is a pump-probe technique which emerged from the development of ultrafast lasers, making possible to study the photoexcited optical properties of a material and the ultrafast phenomena on the sub-picosecond time scale. There are two different experiments which can be performed with TRTS, in one the peak transmission is monitored at a single point as a function of pump-probe time giving frequency averaged dynamics, while the other experiment consists in acquiring full frequency resolved scans collecting the full THz waveform a function of pump-probe time. Ultrashort pulses interact with the material inducing a photoexcitation, the time evolution of the amplitude and phase of the THz pulses are obtained by means of this experiment. Most of the time-resolved studies in the THz region are reported in the spectral region between 0.1 to 3.0 THz [7, 8, 23], however difference frequency generation has opened the window to study properties in the 10 to 72 THz range [24] with phase-stable multi-THz pulses.

THz spectroscopy is a valuable tool for condensed matter physics, since this frequency region covers many fundamental excitations such as the plasma formation in semiconductors [11], lattice vibrations in solids [2], exciton orbital transitions [6, 25] and energy gaps of BCS superconductors [26]. Many of these processes occur beyond the previous probed THz range, hence the great importance to have and ultrabroadband THz setup to characterize the optical properties and photophysical processes in a broad energy range. THz has also found many applications ranging from security through imaging and sensing of explosives, weapons and drugs [27] to non-destructive testing and now high speed wireless communications [12]. THz microscopy has pushed this to sub-wavelength dimensions, enabling microscopic THz responses to be mapped in space and time [28–30]. It is expected in the near future that THz will also have a big impact on biomedical imaging and genetic diagnostics [31]. The future commercial exploitation of the THz spectrum is without a doubt only a matter of time, however enabling technologies are continually being developed.

1.3 Narrowband THz Emission from β-Barium Borate

Terahertz sources with a narrow bandwidth, carrier envelope phase stability and spectral tunability are desirable for applications in imaging and sensing [32], as well as driving material phonon resonances with strong electromagnetic fields [33] or other collective modes. However, narrowband THz generation from bulk nonlinear media usually requires temporal or spatial patterning of the optical photoexcitation [34, 35] or patterning of the nonlinear generation medium [36]. Narrowband THz emission by optical rectification from a bulk crystal of $Bi_4Ge_3O_{12}$ at 2 THz with a ~0.026 THz bandwidth [37] has been reported, however it is currently a challenge to provide narrowband sources in the 5 - 15 THz range [38]. The ultrabroadband nature of the air biased coherent detection (ABCD) THz detection technique, with a bandwidth greater than 30 THz, leads to the detection of any radiation source located within this bandwidth. Owing to this high bandwidth, it was possible to identify and characterize a 10.6 THz narrowband emission arising from of a commonly used non-linear crystal: β -barium borate [39] and is the topic of chapter 3. A linear dependence of the amplitude of the THz field with the incident pump energy was found, and together with an azimuthal angular dependence allowed to identify the THz generation mechanism as an optical rectification process, with the narrowband nature of this emission attributed to efficient phase matching being satisfied only over a narrow range.

1.4 THz Study of Gamma Ray Detector Material

Chalcophospate compounds have been considered as promising new materials for Xray and γ -ray detection. Particularly, heavy metal selenophospates Pb₂P₂Se₆ have an indirect band gap of 1.88 eV and a high dark resistivity around $1 \times 10^{10} \Omega \cdot cm$. The electron carrier mobility-lifetime product of the Pb₂P₂Se₆, used as a figure of merit for high energy photon detection, has been calculated to be 3.5×10^{-5} cm²V⁻¹. This is a relatively low mobility–lifetime product when compared to other X-ray and γ -ray detection materials such as CsPbBr₃ or CdZnTe [40], however the material exhibits good photocurrent response at ~ 40 keV [41]. In order to fully assess the suitability of this material, an optical pump - THz probe characterization was performed [42]. In chapter 4, multi-THz spectroscopy is performed on a single crystal Pb₂P₂Se₆ and the spectral response allowed identification of multiple phonon responses within the bandwidth of the THz pulse, consistent with previously reported studies [43]. Time-resolved THz spectroscopy results revealed a power law photoconductivity decay, which violated the usual assumptions of recombination being governed by a simple exponential relaxation, indicating dispersive transport. An estimate of the charge carrier mobility of $\sim 10 \text{ cm}^2 \text{ (V} \cdot \text{s})^{-1}$ is found, based on the frequency averaged response, which is low when compared with other materials [40]. Given that, improvements on the growth of Pb₂P₂Se₆ is needed to avoid the incorporation of oxygen, this would lead to get a better photoresponse and consequently an improved γ -ray detection [42].

1.5 Hybrid Metal Halide Perovskites

Hybrid inorganic-organic halide perovskites with chemical formula ABX₃, where A is the organic cation (CH₃NH₃⁺ or NH₂CH=NH₂⁺), B is the inorganic metal (Pb²⁺, Sn²⁺ or Ge²⁺) cation and X is the halide (Cl⁻, Br⁻ or I⁻), are solution processable materials that have good absorption across the visible spectrum, efficient mobile charge generation and long carrier lifetimes, making them highly suitable for photovoltaic applications. Solar cell devices based on this material have shown power conversion efficiencies which have climbed in only a few years from 3.8% in 2009 [44] to 22.1% in 2016 [45, 46]. Efforts are being made with already very promising results in the use of these materials as light emitting devices [47] and even lasers [48]. There has been an enormous research effort on these materials towards the understanding their intrinsic photophysical properties, with several open questions relating directly to their use as optoelectronic devices.

Methylammonium lead iodide (CH₃NH₃PbI₃, or MAPbI₃) is the best studied compound having exhibited the highest conversion efficiencies due to good absorption over the visible range with its band gap of 1.56 eV. Most of the reported work on the photoexcited state, and charge carrier dynamics was initially performed on thin films [49], however it is known that the microscopic morphology of films can strongly influence both mobilities and optical properties. Extracted properties can be strongly influenced by the specific deposition process, crystallinity or and grain size, defects, etc. In order to understand the intrinsic properties of MAPbI₃ spectroscopic studies of single crystal samples are desirable just as the knowledge of inorganic semiconductors were driven by improvement in synthesis. Inspiration can be taken from a notable quote by Wolfgang Pauli: *One shouldn't work on semiconductors, that is a filthy mess. Who knows whether*
any semiconductors exist. Synthesis of large perovskite single crystals, on the order of several millimeters in size, have only become available recently and their THz properties are the main topic of this thesis [50, 51].

1.5.1 Charge Carrier Mobility

Charge carrier mobility in hybrid metal halide perovskites is a matter of debate in the community given the wide range of reported values [52]. The fundamental processes that limits the charge carrier mobility still requires a better understanding. Mechanisms that restrain charge carrier mobility in these systems can be separated into extrinsic (such as grain boundaries or impurities) and intrinsic (inherent material properties). Reported mobilities in MAPbI₃ films vary from few cm² (V·s)⁻¹ up to 71 cm² (V·s)⁻¹, with an average of 37 ± 18 cm² (V·s)⁻¹ [52–58]. The principal limiting factor on the mobility in films, and the origin of the large deviation in the reported mobility values is the grain size. In films the microstructure is such that grain sizes are limited from tens to hundreds of nm, where larger grain sizes give higher mobility [57]. Extrinsic scattering mechanisms dominate the mobility in films, and so for devices, these are likely to be the ones that matter. Still, if one would like to push the limits, it is of importance to know what are the intrinsic scattering mechanisms that limit the mobility.

Pursuing this interest, it has recently been possible to grow metal halide perovskites single crystals [50]. Mobilities for MAPbI₃ single crystals are higher than in films (usually around 100 cm² (V·s)⁻¹ [54, 59–61], but up to 600 cm² (V·s)⁻¹ [62]). Different mechanisms have been proposed in order to explain the fundamental limits of the mobility in MAPbI₃. Acoustic phonon deformation potential has been considered to have a low contribution, ab initio theoretical calculations predict mobilities of several thousand

cm² (V·s)⁻¹ [63, 64] which is diminished when including Rashba effects [65]. An experimental study claimed a T^{-1.5} temperature dependence in agreement with acoustic phonon deformation potential, however the room temperature obtained mobilities of 27 cm² (V·s)⁻¹ do not agree with theoretical calculated value [66]. Therein, other studies suggest that Frölich interactions between carriers and LO phonons are the mechanism that limits the mobility at room temperature and is in agreement with theoretical calculations which yields charge carrier mobilities of ~100 cm² (V·s)⁻¹ [67]. It has also been reported that in MAPbI₃ there is a very low deformation potential and strong piezo-electricity. Suggesting that the carrier mobility is limited by piezoelectric scattering yielding mobility values in the range of several thousand cm² (V·s)⁻¹ [68].

It is important to note that dc measurements of carrier mobility typically are sensitive to the surface of materials, which is very sensitive to environmental degradation [69] and can even degrade due to the electric fields applied under test [70]. Non-contact measurements of carrier mobility on large, high quality single crystal samples are required to test these scattering mechanisms, which is addressed in this thesis through multi-THz spectroscopy.

1.5.2 Exciton Binding Energy

As part of the interest to know the nature of photoexcited states of metal halide perovskites, a question arises regarding whether there are free charges upon excitation or if bound excitons are present [49]. If most of the created carriers are excitons, an extra energy needs to be given to the system, the exciton binding energy, E_b , to separate the electron and the hole so that they can contribute to the photocurrent in a solar cell device. Time resolved measurements have found that there are free charges upon excitation in MAPbI₃ within ~1 ps [53, 71]. Many measurements have been performed to determine the intrinsic binding energy of the exciton in MAPbI₃, however there is a large spread in the values between 2-62 meV [72–80]. These values span the room temperature thermal energy of 25 meV, and so no conclusive decision can be made as to whether or not the exciton binding energy is important.

There are some important aspects which must be considered when determining the exciton binding energy. MAPbI₃ undergoes a phase transition at ~162 K, below is orthorhombic, above is tetragonal up to ~327 K where it undergoes another phase transition to cubic [81]. The extraction of E_b from temperature dependence measurements is only valid for certain phase and can not be extrapolated. Furthermore, the issue of morphology arises again, since grain size could affect the E_b value, a recent study found E_b values independent of grain size [82].

The values of E_b previously calculated depend on the electric permittivity, ϵ , given its relationship $E_b \propto 1/\epsilon^2$, however this task should be carefully done since ϵ changes in the THz range as it has a phonon at 1 THz and another at 2 THz [83]. The correct value of ϵ to be used is still under debate, either the high frequency dielectric constant or low frequency component can not be used reliably given that there are phonons located in the same energy range of E_b , for this reason a extraction of E_b assuming a value of ϵ should be avoided. Determining E_b from the analysis of absorption spectra near the band edge as a function of temperature in certain range, has suggested values of 55 \pm 20 meV, assuming the presence of homogeneous and inhomogeneous broadening [77]. Alternative studies, analyze the full shape of the absorption spectra using Elliott's theory to provide a value for E_b but again varies from 5 to 25 meV [72, 79, 84, 85]. Other method which is less sensitive to lineshape broadening, reported values of $E_b = 29 \text{ meV}$ at room temperature [80].

Recently it has been reported the determination of E_b from magneto-absorption measurements [76]. The authors report a value of $E_b = 16$ meV at low temperature in the orthorhombic phase. The advantage of this method is that it is a direct measurement without any assumption of ϵ , however they were unable to go well above the orthorhombic to tetragonal transition temperature at 160 K and still resolve the excitonic signature in the magneto-absorption spectrum. A room temperature estimate of the exciton binding energy, however, has yet to be made and will be presented in this thesis.

1.5.3 Multi-THz time resolved spectroscopy

Several important energy scales in MAPbI₃ are covered by the 4-125 meV bandwidth of the air plasma THz setup, including charge carrier scattering rates, optical phonons and excitons. In chapter 5, multi-THz pulses are used to study single crystal CH₃NH₃PbI₃ perovskites [62]. From time-domain THz spectroscopy, the dark state dielectric function was extracted in the 25 - 100 meV range, and signatures of phonon absorption were identified. Time-resolved THz spectroscopy measurements revealed that MAPbI₃ has band transport that follows a simple Drude response. From this analysis, record high mobilities for a solution processed semiconductor up to ~ 800 cm² (V·s)⁻¹ were obtained. Direct observation of exciton dissociation was possible through these measurements via an orbital transition over picosecond time scales, time correlated with the creation of free charges. This allowed us to estimate an exciton binding energy of 17 meV for MAPbI₃ in the room temperature tetragonal phase.

Chapter 2

Experimental Methods

Research in the THz part of the electromagnetic spectrum grew significantly from the beginning of the 1990s owing to the important advances in femtosecond laser sources and photonics. Starting with classic THz generation mechanisms that have now been used for decades, photoconductive antennas and optical rectification, it has since moved on to more complicated techniques such as tilted pulse front optical rectification, capable of achieving immense peak electric fields in a single cycle THz pulse, or two-colour laser induced plasma THz generation, a recent technique capable of achieving THz bandwidths well over ten times greater than the previous classic methods. These THz pulses can be used in a time domain THz spectroscopy (THz-TDS) to extract the optical properties of materials (complex conductivity, index of refraction or dielectric function, equivalently). With the introduction of a perfectly synchronized femtosecond optical pump pulse for photoexcitation of a sample, time-resolved THz spectroscopy (TRTS) was born. It then became possible to determine the dynamics of these optical response functions after photoexcitation on a sub-picosecond time scale. Measuring THz photoconductivity dynamics, for instance, made it possible to track charge densities and

scattering mechanisms of a material as they evolved through to equilibrium with subps resolution. No other technique was capable of this, and to this day TRTS remains an enormously powerful tool to investigate photoconductivity dynamics in materials [7].

A crucial aspect in extracting the optical properties of a material in TRTS is the data acquisition, which can be performed in two ways, typically: a 1-Dimensional scan only monitors one point in the THz electric field transient and provides a frequency-averaged response of the system while a 2-Dimensional scan measures the full THz waveform for each pump probe delay time, creating a 2-D time-energy map. The aim of this chapter is to briefly present the classical THz generation techniques, then move to a more detailed discussion of the generation of THz in air via a two-colour laser induced plasma and the detection of THz pulses in air with the air-biased coherent detection (ABCD) technique. Then the THz-TDS and TRTS techniques are discussed an some examples are presented. Finally, some technical design considerations used in the air based time-resolved THz spectrometer are presented.

2.1 THz Generation and Detection Mechanisms

This section will present three common ways of generating broadband THz pulses with femtosecond laser pulses, along with their corresponding detection schemes: Photoconductive antennas, optical rectification in a non-linear medium and THz generation through plasma ionization in air, the latter allows for ultrabroadband pulses reaching bandwidths that cover the whole THz gap.

2.1.1 Photoconductive Antenna

One of the first methods used to generate and detect THz pulses was through the use of photoconductive antennas. Their operation is based on the Auston switch developed in 1975, where THz pulses generated were confined to a transmission line, limiting their use in spectroscopy [86]. However at the end of 1980s a breakthrough occurs when it was reported the free space propagation of THz pulses emitted from photoconductive antennas [9, 87–90], this simplified THz spectroscopy since a sample could be placed in between emitter and detector, allowing the measurement of THz absorption by water vapor [21], dielectrics, semiconductors [22] and polar liquids [91] to cite some examples. The basic operation of a photoconductive antenna relies on the acceleration of free carriers in a semiconductor, the schematic diagram of this process is shown in Fig. 2.1(a). A short pulse from a laser with above bandgap energy generates carriers in the conduction band of a semiconductor under an applied bias voltage. The bias voltage accelerate this new charges and creates a current J(t), which in turn yields a THz pulse E(t). The emitted field is directly proportional to the time derivative of the current $E(t) \propto \partial J(t)/\partial t$.

Detection of THz radiation with a photoconductive antenna is similar, with the difference that no bias is applied since the THz transient itself gives the bias and a current amplifier is included, a schematic diagram is shown in Fig. 2.1(b). When the gap is illuminated charges are photoexcited, and in the presence of a THz pulse the charges will move from one side of the antenna to the other. Charge will flow in proportion to the amplitude of the THz pulse when the IR pulse is gated and a current can be measured, the full waveform is obtained by moving a variable delay. Photoconductive antenna switches have reported detection bandwidth up to 5 THz [92], with the high frequency



FIGURE 2.1: Schematic of photoconductive antenna for (a) generation (b) detection of THz pulses. The coupling hyper-hemispherical silicon lenses are not depicted for clarity.

cutoff being typically limited by the response time of the material and the lower cutoff by diffraction. By collecting the backwards THz radiation in a low temperature grown GaAs photoconductive emitter, frequency components up to 30 THz have been achieved with a 12 fs laser pulse [93], however the frequency spectrum is not smooth, as it shows spectral dips at 8 THz due to the TO phonon in GaAs. Photoconductive switches have the advantage that can be used with high repetition rate oscillator laser sources which operate at \sim 100 MHz [7]. Photoconductive antennas can also be used with amplified laser pulses in large aperture switches, with the drawback that since the distance between the electrodes increases, so does the applied bias, needing voltages in the order of 1-10 kV [94]. As described in the next subsection, optical rectification is a more popular technique to generate THz pulses when using an amplified laser source.

2.1.2 Optical Rectification

Optical rectification is a second order non-linear optical process in which THz radiation is generated when an Intense laser pulses transverses a non-linear medium as depicted



FIGURE 2.2: Schematic of optical rectification for generation of THz pulses.

in Fig. 2.2. To explain where it comes from lets consider the relationship between the polarization P(t), and an applied electric field E(t) given by $P(t) = \epsilon_0 \chi^{(1)} E(t)$ where $\chi^{(1)}$ is the linear susceptibility and ϵ_0 the permittivity of free space. non-linear optical properties are obtained by expressing P(t) as a power series of E(t)

$$P(t) = \epsilon_0 [\chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + ...]$$

= $P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + ...$ (2.1)

in Eq. 2.1, $\chi^{(2)}$ and $\chi^{(3)}$ are the second and third order non-linear susceptibilities. Optical rectification comes from the second order non-linear term $P^{(2)}$, when taking two electric fields $E_1 = E_0 \cos \omega_1 t$ and $E_2 = E_0 \cos \omega_2 t$, the second order non-linear non-linear polarization takes the form:

$$P^{(2)}(t) = \chi^{(2)} E_1 E_2 = \frac{\chi^{(2)} E_0^2}{2} [\cos(\omega_1 - \omega_2) + \cos(\omega_1 + \omega_2)]$$
(2.2)

the first term in the right hand side of Eq. 2.2 corresponds to difference frequency and is responsible for THz radiation by optical rectification, while the second term corresponds to sum frequency generation and is responsible for the electro-optic effect used in the detection of THz pulses. Assuming perfect phase matching, the difference frequency term will determine the ultimate bandwidth of the THz radiation, given that it takes the difference of all frequencies within the bandwidth of the fs laser pulse, giving a time domain profile of the THz radiation of the form $E_{THz} \propto \frac{\partial^2 P^{(2)}}{\partial t^2}$. The generation of THz radiation can be described as [10]:

$$E(\Omega, z) = \frac{\Omega^2 e^{ik(\Omega)z}}{k(\Omega)c^2} \chi_{\text{eff}}^{(2)}(\Omega) \frac{e^{i\Delta k(\omega_0,\Omega)z} - 1}{\Delta k(\omega_0,\Omega)} C(\Omega)$$
(2.3)

where $\Omega = \omega_1 - \omega_2$ is the difference frequency, $C(\Omega) = \int A(\omega + \Omega)A^*(\omega)d\omega$ is the autocorrelation of the spectrum of the laser pulse, and $\Delta k(\omega_0, \Omega)$ is the phase matching given by [10]:

$$\Delta k(\omega_0, \Omega) \approx \frac{\Omega}{c} (n_{gr}(\omega_0) - n_{THz}(\Omega))$$
(2.4)

 n_{gr} is the group refractive index of the optical light and n_{THz} the phase refractive index of the THz light. From Eq. 2.3, the bandwidth of the generated THz radiation will be limited by the mismatch between the group velocity at optical frequencies and the phase velocity at THz frequencies [95], however for sufficiently thin crystals phase matching can be achieved and the autocorrelation of the pulse $C(\Omega)$ will limit the THz bandwidth [10].

Optical rectification from a 5 ps duration mode-locked laser pulses was first demonstrated in 1971 in a LiNbO₃ crystal [96, 97]. Currently ZnTe is one of the most widely used crystals used for optical rectification given that is easy to align due to the collinear THz generation but also because it is well phase matched for 800 nm laser pulses [98]. A drawback of optical rectification is that when a short enough fs pulse is used, the bandwidth of the THz pulse will be limited by phonon absorption in the material, in the case of ZnTe this occurs at 5.3 THz [16]. There are other non-linear inorganic crystals that have been used for optical rectification such as GaAs, CdTe [99] and GaP [100], organic non-linear crystals have been used as well such as DAST (4-Dimethylamino-N-methyl-4-stilbazolium Tosylate) [101, 102] achieving a bandwidth up to 20 THz [103]. Multi-THz pulses have also been obtained with very thin GaSe crystals in a difference frequency scheme [104, 105].

Optical rectification in LiNbO₃ using a tilted pulse front excitation is a novel technique that can achieve intense THz fields enabling non-linear spectroscopy studies around 1 THz [106]. LiNbO₃ has a larger non-linear optical coefficient and larger bandgap, that prevent two photon absorption at 800 nm, compared with other conventional materials used for optical rectification [107]; however there is a strong phase mismatch between the optical pump pulse and the phase velocity of the generated THz pulse. The optical pump pulse travels faster than the generated THz pulse, and the THz radiation emitted is conical in a Cherenkov geometry [107]. By tilting the optical pulse front with a grating it is possible to coincide with the Cherenkov emission angle, in this way phase matching is achieved resulting in a enhanced conversion efficiency. With this technique, high electric fields over 1 MV/cm have been achieved [108] and high conversion efficiencies of ~ 0.35 % due to a cascaded THz generation mechanism [109].

Detection of THz pulses in non-linear crystals uses the linear Pockels effect and is know as free space electro-optic detection, first demonstrated in middle of 1990s by three independent groups [110–112]. ZnTe has an excellent performance for free space



FIGURE 2.3: Schematic of free space electro-optic detection for the detection of THz pulses.

electro-optic sampling and therefore is very popular however other materials have been used such as GaAs, GaP, GaSe and DAST [100, 104, 113].

When a linearly polarized optical probe pulse traverses an electro-optic (EO) crystal, as depicted in the top of Fig. 2.3, its polarization remains unchanged. After passing through a quarter wave plate a circular polarization is obtained, this is later separated by a Wollaston prism into their orthogonal polarization components and are sent to a balanced photodetector. The Intensity difference, $\Delta I = I_x - I_y$, measured by the detector in this case is zero. On the other hand, when a THz pulse and a linearly polarized optical probe pulse traverses an electro-optic crystal, as depicted in the bottom of Fig. 2.3, there is a field induced birefringence that will result in a small elliptical polarization of the optical probe pulse. After passing through a quarter wave plate an elliptical polarization is obtained that a Wollaston prism then splits and sends to a balanced photodetector. The intensity difference ΔI in electro-optic detection for ZnTe, can be obtained from the following expression [114]:

$$\Delta I(\alpha,\varphi) = I_p \frac{\omega n^3 E_{THz} r_{41} L}{2c} (\cos\alpha \sin 2\varphi + 2\sin\alpha \cos 2\varphi)$$
(2.5)

where I_p the probe intensity, r_{41} is the electro-optic coefficient, L is the crystal length and α (φ) is the angle of the THz beam polarization (probe-beam polarization) with respect to the crystal (001) axis. From Eq. 2.5 it can be seen that the signal measured by a balanced detector is directly proportional to the electric field. α and φ will directly affect the efficiency of the THz detection, with a maximum signal obtained when $\varphi = \alpha$ or $\varphi = \alpha + 90^{\circ}$. The expression for the intensity difference, although used for ZnTe, is valid for other zinc-blende crystals [114].

Even though optical rectification and photoconductive antennas are popular methods for generating THz pulses, there are limitations to the field strength generation due to saturation or even damage of the material. Furthermore the bandwidth will be limited by the carrier response in photoconductive antennas, or by phase matching as well as phonon absorption when dealing optical rectification, these limitations can be avoided when the THz emission comes from laser induced air plasma [17].

2.1.3 Air Plasma THz Generation

It was first demonstrated in 1993 that weak, sub-picosecond THz pulses could be generated from an 120 fs, 800 nm laser induced plasma. The radiation mechanism was attributed to pondermotive forces [115] in the laser field proportional to E^2 , inducing a net rectified current which radiated. Later in 2000, it was demonstrated that by electrically biasing the plasma it was possible to have a stronger THz emission comparable to



FIGURE 2.4: Schematic for the generation of THz pulses via a two color laser induced plasma.

large area photoconductive antennas [116]. Around the same time, it was shown that by focusing the fundamental frequency ω of the laser along with its second harmonic 2ω intense THz pulses from gases could be generated [18], electric fields of more than 400 kV/cm were reported with this technique [117]. A schematic of THz generation via two color laser induced plasma is shown in Fig. 2.4.

The emitted THz mechanism in the two color laser plasma was initially attributed to four wave mixing (FWM) by means of a third order susceptibility in the gas [118] and became a standard THz generation method due to its simplicity, broad bandwidth and strong THz emission. In the four wave mixing process the THz electric field is given by:

$$E_{THz} \propto \chi^{(3)} E_{\omega} E_{\omega} E_{2\omega} \tag{2.6}$$

where E_{ω} and $E_{2\omega}$ are the electric fields of the fundamental and second harmonic respectively and $\chi^{(3)}$ is the third order non-linear susceptibility. Eq. 2.6 is a basic model that intuitively explains some aspects of the THz generation, however the value of $\chi^{(3)}$ in air is too weak to reproduce the measured signals and the THz emission is linked with the plasma formation at the laser focus [119]. Moreover, scaling of the THz emission has been reported but only over a limited pump energy range where saturation was observed so no conclusive remarks could be done [120].

A more detailed description of the THz plasma generation was later formulated in a photocurrent model, where electrons undergo a tunneling ionization process and respond to an asymmetric two colour laser field inducing transverse currents in the time scale of the laser pulse envelope [121], the following analysis comes from this photocurrent model. The aim is to show that in an alternating laser electric field, it is possible to have a non-zero photocurrent. The laser electric field E_L can be expressed in terms of the fundamental ω and its second harmonic 2ω as:

$$E_L(t) = E_1 \cos(\omega t + \phi) + E_2 \cos[2(\omega t + \phi) + \theta]$$
(2.7)

where E_1 and E_2 in Eq. 2.7 are the amplitudes of the fundamental and second harmonic fields, θ is the relative phase between the ω and 2ω fields and it is assumed that when the electrons are photoionized have a phase ϕ . The laser field amplitudes are plotted for $\theta = 0$ and $\theta = \pi/2$ in Fig. 2.5, where the laser intensities are $I_{\omega} = 5I_{2\omega} = 1 \times 10^{15} \text{W/cm}^2$.

Once the electrons are photoionized, the trajectories and velocities are calculated with classical mechanics in a similar way of the high harmonic generation [122], when



FIGURE 2.5: Laser field obtained from Eq. 2.7 of the fundamental ω and second harmonic 2ω (relative intensity $I_{2\omega}/I_{\omega} = 0.2$) with a relative phase of (a) $\theta = 0$, and (b) $\theta = 90$.

the magnetic field is also neglected a drift velocity ν_d is obtained:

$$\nu_d = \frac{eE_{1\omega}\sin\phi}{m_e\omega} + \frac{eE_{2\omega}\sin\left(2\phi + \theta\right)}{2m_e\omega}$$
(2.8)

as seen in Eq. 2.8, the electron drift velocity per optical cycle will be dependent on the relative phase θ between the ω and 2ω pulses, the electrons that gain drift velocity will create an asymmetric current that will radiate a THz pulse. As seen from Fig. 2.6, relative phase $\theta = 0$ will give an average velocity of 0, however, by using a relative phase $\theta = 90$ a non-zero average velocity is obtained. The non-zero average velocity will give rise to a transient asymmetric current *J* [121] and in turn this current will radiate a THz pulse according to:

$$E_{THz} \propto \frac{dJ}{dt} = e \frac{d}{dt} \int_{t_0}^t \nu_e(t, t') N_e(t') dt'$$
(2.9)



FIGURE 2.6: Electron drift velocity (v_e) as a function of ϕ for (a) θ = 0, and (b) θ = 90. The laser field (E_L) is the plotted dotted line, the shaded regions represent ionization electrons due to the high laser field.

where $\nu_e(t, t')$ is the velocity of electrons ionized at t = t' and $N_e(t')$ is the electron density in Eq. 2.9.

When performing air plasma THz generation, the laser pulse duration will limit the bandwidth. It has been reported that by using 10 fs laser pulses in an air plasma setup, ultrabroadband pulses up to 200 THz have been generated [123]. The shape of the THz pulse emitted from an air plasma has been studied, and has been described as a conical emission pattern with a donut-shaped beam profile due to constructive interference between the THz waves emitted along the plasma filament [124–126]. The air plasma THz generation has a strong dependence on the wavelength, a longer wavelength boosts the down-conversion efficiency in the THz region where electric field strengths as high as 4.4 MV/cm have been reported [127].

2.1.4 Air Plasma THz Detection - ABCD

Air can also be used as a medium to detect THz pulses. Due to the lack of dispersive excitations in dry air, the bandwidth limitations present in electro optic detection or photoconductive antennas can be avoided. The main limitation is the laser pulse duration. In this way, detection bandwidths greater than 100 THz have been reported when using laser pulses employing sub 20 fs duration laser pulses [128].

The detection of ultrabroadband pulses can be achieved in air and other gases owing to a third order nonlinearity in the gas medium, and can be explained as a four wave mixing process [120, 129]. A THz photon E_{THz} and two laser photons E_{ω} are focused and mix to generate a second harmonic photon $E_{2\omega}$ in a third order non-linear process know as terahertz field induced second harmonic (TFISH)

$$E_{2\omega} \propto \chi^{(3)} E_{THz} E_{\omega} E_{\omega} \tag{2.10}$$

from Eq. 2.10, the intensity of the measured signal is proportional to the intensity of the THz field. This is $I_{2\omega} \propto (\chi^{(3)}I_{\omega})^2 I_{THz}$, then only an incoherent measurement can be performed where the phase information is lost. By introducing an external local oscillator (LO) bias field, composed of and AC and a DC term $E_{2\omega}^{LO} = E_{bias}^{AC} + E_{bias}^{DC}$, to the optical focus it is possible to obtain a coherent measurement [130]. The additional field will act as a local oscillator and will mix with the TFISH field:

$$I_{2\omega} \propto \langle E_{2\omega}^2 \rangle = \langle (E_{2\omega}^{THz} + E_{2\omega}^{LO})^2 \rangle = \langle (E_{2\omega}^{THz} + E_{bias}^{AC} + E_{bias}^{DC})^2 \rangle$$
$$= (E_{2\omega}^{THz})^2 + (E_{2\omega}^{AC})^2 + (E_{2\omega}^{DC})^2$$
$$+ 2\langle E_{2\omega}^{THz} E_{2\omega}^{AC} \rangle + 2\langle E_{2\omega}^{THz} E_{2\omega}^{DC} \rangle + 2\langle E_{2\omega}^{AC} E_{2\omega}^{DC} \rangle$$
(2.11)

the field induced second harmonics $E_{2\omega}^{THz}$, $E_{2\omega}^{AC}$ and $E_{2\omega}^{DC}$ can be written as:

$$E_{2\omega}^{THz} \propto \chi^{(3)} I_{\omega} E_{THz}$$

$$E_{2\omega}^{AC} \propto \chi^{(3)} I_{\omega} E_{bias}^{AC}$$

$$E_{2\omega}^{DC} \propto \chi^{(3)} I_{\omega} E_{bias}^{DC}$$
(2.12)

so that Eq. 2.11 can be rewritten as:

$$I_{2\omega} \propto (\chi^{(3)}I_{\omega})^{2}[(E_{THz})^{2} + (E_{bias}^{AC})^{2} + (E_{bias}^{DC})^{2} \\ \pm 2E_{THz}E_{bias}^{AC} \pm 2E_{THz}E_{bias}^{DC} \pm 2E_{bias}^{AC}E_{bias}^{DC}]$$
(2.13)

By means of a lock-in technique, it is possible to reference only to the terms containing AC bias signals. Furthermore, the 2nd and 6th terms in Eq. 2.13 can be made to cancel out by changing the applied DC bias field, this allows a zero baseline in $I_{2\omega}$. The 4th term of Eq. 2.13 will give the desired $I_{2\omega}$, where the intensity is directly proportional to THz electric field:

$$I_{2\omega} \propto 4[\chi^{(3)}I_{\omega}]^2 E_{THz} E_{bias}^{AC}$$

$$(2.14)$$

This process is know as Air Biased Coherent Detection, or ABCD, a schematic is shown in Fig. 2.7. An all air plasma THz spectroscopy is also possible where no electrodes are used for detection [131]. From Eq. 2.14 it is seen that $I_{2\omega} \propto [\chi^{(3)}]^2$, then the dynamic range can be improved by choosing a gas with high third order non-linear susceptibility and low THz absorption, such as Xenon or alkane gases. Elevating the pressure also enhances the detection since the effective $\chi^{(3)}$ is proportional to the total number of molecules [129].



FIGURE 2.7: Schematic for the detection of THz pulses with the air biased coherent detection technique (ABCD).

The generation and detection of THz pulses in air extends the range of frequencies that can be measured to cover the entire THz gap, and have already been used to study optical properties of α -BBO and β -BBO [132, 133], charge generation in polymerfullerene film [134], THz static properties of common polymers [135], phonon-scattering in perovskite thin films [66], femtosecond buildup of electron mobility GaAs [136], and has been used as a tool to analyze the validity of thin film approximation [137].

Working on air to generate and detect THz has many advantages over other conventional methods, since the emitter and the sensor medium can be ambient air, where no phonon absorption is present. This method is capable of reaching peak electric field strengths in the order of MV/cm and can reach bandwidths greater than 100 THz. The requirements of this method is that intense laser pulses are needed, usually coming from a large amplified laser system. Also, the optical to THz conversion efficiency is low and a precise alignment is necessary to detect such wide bandwidths [19]. In spite of this, the advantages of working in an air plasma THz system overshadow the drawbacks, and make this system excellent to perform THz spectroscopy.

2.2 Time-Domain THz Spectroscopy

In time-domain THz spectroscopy, the electromagnetic field of the THz pulse is measured in time and hence the amplitude and phase changes are detected, allowing the extraction of optical properties such as the complex refractive index, absorption coefficient and the complex conductivity without the use of the Kramers-Kronig relations. These measurements are performed in a non contact way, and thus are not destructive for the sample. This coherent measurement of the electric field of THz pulses in the time domain is know as THz time domain spectroscopy (THz-TDS).

This technique was first used in 1989 to study THz absorption by water vapor [21], and has since been used in a variety of materials such as dielectrics and semiconductors[22], water [138], in biological systems to study vibrational spectra of retinal isomers [139], DNA [140, 141] and biological molecules [142]. Full analysis as well as algorithms have been developed in order to correctly extract the optical constants with high precision when doing THz-TDS [143–145].

2.2.1 Fresnel Equations

The fundamental expressions of light matter interactions which describe the transmission and reflection of an electromagnetic field at an interface are known as Fresnel equations. Transmission and reflection of light at an interface between air and a medium with a refractive index n are illustrated in Fig. 2.8.

Consider an x-polarized beam propagating along the z direction, in a normal incidence geometry. From the boundary conditions at the interface between two dielectrics, the tangential components of the electric and magnetic fields are continuous. In other



FIGURE 2.8: Transmission and reflection of light at an interface between two different refractive index mediums.

words, the electric and magnetic fields must be the same on either side of the interface and can be expressed as follows:

$$E_x^i + E_x^r = E_x^t \tag{2.15}$$

$$H_{y}^{i} - H_{y}^{r} = H_{y}^{t}$$
(2.16)

where *i*, *r* and *t* superscripts represent the incident, reflected and transmitted light, respectively. Given that electric and magnetic fields are related to each other by: $H_{y0} = E_{x0}/Z$ where *Z* is the wave impedance, $Z = 1/c\epsilon_0 n$, Eq. 2.16 can be rewritten as:

$$E_t n_t = E_i n_i - E_r n_r \tag{2.17}$$



FIGURE 2.9: Incident, transmitted and reflected electric fields in a sample of thickness *d*.

By combining Eq. 2.15 and Eq. 2.17 the reflection and transmission coefficients at normal incidence are obtained:

$$\tilde{r} = \frac{E_r}{E_i} = \frac{\tilde{n}_i - \tilde{n}_t}{\tilde{n}_i + \tilde{n}_t}$$
(2.18)

$$\tilde{t} = \frac{E_t}{E_i} = \frac{2\tilde{n}_i}{\tilde{n}_i + \tilde{n}_t}$$
(2.19)

The change in amplitude and phase of the electromagnetic field as it passes through the interface of a given medium is described by these coefficients. To illustrate this, consider a material of thickness d and refractive index $\tilde{n}_2 = n$ (medium 2). This material is placed on air (medium 1) with a refractive index $\tilde{n}_1 \simeq 1$, as shown in Fig. 2.9. The complex transmission function, defined as the ratio between the transmitted field E_t and the incident field E_i for this example, is represented by Eq. 2.20:

$$\frac{E_t(\omega)}{E_i(\omega)} = T(\omega)e^{i\varphi(\omega)} = \frac{t_{12}t_{21}P_2}{P_1} = \frac{4\widetilde{n}}{(1+\widetilde{n})^2}e^{i(\widetilde{n}-1)\frac{\omega}{c}d}$$
(2.20)

This function includes the complex Fresnel transmission coefficients from medium 1 to medium 2 and from medium 2 to medium 1 and an additional transmission factor



FIGURE 2.10: Time domain electric field of a THz pulse propagated in air (blue) and passing through a 500 µm Silicon sample (doted red).

 $P = e^{i\frac{\omega}{c}\tilde{n}d}$. By writing this expression in terms of the real and imaginary part of the refractive index the following expression is obtained:

$$T(\omega)e^{i\varphi(\omega)} = \frac{4\widetilde{n}}{(1+\widetilde{n})^2} e^{i\frac{\omega}{c}(n-1)d} e^{-k\frac{\omega}{c}d}$$
(2.21)

The spectral phase $\varphi(\omega) = (n-1)\frac{\omega d}{c}$ encodes important information about the optical properties of the material in this case, the refractive index, and in the limit where the phase accumulated through the bulk of the crystal is much larger than the phase change occurring at the interface, it is possible to extract the index directly from the spectral phase analytically:

$$n(\omega) = \frac{\varphi(\omega)c}{\omega d} + 1$$
(2.22)

Eq. 2.21 also shows an attenuation term, the extinction coefficient $k(\omega) = \alpha(\omega)c/(2\omega)$



FIGURE 2.11: Extracted refractive index of a 500 µm Silicon sample.

which is proportional to the absorption coefficient which in turn can be extracted by the following expression:

$$\alpha(\omega) = -\frac{2}{d} ln\left(\frac{(n+1)^2}{4n}T(\omega)\right)$$
(2.23)

By measuring the time shift between these two pulses it is possible to estimate the refractive index of the sample, as an example a high resistivity silicon sample was measured and is shown in Fig. 2.10. The time delay introduced by the silicon sample is given by $\Delta t = (n - 1)d/c$, from this the refractive index can be calculated. Taking $\Delta t = 4.12$ ps in a d = 500 µm sample a refractive index for silicon of n = 3.46 is obtained, in fair agreement to the literature value of n = 3.42 for high resistivity silicon [146]. By employing Eq. 2.22 it is possible to extract the frequency dependent refractive index in silicon, this is shown in Fig. 2.11.

2.3 Time-Resolved THz Spectroscopy

The THz radiation can be used in a pump-probe configuration in order to perform spectroscopy. In this technique, an ultrafast pump pulse is used to photo excite the sample while a THz pulse is used as a probe to monitor the pump induced change in photoconductivity. The THz pulse is moved in time with respect to the pump pulse, called pump-probe time delay, where it can probe the appearance, increase and decrease of the induced photoconductivity over ps time scales. A big advantage of working with air plasma THz generation and ABCD detection is that the time resolution will be limited by the laser pulse duration. Many systems have been studied with TRTS such as bulk semiconductors [1, 147–151], semiconductor nanostructures [152–158], organic semiconductors [159–161], thin gold films [162], superconductors [163], dielectrics [164], liquids [165] among many others [10]. The data acquisition in TRTS can be done in two different modes: a 1-Dimensional (1-D) scan where only the pump line is moved while monitoring the peak of the THz pulse, and a 2-Dimensional (2-D) scan where two delay lines are moved, one for the pump photoexcitation, and another to obtain a full THz waveform.

2.3.1 1-Dimensional Scan

In order to perform this type of scan it is necessary to identify the maximum of a THz pulse and move to that position, this will correspond to the maximum electric field of the THz pulse, where all the frequency components of the pulse are in phase. A pump beam, that can be moved in time through a delay stage and is modulated by an optical chopper, is used to photoexcite the sample. The peak of the THz electric field, and the



FIGURE 2.12: 1-Dimensional differential THz transmission ($\Delta T/T$) after 400 nm photoexcitation in a silicon sample.

pump induced change are measured simultaneously, by means of a two lock-in technique, in order to eliminate systematic timing variations [166]. The data acquisition in a 1-D scans is relatively fast, usually taking a few minutes per scan allowing a finer pump-probe resolution, however a drawback of this technique is that the phase information is ignored. An example of a 1-D scan of a silicon sample taken in transmission geometry, is shown in Fig. 2.12. Here, the induced photoconductivity reduces the THz transmitted signal due to the free carrier absorption.

2.3.2 2-Dimensional Scan

The generation and detection of THz pulses is done in a coherent way, where the amplitude and phase are resolved. Thus it makes sense to use the full waveform to map the photoconductivity dynamics, this is done on a 2-Dimensional scan. A full waveform is



FIGURE 2.13: 2-Dimensional map of the differential change of the electric field (ΔE) in a silicon sample, the dashed line corresponds to the time of the pump arrival $\tau_p = 0$.

measured while a pump pulse photoexcites the sample, with the help of a delay stage the pump excitation is moved in time with respect to the THz pulse creating a 2-D map. In this way the induced photoconductivity can be mapped. A full 2-D map contains all the information needed to extract a 1-D scan (described in the previous subsection), this can be obtained by looking at the peak of the THz pulse in the 2-D map. The main drawback of this measurement is that taking the full THz waveform for each pump probe delay greatly increases time needed to record the data. As an example the pump induced change in the THz field for silicon has been measured, pumped at 400 nm, this is shown in Fig. 2.13.



FIGURE 2.14: Schematic of the pump, THz and gating pulses used in a TRTS experiment and their relative delay times.

2.3.3 Time-Resolved THz Spectrometer - Delay Lines

In a TRTS experiment three pulses are needed, one to photoexcite the sample, one to generate a THz pulse and another to probe the THz pulse. Those pulses can be moved in time with delay stages, so its convenient to label the time of arrival for each pulse as follows: t_e is the time of the optical excitation, t is the time when the value of the polarization ΔP is measured through the emitted THz pulse and t_p is the THz probe pulse arrival (gating pulse). It is also convenient to see how the pulses are related to each other and to label them accordingly. There are three relative delay times: $\tau = t - t_p$ is the probe-measurement delay, $\tau_e = t - t_e$ the pump-sampling delay and $\tau_p = t_p - t_e$ is the pump-probe delay, these times are schematically shown in Fig. 2.14. If a 2-D scan wants to be made, one of these three delays needs to be fixed, while the other two delays are moved, this leaves three ways of performing a 2D scan as shown in table 2.1.

	Pump Delay	THz Delay	Gating Delay
Ι	$ au_{e}$	τ	Fixed
II	$ au_{ m p}$	Fixed	τ
III	Fixed	$ au_p$	$ au_{e}$

TABLE 2.1: TRTS Delay Selection.

The selection of the delays in either the optical excitation, the THz generation or the gating pulse arms will give you different responses in the non-linear induced polarization ΔP [167]:

$$\Delta P(t-t_p, t-t_e) = \epsilon_0 \int_{-\infty}^t E_{THz}(t'-t_p) \Delta \chi(t-t', t-t_e) dt'$$
(2.24)

Eq. 2.24 can also be rewritten in terms of the relative times

$$\Delta P(\tau, \tau_e) = \epsilon_0 \int_{-\infty}^{\tau} E_{THz}(t' - t_p) \Delta \chi(\tau - t', \tau_e) dt'$$
(2.25)

Eq. 2.25 can also be expressed in the frequency domain

$$\Delta P(\omega, \omega_e) = \epsilon_0 E_{THz}(\omega) \Delta \chi(\omega, \omega_e)$$
(2.26)

A THz waveform will be needed in all cases to perform a 2-D scan, this means that the probe-measurement delay τ is needed. Table 2.1 shows that method III does not have this delay and thus is not suitable to be used while method I and II are viable options.

In method II, the THz delay is fixed. A single THz pulse is measured but the pulse

itself experiences different excited states of the medium as it traverses the sample. This method has the disadvantage that one must project the data numerically after acquisition, as your induced response will be shifted in time. A zero padding to the data is also necessary in order to perform a Fourier transform. Many examples in the literature can be found using this method [1, 168].

In method I, the gating delay is fixed. The measured THz pulses are composed of time-projected fields that all experience the same excited state. The THz spectrometer in this thesis built was based on this method. This has the advantage that the data already has a rectangular window and the Fourier transform can be directly performed, without any data manipulation. Moreover, application of Method II requires long term stability in the laser and spectrometer over hours of acquisition time, as one must project information from later pump-probe delays onto a single time axis. Method I reduces the requirement for stability to the length of a single scan, approximately 1 minute [166]. Propagation after the sample, however, has to be taken in account as will be discussed.

2.3.4 Thin Film Approximation

Many times the pump excitation penetrates over a very thin region of the sample, in this case data analysis is simplified when the thin film approximation is used. The Tinkham equation, gives the transmission through a thin conducting film going from air to a medium of refractive index n [169]:

$$\tilde{t}_{film} = \frac{2}{n+1+Z_0\tilde{\sigma}(\omega)d}$$
(2.27)

Eq. 2.27 is valid in the limit of small pump penetration depth $d \ll c/n\omega$. The complex transmission function $\widetilde{T}(\omega)$ is obtained from the Fourier transform of the time domain electric fields in the presence of an excitation pulse \widetilde{E}_{pump} , and without excitation \widetilde{E}_{ref} :

$$\widetilde{T}(\omega) = T(\omega)e^{i\varphi(\omega)} = \frac{\widetilde{E}_{pump}(\omega)}{\widetilde{E}_{ref}(\omega)} = \frac{\widetilde{t}_{film}}{\widetilde{t}_{subs}} = \frac{n+1}{n+1+Z_0\widetilde{\sigma}(\omega,\tau_p)d}$$
(2.28)

Eq. 2.28 can be inverted in order to extract the complex conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$

$$\sigma(\omega) = \frac{n+1}{Z_0 d} \left(\frac{1}{T(\omega)e^{i\varphi(\omega)}} + 1 \right)$$
(2.29)

Eq. 2.29 can be split into its real an imaginary parts giving respectively σ_1 and σ_2 .

$$\sigma_1(\omega) = \frac{n+1}{Z_0 d} \left(\frac{1}{|T|} \cos \varphi + 1 \right)$$
(2.30)

$$\sigma_2(\omega) = -\frac{n+1}{Z_0 d} \frac{1}{|T|} \sin\varphi$$
(2.31)

The maximum carrier density n_{max} that can be injected is given by [169]:

$$n_{max} = \frac{\eta(1-R)F}{dh\nu}$$
(2.32)

where η the quantum efficiency, R the intensity reflection coefficient, F the incident pump fluence in J/cm², d the pump penetration depth and $h\nu$ the photon energy in Eq. 2.32.

The Tinkham equation can also be used in the reflection geometry, in this case the complex reflection function $\widetilde{R}(\omega)$ is:

$$\widetilde{R}(\omega) = R(\omega)e^{i\varphi(\omega)} = \frac{\widetilde{E}_{pump}(\omega)}{\widetilde{E}_{ref}(\omega)} = \frac{\widetilde{r}_{film}}{\widetilde{r}_{subs}} = \left(\frac{1 - n - Z_0\widetilde{\sigma}(\omega, \tau_p)d}{1 + n + Z_0\widetilde{\sigma}(\omega, \tau_p)d}\right) \left(\frac{1 + n}{1 - n}\right)$$
(2.33)

2.3.5 Drude Model

The Drude model is a simple conductivity model that explains the transport of electrons in metals and was proposed by Drude in 1900 [170]. Even though this model has many shortcomings, is still of great importance to describe concepts related with the electrical conductivity. This model consider the following assumptions:

- There is no Coulomb interaction between the electrons and no collisions with each other either, the model then neglects electron-electron interaction.
- The ions are stationary while the electrons are free to move, but can collide with the ions in the solid with a time constant 1/τ, where τ is known as scattering time or relaxation time.
- The relaxation time leads to other important concept, the mean free path between two scattering processes given by λ = τv_t, where v_t is the average speed and at room temperature v_t ≈ 1 × 10⁻⁵ m/s. For example, if the scattering is generated by the collision with ions λ ≈ 1 nm, then τ ≈ 1 × 10⁻¹⁴ s.
- The electrons in the material will move in a straight line unless an electric field is applied, and will follow Newton's law. There will be collisions of electrons with the ion cores with a probability of 1/τ, these collisions change their velocity, instantaneously.

In the presence of an electric field, the electron will move according to the following equation of motion:

$$m\frac{d\boldsymbol{v}(t)}{dt} = -m\frac{\boldsymbol{v}}{\tau} - e\boldsymbol{E}(t)$$
(2.34)

In a dc field, dv/dt = 0, then a dc conductivity σ_{dc} can be obtained, from the current density given by J = -nev. The current density is directly proportional to the electric field strength and follows Ohm's law. The constant of proportionality between the current density and the electric field will be the conductivity:

$$\sigma_{dc} = \frac{J}{E} = \frac{ne^2\tau}{m} = \omega_p^2 \epsilon_0 \tau = ne\mu$$
(2.35)

from Eq. 2.35 an important concept is derived, the plasma frequency ω_p :

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m} \tag{2.36}$$

If $\omega < \omega_p$, the dielectric function ϵ is a real and a negative number, this implies that $\epsilon^{1/2}$ is imaginary and the complex index of refraction includes the imaginary part $i\kappa$, then the light is not transmitted within the solid and must be reflected. If $\omega > \omega_p$, ϵ is positive and real, then light will be propagated into the metal. Low frequency light is reflected by the metal which becomes transparent to a high frequency light. The mobility, is defined as the ratio of the average drift velocity of the carrier to the electric field:

$$\mu = \frac{\boldsymbol{v}}{\boldsymbol{E}} = \frac{e\tau}{m} \tag{2.37}$$

Now, if the applied field is ac of the form $\boldsymbol{E}(t) = Re[\boldsymbol{E}(\omega)e^{-i\omega t}]$, then the velocity is of the form $\boldsymbol{v}(t) = Re[\boldsymbol{v}(\omega)e^{-i\omega t}]$, inserting this into Eq. 2.34 together with $\boldsymbol{J} = -ne\boldsymbol{v}$ and



FIGURE 2.15: Drude model conductivity example showing the real (blue line) and imaginary (green line) parts of the conductivity for the case where (a) $\sigma_1 \approx \sigma_2$ and (b) $\sigma_1 \gg \sigma_2$

 $\boldsymbol{J} = \widetilde{\sigma}(\omega) \boldsymbol{E}$ gives the complex conductivity $\widetilde{\sigma}(\omega)$

$$\widetilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{\sigma_{dc}}{1 - i\omega\tau}$$
(2.38)

The conductivity can be separated into the real or imaginary parts

$$\sigma_1(\omega) = \frac{\sigma_{dc}}{1 + (\omega\tau)^2} \tag{2.39}$$

$$\sigma_2(\omega) = \frac{\omega \tau \sigma_{dc}}{1 + (\omega \tau)^2} = \omega \tau \sigma_1(\omega)$$
(2.40)

An example of the Drude model is shown in Fig. 2.15 for the case of (a) $\sigma_1 \approx \sigma_2$ and (b) $\sigma_1 \gg \sigma_2$. Typical scattering times of metals are in the tens of fs range while semiconductors are in the hundreds of fs range.

To illustrate the Drude model, a high resistivity silicon wafer was measured in the TRTS setup. The conductivity of silicon was obtained by using Eq. 2.29 and is plotted



FIGURE 2.16: Optical conductivity of a high resistivity silicon wafer. The dots denote the extracted data, while the lines are fits to (a) the Drude model (b) The Drude and the Cole-Davidson model.

in Fig. 2.16(a), the blue dots are the real part of the obtained conductivity while the red dots are the imaginary part of the conductivity. The blue and red lines are simultaneous fits to the data and were performed by using the Drude model as in Eq. 2.38. At 1 ps a scattering time of $\tau \sim 35$ fs was obtained, this corresponds to a mobility of 240 cm²/Vs, and a carrier density of $n_d = 1.5 \times 10^{18}$ cm⁻³, taking into account a measured fluence of 16 µJ/cm², this corresponds to charge generation efficiency of ~ 50 %. The data fits well to the Drude model, and initially it was considered correct [171]. However later on it was shown that at high fluences the data is not well described by a simple Drude model, it was demonstrated that by modification of the Drude theory to include a Cole-Davidson type distribution a better agreement with the data was achieved [172]. Knowing that the Cole-Davidson model applies to doped silicon it was demonstrated that it is valid even for low carrier densities [173].

In the Cole-Davidson distribution, the conductivity is given by [172]:
$$\widetilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{\sigma_{dc}}{(1 - i\omega\tau)^{\beta}}$$
(2.41)

where β is a fractional exponent that reduces to the Drude model when $\beta = 1$. A high resistivity silicon wafer was measured in the TRTS setup at higher fluences to test the Cole-Davidson model. The conductivity of silicon was again obtained by using Eq. 2.29 and is plotted in the Fig. 2.16(b), the blue and red dots are obtained from the measured data, the dashed lines are fits to the Drude model and the continuous lines come from fits to the Cole-Davidson model. As expected the Drude model fails at this higher fluence, while the Cole-Davidson model correctly describes the conductivity of Silicon. At 1 ps a value of $\beta \sim 0.70$ was found, with a scattering time of $\tau \sim 120$ fs, this corresponds to a mobility of 810 cm²/Vs, and a carrier density of $n_d = 3.3 \times 10^{18}$ cm⁻³, taking into account a measured fluence of 35 µJ/cm², this corresponds to a charge generation efficiency of ~ 50 %.

2.3.6 Lorentz Model

Light matter interactions can be described in terms of the electric field of the light which induces oscillations of the atomic dipole by the driving forces which acts on the electrons. The displacement x of the atomic dipoles is modeled as damped harmonic oscillators. Damping emerges from collision processes by which the oscillating dipoles lose their energy. One of the main effects of damping term is the absorption line broadening.

Since the nuclear mass is much greater than the electron mass, the motion of the nucleus can be neglected and the displacement x of the electrons is described by the

equation of motion:

$$m\frac{d^2\boldsymbol{x}(t)}{dt^2} + \frac{m}{\tau}\frac{d\boldsymbol{x}(t)}{dt} + k\boldsymbol{x}(t) = -e\boldsymbol{E}(t)$$
(2.42)

where $1/\tau$ is the damping rate, -e is the electron charge and E is the electric field of the light wave. Each term from left side of equation represent the acceleration, damping and restoring force. Right side term represents the driving force exerted by the electric field of the light of the form $\boldsymbol{E}(t) = E(\omega)e^{-i\omega t}$, by substituting this equation into Eq. 2.42 and looking for solutions of the form: $\boldsymbol{x}(t) = \boldsymbol{x}(\omega)e^{-i\omega t}$ gives:

$$\boldsymbol{x}(\omega) = -\frac{e}{m} \frac{1}{(\omega_0^2 - \omega^2) - i\omega/\tau} \boldsymbol{E}(\omega)$$
(2.43)

The displacement of electrons produces a dipole moment which varies on time p(t) and contributes to the macroscopic polarization that is, the dipole moment per unit volume: P = -nex. This macroscopic polarization is related to the electric susceptibility by $P = \epsilon_0 \chi E$ and dielectric function and the electric susceptibility are related each other by $\epsilon = \epsilon_0 (1 + \chi)$ together with Eq. 2.43 gives:

$$\frac{\widetilde{\epsilon}(\omega)}{\epsilon_0} = 1 + \frac{ne^2}{m} \frac{1}{(\omega_0^2 - \omega^2) - i\omega/\tau}$$
(2.44)

Recalling that the dielectric function is related to the conductivity by:

$$\widetilde{\epsilon}(\omega) = 1 + \frac{i\sigma(\omega)}{\epsilon_0\omega}$$
(2.45)

Combining Eq. 2.45 and Eq. 2.17 the conductivity in the Lorentz model is obtained:

$$\widetilde{\sigma}(\omega) = \frac{ne^2}{m} \frac{\omega}{\omega/\tau + i(\omega_0^2 - \omega^2)}$$
(2.46)



FIGURE 2.17: Lorentz model conductivity example showing the real (blue line) and imaginary (green line) parts of the conductivity for $\omega_0 = 8$ THz, $\omega_p = 3 \times 10^{13}$ and $\tau = 200$ fs.

Eq. 2.46 can be separated into its real and imaginary parts:

$$\sigma_1(\omega) = \frac{Ne^2}{m} \frac{\omega^2/\tau}{(\omega/\tau)^2 + (\omega_0^2 - \omega^2)^2}$$
(2.47)

$$\sigma_2(\omega) = -\frac{Ne^2}{m} \frac{\omega(\omega_0^2 - \omega^2)}{(\omega/\tau)^2 + (\omega_0^2 - \omega^2)^2}$$
(2.48)

The real and imaginary parts of the conductivity, σ_1 and σ_2 (Eq. 2.47 and Eq. 2.48), are plotted as shown in Fig. 2.17, taking $\omega_0 = 8$ THz, $\omega_p = 3 \times 10^{13}$ and $\tau = 200$ fs.



FIGURE 2.18: Schematic of the Laser System used in the THz lab.

2.4 System for Multi-Transient THz Spectroscopy -Technical Description

2.4.1 Ultrafast Ti:Sapphire Amplifier

Multi-transient THz spectroscopy requires the use of ultrashort pulses to study the ultrafast dynamics in materials and to characterize their optical properties. This section will describe briefly ultrafast amplified pulse generation, which is the light source driving the THz spectrometer. A schematic of the laser system used is shown in Fig. 2.18

Ultrashort pulses are generated from a Ti:sapphire oscillator which produces ~ 400 mW pulses centered at 810 nm with a full width at half maximum (FWHM) of 77 nm when mode locked. Mode locking process is achieved through the Kerr lens which is induced by the Ti:sapphire crystal. To amplify the energy of this ultrafast pulse, it is necessary to send it to a stretcher stage which lengthens the duration of the pulse by

Technical Description

approximately three orders of magnitude generating pulses in the order of ps, which decrease the peak power below the optical damage threshold for its safe further amplification. The pulse is then amplified by a regenerative amplification, where a pump frequency-doubled Q-switched Nd:YLF laser is focused into the Ti:sapphire crystal along with the mode of laser cavity itself to produce pulses of 6 mJ. Thereafter the optical amplification, the pulse is sent through a compressor stage to bring the pulse back to the femtosecond temporal scale, finally obtaining 40 fs, 5 mJ pulses centered at 795nm at a repetition rate of 1 kHz. An optical parametric amplifier may be used as needed in order to have a selection of pump pulses from 460 nm to 1100 nm. The 5 mJ output energy per pulse from the laser is large enough to damage the laboratory optics. For this reason the specification data from the manufacturer must be consulted to confirm that all the optics are working under the damage threshold, otherwise the pulse energy per unit area needs to be decreased, which can be achieved by expanding the laser beam.

2.4.2 Time-Domain THz Spectrometer

A schematic diagram of the Time-Domain THz Spectrometer is shown in Fig. 2.19. The fs pulses are sent to a 85/15 beam splitter. The higher power beam goes through a delay line, then passes through a 100 μ m thick β -barium borate or β -BBO for second harmonic generation through a non-linear process. After the β -BBO the fundamental and second harmonic polarizations are orthogonal, a dual wave plate is used to control the polarization of both beams to make them parallel [174]. Both the fundamental and second harmonic beams are focused with a 2" focal length parabolic mirror to create a plasma. The optical beams are sent to a high resistivity silicon wafer which allows the



FIGURE 2.19: Experimental setup for TDS in the transmission geometry.

transmission of the THz pulse but blocks the fundamental and second harmonic beams. The THz pulse is collected with a 4" parabolic mirror and then sent to a 3" parabolic mirror to focus into the sample. The sample response is collected and collimated by a pair of 3" parabolic mirrors and is focused along with the fundamental to detect the THz through the ABCD method. Finally, a 400 nm filter is used to select the THz field induced second harmonic and is detected with an avalanche photodiode.

2.4.3 Time-Resolved THz Spectrometer in Transmission

A schematic diagram of the Time-Resolved THz Spectrometer in transmission mode is shown in Fig. 2.20. The setup for time resolved THz spectroscopy is similar to the one described above for time domain spectroscopy, with the only difference that the setup adds an additional pump beam that can be delayed and is used to photoexcite the sample. The femtosecond train pulses are sent to a 70/30 beam splitter, the higher power is used as described in the previous subsection to generate and detect the THz pulse. The lower power beam is sent to a delay line and then guided to the sample,





FIGURE 2.20: Experimental setup for TRTS in the transmission geometry.

through a small hole in the parabolic mirror, to be used as a pump. When a different pump excitation energy is needed, a second harmonic generation crystal such as β -BBO can be put in on the optical path, alternatively the output of and optical parametric amplifier can be used to photoexcite the sample.

Some of the studied materials have strong absorption in the multi-THz range. As an example, the transmission of a THz pulse through a 500 µm GaAs wafer is shown in Fig. 2.21. The time domain data shows strong dispersion and attenuation when compared to the air reference pulse, the frequency domain shows a strong attenuation between ~7.5 and ~10 THz, this is the reststrahlen band in GaAs where the THz field is perfectly reflected and correspond to the frequency region between the transverse optical ω_{TO} and longitudinal optical ω_{LO} phonons in GaAs.



FIGURE 2.21: THz Propagation through GaAs (a) Time domain where the gray line is the air reference, and the blue line the THz pulse transmitted through a 500 µm GaAs wafer. (b) Their corresponding Fourier spectrum showing the reststrahlen band in the GaAs sample.

2.4.4 Artifacts that can Arise - Group Delay

When a THz pulse goes through a sample with active phonons, the pulse will be strongly dispersed when coming out of the sample. If an optical photoexcitation is included, artifacts on the data can arise. Take for example the transmission of a multi-THz pulse through a CH₃NH₃PbI₃ single crystal sample. This material has strong dispersion near a phonon located at 2 THz. When the sample is photoexcited, at the surface of the crystal the THz pulse is transform limited, all frequencies are in phase and are photo-excited at the same time $\tau_p = 0$. As the pulse propagates in the sample, and due to the high dispersion, the frequency components will disperse temporally and the detected pulse will have low frequency components that arrive later than the high frequency components as can be seen in Fig. 2.22(a). All the frequency components were photoexcited at the same pump probe delay time $\tau_p = 0$, so a compensation for the

Τω 0.85 0.90 0.95 1.00 1.05 Group Delay (b) (a) Τ (ω) 0.85 0.90 0.95 1.00 1.05 1.4 1.4 1.4 1.2 1.2 1.2 (sd) 1.0 1.0 1.0 0.8 0.8 (sd) (sd) 0.6 0.6 ے م പ്പ 0.4 0.4 0.2 0.2 0.0 0.0 -0.2 -0.2 -0.2 -0.4 -0.4 -0.4 8 10 12 14 16 18 20 8 10 12 14 16 18 20 Frequency (THz) Frequency (THz)

FIGURE 2.22: multi-THz propagation through single crystal CH₃NH₃PbI₃ (a) 2D map of real transmission, the dotted lines is the group delay calculated from refractive index (b) Real transmission with low frequency components shifted with the group delay, the black region have no information.

group delay is needed, a numerical redistribution of the frequency components along the pump-probe time axis. In order to do this the refractive index of the material is needed to calculate the group velocity, previously obtained data for *n* correlates well with the data. In the end, the time domain response will be convoluted with the frequency response and enough resolution in the pump probe time is needed to project the data to earlier delay times. This procedure was done in Fig. 2.22(b), now all the frequency components arrive at the same time $\tau_p = 0$, but as a consequence of this, at early times some of the response is missing (black regions). Performing time resolved spectroscopy in such materials with this strong dispersion leads to a complicated and cumbersome analysis, which can be avoided if the TRTS is operated in a reflection geometry. Experimentally this is a more challenging setup to implement, however because of the benefits in the simplification of the data analysis as well as a decrease in

Technical Description



FIGURE 2.23: Experimental TRTS setup for (a) transmission compared with (b) reflection geometry.

the requirement for long term stability of the laser make it beneficial to use in the long term.

2.4.5 Time-Resolved THz Spectrometer in Reflection

There are samples that interact strongly with the THz radiation, blocking a portion of the incoming THz pulse and strongly dispersing a transmitted pulse, this would complicate the data analysis. In this cases, it will be more convenient to work in a reflection geometry. The TRTS setup is designed to switch between a transmission or reflection geometry with ease. This is achieved with a silicon wafer that is used as a beam splitter, and metallic mirror on a flip mount. The schematic diagram of both transmission and reflection geometries are shown in Fig. 2.23. In the transmission geometry the silicon wafer is only used to block the unwanted optical light, but in the reflection geometry the silicon wafer also serves as a beamsplitter, and sends a THz



FIGURE 2.24: THz water vapor absorption example (a) Time domain comparison of dry air (blue line) versus humid air (red line) (b) their corresponding Fourier spectrum.

pulse reflected from a sample to a metallic mirror mounted on a flip mount for its detection.

2.4.6 Technical Details

THz Propagation in Air

THz radiation is strongly absorbed by water, so even the propagation of a THz pulse through ambient air will lead to attenuation and free induction decay fields. To avoid this effect, an atmosphere of dry air is used, supplied by a purge gas generator. Fig. 2.24 shows the difference when a THz pulse propagates in dry air (blue line) compared with a THz pulse propagating in ambient humid air (red line), with a relative humidity of \sim 30 %. In the time domain it is seen that the peak electric field decreases for the humid air due to the absorption and dispersion of molecules, free induction decay is seen as well. In the frequency domain, the bandwidth of the pulse remains about the same, but

with lower amplitude and clear absorption lines are seen. The water absorption lines correlate well with previously reported values [175].

Dispersion Control

Dispersion control needs to be taken into account when dealing with ultrashort laser pulses in the fs time scale, since the more dispersed the pulse is, less broadband THz generation is obtained. Even when propagating in air fs pulses will disperse slightly, dispersion is even greater when the pulse propagates through a medium, for this reason the THz spectrometer is designed and built with this in mind. The vast majority of the optics in the spectrometer are reflective while the number of transmissive optics is kept at a minimum.

Pump Photoexcitation Conditions

The photoexcitation pulse needs to spatially overlap and be uniform over the whole region probed with a THz pulse, which is focused to a diffraction limited spot. An inhomogeneous excitation would map to the frequency dependent response through the overlap with the diffraction limited spot size at that given frequency in the pulse [1]. Remembering that 1.0 THz corresponds to 300 μ m, then if frequency components up to 0.25 THz want to be modulated, the pump beam needs to be homogeneous over a 1.2 mm diameter.

Phase Difference Between ω and 2ω Pulses

The relative phase θ between the ω and 2ω beams, can be controlled by spatially moving the position where the 2ω beam is generated relative to the focus, this is done by





FIGURE 2.25: (a) Schematic of the ω and 2ω phase difference at the plasma position (b) Compensation for ω and 2ω phase resulting in a more efficient THz generation.

moving the SHG non-linear crystal, β -BBO in this case. This is because in air, the refractive index at frequency ω is slightly lower than at 2 ω . To achieve a phase difference of $\theta = \Delta n \omega d/c = \pi/2$, the β -BBO will have to be moved a total of d = 8.23 mm, where a value of $\Delta n = 2.43 \times 10^{-5}$ was taken from [176]. In this way, the THz generation can be optimized by changing the position of the β -BBO crystal and the focus some millimeters along the propagation direction.

However the THz efficiency can be further optimized when the walk off between the ω and 2ω pulses in all transmissive optical media is compensated [174]. The 2ω beam is generated perpendicular to ω , due to the birefringence of the medium the beams will have a ~19 fs walk off at the exit of a 100 µm β -BBO crystal. An additional walk of is introduced given that the two beams propagate in air, a propagation of ~150 mm will further separate the pulses by ~12 fs. Only the tail of the pulses will spatially overlap and contribute to the THz emission. This is shown schematically in Fig. 2.25(a). This emission can greatly be enhanced by compensating the walk off of the pulses. To compensate for the walk off of the ω and 2ω pulses, a birefringent material such as α -BBO is introduced so that the 2ω pulse leads the ω pulse, then quartz wedges are introduced to fine tune the walk off of the pulses. With this a better overlap can be achieved resulting in a greater overall THz signal, as shown schematically in Fig. 2.25(b).

Linearity of ABCD

It is desired to have a linear relationship between the THz electric field and the detected ABCD signal in order to perform reliable spectroscopy, since a non-linear response may lead to artificial gains in the spectroscopy. For this reason, the setup was tested with a photomultiplier tube (PMT) and showed that the technique of ABCD was linear with applied electric field for the applied bias voltages as shown in Fig. 2.26. However, it has been shown that a PMT can present a non-linear response on the THz electric field amplitude, while an avalanche photodiode (APD) presents a linear response [177], the fact that this non-linear behavior was not seen for this setup may be due to greater electrode distance, an thus an overall lower electrical bias per meter. Besides, the APD has other advantages over the PMT: it has a greater signal to noise ratio (SNR) and and greater dynamic range (DR)[177]. For this reason the THz detection setup was upgraded resulting in the replacement of the PMT with a boxcar integrator and an

Technical Description



FIGURE 2.26: Linearity of peak electric field with applied bias voltage in the ABCD technique.

APD.

Detection Electronics

As discussed in section 2.1.4, in the detection of THz pulses based on the ABCD method a second harmonic signal will be obtained proportional to the THz radiation ($I_{2\omega} \propto \chi^{(3)}I_{\omega}^2 E_{bias}E_{THz}$), a 400 nm bandpass filter is used to send only the second harmonic to an avalanche photodiode (APD). The output of this APD is then sent to a boxcar gated integrator to integrate over narrow gate the fast transient from the APD, the output of this gated integrator is then sent for lock-in detection [177]. The lock-in amplifier is locked to the modulating high voltage bias used in the ABCD technique. The output of the lock-in is finally sent to a computer through a General Purpose Interface Bus (GPIB) to USB interface and a custom made LabVIEW program collects and saves the THz waveform.

Dual lock-in Detection

When performing a TRTS experiment, both pumped and reference signals can be obtained simultaneously. This is done with the purpose of eliminating systematic timing variations [166] from scan to scan. In order to do this, two lock-in amplifiers are used. One lock-in measures a THz waveform, locked to the modulation frequency of the applied electrical bias in the ABCD technique, while the second lock-in measures a pump induced change in the THz waveform, locked to a modulation of the pump photoexcitation beam, introduced by an optical chopper.

Frequency Resolution of a THz Scan

The laser amplifier used for this TRTS setup had pulses of typically 40 fs. In the air plasma THz setup this produced pulses that extended above 30 THz, thus it is important to take measurements that allows the recovery of such high frequency components. To cover the desired frequency components of a waveform, a sampling f_s of at least twice of the highest waveform frequency is needed, according to the Nyquist frequency,

$$f_{Nyquist} = 0.5f_s \tag{2.49}$$

With $f_s = 1/10$ fs = 100 THz, the maximum frequency that can be recovered is 50 THz. This step size is enough to cover the desired bandwidth and was used for most of the experiments. The frequency resolution is another important parameter that needs to be taken into account when performing measurements. The frequency resolution is given by f = 1/N thus, in order to have a resolution of at 0.5 THz, a 2 ps scan is needed while 0.1 THz resolution is obtained with a scan length of 10 ps.

Chapter 3

Narrowband THz Emission from β-Barium Borate

This chapter is based on

Multi-Cycle Terahertz Emission from $\beta\mbox{-Barium}$ Borate

David A. Valverde-Chávez and David G. Cooke. *Journal of Infrared, Millimeter, and Terahertz Waves* 38, **1** (2017), pp. 96-103.

3.1 Abstract

We report the observation of strong narrowband terahertz emission at 10.6 THz from the common nonlinear second harmonic generation crystal β -barium borate crystal excited by 40 fs laser pulses at a 800 nm center wavelength. The emitted THz field amplitude is linear with incident pump energy with no saturation observed up to 2 mJ of pump pulse energy, and exhibits a crystal azimuthal angular dependence consistent with an optical rectification process. The narrowband emission can be explained by the large dispersion caused by optical phonons in the vicinity of the emission energy.

3.2 Introduction

Optical rectification of femtosecond pulses in a $\chi^{(2)}$ medium is a common mechanism for generating single cycle character, broadband terahertz (THz) pulses [13–15]. The phase matching condition requires the THz phase index and optical pulse group index to be similar, and dispersion of these quantities typically limits the bandwidth of the emitted THz pulse. In addition, the absorption due to phonons must allow for transparency in emitted THz bandwidth, or the effective conversion length is limited to the THz skin depth of the crystal. The ease of optical alignment due to the co-linearity of the THz emission and the pump beam, as well as the availability of high damage threshold, phase matched crystals has made a considerable impact on the accessibility of the THz frequency band and subsequently THz science [10]. Optical rectification in a nonlinear crystal, such as ZnTe, is the method of choice for many laboratories. ZnTe is phase matched for collinear generation with 800 nm pulses emitted from commercially available Ti:sapphire femtosecond oscillators and amplifiers [15]. Recently, however, tilted pulse front optical rectification in LiNbO₃ is becoming more prevalent, capable of reaching very high optical-to-THz conversion efficiencies due to a cascaded nonlinearity [107–109].

The generation of phase-stable, narrowband THz pulses from a simple bulk nonlinear crystal, however, is less prevalent in the literature. Narrowband THz emission from nonlinear crystals has been demonstrated by two-color difference frequency mixing in organic nonlinear crystals [178], temporal patterning of the optical photoexcitation [34, 179], quasi-phase matching via periodic poling of stacked crystals [36], multiple line excitation and out-coupling of consecutive Cherenkov wavefronts in lithium niobate [35, 180] and chirped pulse optical rectification [181]. Quantum cascade lasers are monochromatic THz emitters, however their processing requires sophisticated fabrication methods[182–184] and high efficiencies are limited to cryogenic temperatures [183]. Recently there have been reports of narrowband THz generation in the scintillator crystal bismuth germanate crystal at 2 THz, matching the transverse optical (TO) phonon frequency, with a narrow bandwidth of ~ 26 GHz [37].

Beta-barium borate (β -BaB₂O₄) or β -BBO is a birefringent inorganic compound widely used in nonlinear frequency mixing [185] and is found in virtually every femtosecond laser laboratory. It has a high optical damage threshold and exhibits suppressed twophoton absorption with a band gap energy of 6.43 eV [186], allowing high peak power excitation with pulses of center wavelength of 800 nm from commercially available Ti:sapphire laser systems. In the case of THz emission from laser-induced plasmas in gases, β -BBO plays an important role in very broadband THz generation, where ultra-broadband THz pulses are generated [18]. It has also been used for the coherent detection of intense THz fields [187] and has been proposed as a good candidate for



FIGURE 3.1: Schematic of THz generation, a 40 fs, 800 nm laser pulse goes through a β -BBO generating narrowband THz pulses, ϕ is the angle between the *y* axis and the extraordinary axis of the crystal (white mark).

THz waveplates [133]. In this work, we add one more item to the already long list of applications for β -BBO: narrowband emission of phase stable THz pulses at 10.6 THz. We show that the emission is consistent with optical rectification and the angular dependence of the polarized emission is in accordance with the trigonal symmetry of the crystal.

3.3 Experimental

A simple schematic of the THz generation is shown in Fig. 3.1. A collimated NIR laser pulse with a $1/e^2$ beam diameter of ~ 11 mm, linearly polarized along the laboratory x-axis (indicated) excites a 100 μ m-thick β -BBO crystal (Eksma Optics cut at θ = 29.2°, with a clear aperture diameter of 10 mm). We define the crystal azimuthal angle ϕ as between the laboratory y axis and the extraordinary axis of the crystal (white mark on figure). The β -BBO crystal is cut for phase matched second harmonic generation (SHG) at 800 nm, and so is commonly found in many laboratories. The experimental THz detection setup is depicted in Fig. 3.2 based on air biased coherent detection [130, 188],



FIGURE 3.2: Experimental setup used to observe narrowband THz emission β -BBO.

capable of detecting frequency components of the pulse up to 30 THz. The p-polarized, 40 fs laser pulse from a 1 kHz regenerative Ti:sapphire femtosecond amplifier at a pulse energy of 3.3 mJ and center wavelength of 800 nm is split at an 80/20 beamsplitter to form the generation and detection beams. The generation pulse is delayed with respect to the detection pulse by a retro-reflecting delay stage, and pumps a β -BBO crystal with polarization aligned along the extraordinary axis of the crystal unless otherwise stated. The transmitted optical pulse is blocked by a thin Teflon (PTFE) film and a black polyethylene (PE) film, both polymers show a flat response in the THz region of interest [135], and thus, the emitted THz pulse is transmitted and is imaged by a series of off-axis parabolic mirrors to be focused at a spot between two high voltage electrodes, separated by a ~ 2 mm spacing. The high voltage is modulated between ± 7 kV at 500 Hz, half the repetition rate of the laser, and is used as a local oscillator for phase sensitive detection of the THz pulse. The optical detection pulse travels through a small hole in the last parabolic and is overlapped in space and time with the instantaneous electric field of the THz pulse. The instantaneous THz pulse electric field is mapped onto the intensity of the field-induced 400 nm pulse measured with an avalanche photodiode



FIGURE 3.3: Time domain electric field emitted from the β -BBO crystal with 800 nm pump pulse at a pump energy of 2.65 mJ.

[130, 188], and the entire THz pulse waveform is determined by recording this signal while the optical delay line is scanned.

3.4 **Results and Discussion**

The electric field waveform of an emitted THz pulse is shown in Fig. 3.3 at the maximum pump pulse energy of 2.65 mJ. The polarization of the pump pulse is aligned to the extraordinary axis of the β -BBO crystal, corresponding to $\phi = 90^{\circ}$ in Fig. 3.1. The emission obtained from the β -BBO is a multi-cycle THz pulse with the corresponding power spectrum is shown in Fig. 3.4. A Gaussian fit to the power spectrum reveals a 10.6 THz center frequency with a full-width at half-maximum of 0.85 THz. In addition to the strongest 10.6 THz narrowband peak, broadband emission can be observed from 1 to 15 THz as a background in the spectrum. Weak emission from a β -BBO crystal cut



FIGURE 3.4: (a) Fourier power spectrum (dots) and a fit to a Gaussian (red line) showing a narrowband peak at 10.6 THz with a full width at half maximum of 0.85 THz (b) Fourier power spectrum in Log scale.

for SHG at 800 nm has been previously reported and identified as a $\chi^{(2)}$ based optical rectification process with Fourier components up to 3 THz [119, 189, 190].

A likely source of the narrowband emission is therefore also optical rectification, however with phase-matching achieved only over a small frequency range dictated by the dispersion of the THz phase index in the vicinity of an optical phonon. The temporal shape and bandwidth of the emitted THz depends on the excitation pulse temporal duration, phase matching and reabsorption of the THz field within the medium [10]. The 40 fs duration optical pulses, with a FWHM bandwidth of 29 nm or 13.6 THz, permits the generation of such high frequency narrowband THz light via nonlinear difference frequency mixing between longitudinal modes in the pulse. The THz electric field emitted via a second order nonlinear optical rectification process is linearly proportional to the intensity of the pump pulse $E_{THz} \propto |E_{800nm}|^2$ [191]. A pump energy dependence of the THz field amplitude E_{THz} was measured with an incident energy



FIGURE 3.5: Amplitude of the emitted THz electric field dependence on the pump pulse energy, showing the linear relation $E_{THz} \propto \chi^{(2)} E_{800 nm}^2 \propto I_{800 nm}$.

varying from 8 μ J to 2.1 mJ, covering more than two decades and shown in Fig. 3.5, the data is well described by a linear fit consistent with optical rectification. Fabry-Perot transmission resonances can partially account for the narrowband emission, combined with the 11 THz cutoff observed in the measured field transmission coefficient shown in Fig. 3.6 for polarizations aligned along the ordinary (T_{||}) and extraordinary (T_⊥) axes, however, these resonances cannot account for the large enhancement in conversion efficiency at the 10.6 THz center frequency. These transmission spectra were obtained in a plasma THz generation setup with ABCD detection [130, 135] and are in good agreement with previously reported transmission measurements [132].

The origin of this narrowband terahertz emission can be explained by a sudden increase in the coherence length l_c , defined as the interaction length corresponding to a phase mismatch of π between the optical and THz pulses [15]:



FIGURE 3.6: Transmission of a THz pulse along the ordinary (T_{\parallel}) and extraordinary (T_{\perp}) axis.

$$l_c(\nu_{THz}) = \frac{c}{2\nu_{THz}|n_{gr}(\nu_0) - n_{THz}(\nu_{THz})|}$$
(3.1)

where *c* is the speed of light, ν_{THz} the THz frequency, ν_0 the near infrared frequency, n_{gr} the group velocity refractive index of the pump and n_{THz} is the THz refractive index [15]. When the phase matching condition $n_{THz} \approx n_{gr}$ is satisfied, l_c will rapidly increase to exceed the thickness of the crystal allowing for efficient optical to THz energy conversion. The optical group refractive index n_{gr} for β -BBO is 1.68 (1.56) for the ordinary (extraordinary) axis respectively [192, 193], while n_{THz} has been measured by reflection THz time-domain spectroscopy as 2.23 (2.75) for the ordinary (extraordinary) axis respectively at 10 THz [133], close to the emission frequency of 10.6 THz. For THz polarization aligned along the extraordinary axis and corresponding to the highest emission



FIGURE 3.7: Extraordinary index of refraction (n_{THz}) extracted from THz-TDS data and group index (n_{gr}) of 800 nm pump pulse indicated with a dashed line.

efficiency, this would yield a coherence length $l_c = 12 \ \mu m$, which is much shorter than the 100 μm thickness of the crystal and would not explain the narrowband emission. On the other hand, narrowband emission can occur if phase matching is satisfied only over a narrow frequency region in a bulk crystal. This might be the case for β -BBO, where the transmission spectra shown in Fig. 3.6 shows regions of strong absorption in this spectral region above the reststrahlen band between 4 and 8 THz. This would indicate a corresponding change in the refractive index, so that for a narrow range of frequencies phase matching can be satisfied.

Fig. 3.7 shows the extracted extraordinary index n_e and n_o in the vicinity of the emission energy following inversion of the Fresnel transmission coefficients using the complex valued THz transmission spectra. Phase-matching $n_e = n_{gr}(800 \text{ } nm)$ occurs at 10.9 THz, on a side of an optically active phonon absorption feature centered at



FIGURE 3.8: The coherence length where blue regions are below the 100 μ m crystal thickness (dashed line) and THz absorption coefficient indicated by the red line.

11.7 THz. The corresponding coherence length is calculated in Fig. 3.8 based in this n_e spectra, showing that narrowband emission is expected in the frequency range where the coherence length is larger than the crystal thickness. The absorption coefficient α_e is also shown in Fig. 3.8, showing strong attenuation of THz emitted above 11 THz. It is worth mentioning that in the ABCD technique, the geometry of the THz detection is fixed and co-polarized with the optical pump pulse for THz generation such that we were sensitive only to an $e + e \rightarrow e$ phase matching condition, but not $o + o \rightarrow e$.

The polarization dependence of the THz emission was investigated by rotation of the crystal around the azimuthal angle ϕ and measuring the resulting THz field amplitude with fixed optical pump and THz polarization. The corresponding spectral amplitude is shown in a two-dimensional angle-frequency map in Fig. 3.9 Besides the strong narrowband 10.6 THz emission, weaker emission is observed in other spectral



FIGURE 3.9: Two dimensional map of the spectral amplitude vs azimuthal angular dependence.

regions, notably also near transmission edges seen by inspection of Fig. 3.6. The three most intense emission frequencies, 4.3, 7 and 10.6 THz are plotted in polar coordinates in Fig. 3.10. The obtained radiated patterns can be explained by the symmetry of the crystal. β -BBO has a trigonal crystal structure with point group 3m and the expected azimuthal angular dependence of the radiated electric field emitted via an optical rectification process can be obtained from the general equation [190, 194]:

$$E_{THz}(\theta) \propto \alpha \cos^3 \phi + \beta \cos^2 \phi \sin \phi + \gamma \cos \phi \sin^2 \phi + \delta \sin^3 \phi$$
(3.2)

where α , β , γ , δ are fitting parameters that contain the *d* nonlinear optical coefficients of the crystal. Fig. 3.10 shows the angular distributions of THz emission, with fits using Eq. (3.2). The fits closely replicate the expected theoretical emission for the trigonal



FIGURE 3.10: Polar plot of the angular dependence for the selected frequencies 4.3, 7 and 10.6 THz, the lines are fits to the amplitude of Eq. (3.2).

structure, and together with the emitted field amplitude obeying the linear intensity dependence, we conclude that the optical rectification is the mechanism involved in the THz generation, with the strong narrowband emission due to a region with good phase matching because of a sudden change in the THz refractive index.

3.5 Conclusion

We detected multi-cycle THz pulses that correspond to a narrowband emission peaked at 10.6 THz by pumping a 100 μ m thick β -BBO phase matched for SHG, with 40 fs, 800 nm pulses from a regenerative Ti:sapphire amplifier. The THz field amplitude displays a linear pump energy dependence consistent with an optical rectification process and the angular dependence corresponds to that of trigonal crystal. The origin of the narrowband emission comes from phase-matching over a small frequency range. β -BBO is a widely used nonlinear crystal, and so the generation of these phase-stable narrowband THz pulses is likely, and unknowingly, occurring already in many labs around the world.

Chapter 4

Charge Transport Mechanisms in a New Gamma Ray Detector Material

This chapter is partially based on

Charge Transport Mechanisms in a Pb₂P₂Se₆ Semiconductor

Svetlana S. Kostina , Micah P. Hanson, Peng L. Wang, John A. Peters, David A.

Valverde-Chávez, Pice Chen, David G. Cooke, Mercouri G. Kanatzidis, and Bruce W.

Wessels. ACS Photonics 3, 10 (2016), pp. 1877–1887.

4.1 Introduction

Given the important applications of gamma ray detection within high energy physics, astrophysics, medical imaging and nuclear security [195], there has been a special interest on creating low cost detectors. However the development of new detectors faces different challenges. There is a limited quantity of prospective materials, which possess both high resistivity and wide bandgap, in the range from 1.6 to 3.0 eV [40]. Wide bandgap semiconductors such as cadmium telluride and cadmium zinc telluride (CZT) have been promising materials for gamma and X-ray detection, however their fabrication involves not only expensive methods but also it introduces defects causing a poor hole charge collection [196]. According to this, recent research has aimed to discover alternative materials and found chalcophosphate compounds as a promising new materials for X-ray/ γ -ray detection. In particular, heavy metal selenophospate Pb₂P₂Se₆ is of great interest since it has an indirect band gap of 1.88 eV and electrical resistivity around 1 x 10¹⁰ Ω cm. Pb₂P₂Se₆, is composed by abundant elements and the process involved in the crystal growth is less challenging compared with other materials such as CZT [41].

The figure of merit for detectors is the the mobility lifetime product, which gives an indication of how long created charges can travel and thus if the charge can be extracted, being a key parameter to determine the quality of any detector material. The mobility lifetime product is also the material parameter which describes the dependence of the charge collection efficiency of a certain detector under an applied bias and it is assumed that the lifetime τ decays exponentially [197]. The electron carrier mobility-lifetime product of the Pb₂P₂Se₆ has been calculated to be 3.5 x 10⁻⁵ cm² V⁻¹



FIGURE 4.1: Picture of γ -ray material Pb₂P₂Se₆.

[41], this value is lower than the calculated for CZT, in spite of this the attractive properties of chalcophosphate motivates to perform a more complete optical characterization. Terahertz spectroscopy is an extremely useful technique which allows the measurement of both mobility and carrier lifetime independently. In the present chapter, the multi THz response of single crystal $Pb_2P_2Se_6$ through Time Resolved Terahertz Spectroscopy (TRTS) is discussed.

4.2 Optical Pump – THz Probe in Reflection

An air based TRTS setup, described in chapter 2, was used to perform measurements in a $Pb_2P_2Se_6$ crystal (picture of the measured crystal is shown in Fig. 4.1) in order to determine the temporal dynamics of the photo-excited carriers. The measurements were done at room temperature, in a dry air purge gas environment and for various pump fluences. 40 fs pulses coming from a Ti:sapphire regenerative laser amplifier were used to generate phase stable terahertz pulses in dry air from a two color laser plasma, the THz pulse electric field was detected in an air-biased coherent detection (ABCD) scheme. An ultrabroadband THz pulse was incident on the Pb₂P₂Se₆ sample in normal reflection mode, and the full time domain profile of the THz pulse was recorded. A second femtosecond pump pulse with wavelength of 560 nm (2.21 eV in energy) collinear with the incident THz field was used to photoexcite the sample at different pump probe delay times (τ_p) with respect to the time of arrival of the THz pulse. The pump induced change in the reflected THz electric field waveform is given by $\Delta E(t, \tau_p) = E_{pump}(t, \tau_p) - E_{Ref}(t)$, where $E_{pump}(t, \tau_p)$ is the electric field of the reflected THz pulse in the presence of the pump pulse and $E_{Ref}(t)$ is the reference THz waveform in the absence of optical photoexcitation. The complex differential reflectance $\Delta \tilde{r}(\omega, \tau_p)/\tilde{r}_0$ is defined in terms of the spectral amplitude and phase of the respective Fourier transformed fields $\Delta \tilde{E}(\omega, \tau_p)$ and $\tilde{E}_{ref}(\omega)$:

$$\frac{\Delta \widetilde{r}(\omega, \tau_p)}{\widetilde{r}_0} = \frac{\Delta \widetilde{E}(\omega, \tau_p)}{\widetilde{E}_{ref}(\omega)}$$
(4.1)

where $\tilde{r}_0 = (1 - n(\omega))/(1 + n(\omega))$ is the reflection coefficient of the unexcited sample and $n(\omega)$ the frequency dependent refractive index in the dark state.

The reflected THz waveform, $E_{ref}(t)$, from the surface of a Pb₂P₂Se₆ sample was measured and compared with the THz waveform reflected after a pump pulse excited the sample $E_{pump}(t, \tau_p)$, this waveforms are shown in Fig. 4.2. The maximum of ΔE was found at $\tau_p \approx 300$ fs, where the photoconductivity is fully developed at this time.

The amplitude (blue line) and phase (green line) of the complex differential reflectance $\Delta r(\omega)$, recorded at $\tau_p \approx 300$ fs, are shown in Fig. 4.3. It presents multiple


FIGURE 4.2: (a) Reflected THz pulse $E_{ref}(t)$ from unexcited Pb₂P₂Se₆ (b) differential reflected THz pulse $\Delta E(t, \tau_p)$ for pump-probe delays of 0.2 and 3 ps. The dashed line indicates the region where the reflectance was monitored in the 1-D scan.

resonant features due to charge carrier induced screening of optically active phonons with frequencies at 3.2, 5.5, 8.8 and 13.8 THz. These features are in fair agreement with previously reported infrared (IR) active B_u phonons (molecular vibrational frequency in a C_{2h} symmetry group) in Pb₂P₂Se₆ located at 4.0, 5.0, 8.6, 13.3 THz [43]. The fact that the phonon feature at ~ 14 THz is screened by the mobile carriers at this frequency, indicates that the Drude momentum scattering time τ is at least as small as 1 / ω = 1 / (2 π 14 THz) ~ 10 fs due to the 1/ ω ² roll off of the real ac conductivity above $\omega \tau$ = 1. This scattering time is of the same order of magnitude as is typically observed in organic polymers [134]. In the Drude model, the mobility is given by $\mu = e\tau/m$, thus a high mobility-lifetime product requires a long Drude scattering time.



FIGURE 4.3: Amplitude (blue) and phase (green) of the differential multi-THz reflectance at 300 fs following photoexcitation at 2.21 eV for a pump fluence of 700 μ J/cm².

4.3 Non-Drude Conductivity

At the peak of the THz pulse, all Fourier components in the pulse are in phase. Monitoring the pump induced change in reflectance of this peak, in absence of any strong transient phase shifts, amounts to measuring the frequency averaged THz photoconductivity over the entire bandwidth of the pulse [134]. This method of data acquisition contains less information than the full waveforms, however it allows to observe the relaxation dynamics with greater pump-probe delay resolution. The pump-induced change in the reflected amplitude of the THz pulse normalized to the dark state reflectance, $\Delta r/r_0$, was recorded as a function of different fluence at a pump energy of 2.21 eV, this is shown in Fig. 4.4. It was found that $\Delta r/r_0$ is linear with photoconductivity in the limit of small $\Delta r/r_0$. The rise time of the photoconductivity, shown on the



FIGURE 4.4: Fluence dependence of the differential reflection of the peak of the THz pulse as a function of pump-probe delay time with a pump energy of 2.21 eV. The inset shows a 10% - 90% rise time of ~ 200 fs.

inset of Fig. 4.4, was determined to be ~ 200 fs, approximately five times our temporal resolution. This risetime can be explained either by the generation dynamics of free charge density or a transient increase of the charge carrier mobility, or both, as the photoconductivity is a product of these two quantities. To visualize the photoconductivity dynamics better, $\Delta r/r_0$ is also presented in a log-log scale as shown in Fig. 4.5, the data plotted this way shows hints of an exponential decay. The $\Delta r/r_0$ relaxation dynamics are indeed well described by a power law decay of the type:

$$\frac{\Delta r(\tau_p)}{r_0} = A \cdot \tau_p^{-\beta} \tag{4.2}$$



FIGURE 4.5: Log-log fluence dependence of the differential reflection of the peak of the THz pulse as a function of pump-probe delay time with a pump energy of 2.21 eV. The line of slope m = -0.5 is a guide for the eye for a power law decay of $t^{-0.5}$.

with a slope of $\beta \approx 0.5$. This power law type of decay can be attributed to dispersive transport, which is present in disordered systems where conduction proceeds by a sequence of charge transfer steps through distributed localized trap states to another trap state in the presence of an electric field, located energetically below a mobility edge [198]. The power law arises from a distribution of trapping times into localized states which are energetically or spatially disordered [199]. In multiple trapping models of dispersive transport, the photoconductive decay follows a power law given by $t^{\alpha-1}$ where α is the dispersion parameter, and $t^{\alpha-1} = t^{-\beta}$ giving $\alpha = 1 - \beta$ [200].

This power law model was used to fit $\Delta r/r_0$ and obtain the *A* and β parameters, the fit was made starting from ~ 2 ps after the onset of photoconductivity, for the measured



FIGURE 4.6: Fits to a power law decay $\Delta r(\tau_p)/r_0 = A\tau_p^{-\beta}$ as a function of pump fluence for the amplitude *A* and the decay exponent β .

pump fluences, the results of the fits are shown in Fig. 4.6. The linear increase of amplitude A with increasing pump fluence is consistent with direct generation of charges and indicates the absence of any nonlinear charge generation mechanism. The value of the β coefficient ranges from 0.5 to 0.6 and is not strongly dependent on pump fluences, showing only a slight increase at the highest two pump fluences. The observed dispersive transport is consistent with photoconductivity being dominated by transport via a distribution of trap states. This picture is incompatible with the often used maximal charge collection efficiency analysis [41], where an exponential decay of charges is assumed.

The magnitude of the THz response can be quantitatively used to roughly estimate the charge mobility using the photoinduced reflectivity spectra in 4.3. Because of the



FIGURE 4.7: Reference THz pulse (blue) and THz pulse after transmission through a 0.815 mm thick Pb₂P₂Se₆ sample (green). The time delay $\Delta t \sim 12.85$ ps is shown on the plot.

presence of phonons at various THz frequencies, $\tilde{n}(\omega)$ and $\tilde{r_0}(\omega)$ are frequency dependent with four resonances in the frequency window of 2 - 14 THz, however below 2 THz no resonance is present and the Δr in this region could be used to make an estimate of the mobility. It is the necessary to determine the background refractive index of the crystal. The refractive index in this frequency range can be estimated by measuring the optical path delay of a 3 THz bandwidth limited reference THz pulse through the Pb₂P₂Se₆ sample in reference to a pulse traveling through only air, this is shown in Fig. 4.7. In this experiment, the time delay introduced by the sample of thickness d =815 µm is given by $\Delta t = (n - 1)d/c$. With a THz reference pulse containing frequency components in the range from 0.1 to 3 THz, a value of $\Delta t =$ 12.85 ps was measured, consequently a frequency averaged refractive index of 5.78 was obtained.

4.4 Mobility Estimation

Information on the subpicosecond complex THz photoconductivity $\tilde{\sigma}(\omega, \tau_p)$ of the sample after excitation at delay τ_p can be extracted from the differential reflectance $\Delta \tilde{r}(\omega, \tau_p)$ spectra by employing the following analytic relationship:

$$\frac{\Delta \widetilde{r}(\omega, \tau_p)}{\widetilde{r}_0} = -\frac{1 + \widetilde{r}_0}{\widetilde{r}_0} \frac{dZ_0 \widetilde{\sigma}(\omega, \tau_p)}{1 + \widetilde{n}(\omega) + dZ_0 \widetilde{\sigma}(\omega, \tau_p)}$$
(4.3)

where Z_0 is the impedance of free space and d is the pump pulse penetration depth. A sample from the same ingot showed a low photoresponse of ~ 2 x 10⁻⁸ Ω^{-1} cm⁻¹ [42], therefore it is expected that the scattering mechanisms that limit the photoresponse of other Pb₂P₂Se₆ samples to be also strongly present in this specimen. From the change in peak conductivity, Eq. 4.3, a sheet conductivity of 0.003 Ω^{-1} m⁻¹ was calculated.

While often not applicable in disordered systems, if a Drude form for the ac conductivity is assumed then the mobility can be obtained for estimation purposes. In the limit of $\omega \tau \ll 1$, where τ is the Drude momentum scattering time, the change in photoconductivity σ is directly related to mobility μ by $\sigma = n_{max}e\mu$. The maximum carrier density injected, n_{max} , is given by

$$n_{max} = \frac{\eta(1-R)F}{dh\nu} \tag{4.4}$$

where η the quantum efficiency, R the intensity reflection coefficient, F the incident pump fluence, d the pump penetration depth and $h\nu$ the photon energy. Assuming quantum efficiency of 1, and ignoring the reflection of the pump pulse, a mobility μ on the order of 10 cm²/(Vs) is estimated according to: 90 Chapter 4. Charge Transport Mechanisms in a New Gamma Ray Detector Material

$$\mu = \frac{-h\nu(1+n)}{eZ_0F} \frac{\Delta r}{1+r_0+\Delta_r}$$
(4.5)

The relatively low mobility in Pb₂P₂Se₆ further suggests that the photoresponse in Pb₂P₂Se₆ is being limited by a distribution of trapping and recombination sites within the crystal. With a mobility of ~ 10 cm²/(Vs) and a carrier lifetime of ~ 5 ps it is possible to obtain a figure of merit, the mobility lifetime product: $\mu\tau = 5 \times 10^{-11}$ cm² V⁻¹, this is orders of magnitude lower than what was previously reported for this material, 3.5×10^{-5} cm² V⁻¹ and is attributed to the fact that the latter lifetime product was obtained with the maximal charge collection efficiency analysis which wrongly assumes an exponential lifetime decay.

Chapter 5

Hybrid Metal Halide Perovskites

This chapter is based on

Intrinsic femtosecond charge generation dynamics in single crystal CH₃NH₃PbI₃ David A. Valverde-Chávez, Carlito S. Ponseca, Constantinos C. Stoumpos, Arkady Yartsev, Mercouri G. Kanatzidis, Villy Sundström, and David G. Cooke. *Energy & Environmental Science* 8, **12** (2015), pp. 3700-3707.

5.1 Abstract

Hybrid metal-organic perovskite solar cells have astounded the solar cell community with their rapid rise in efficiency while maintaining low-cost fabrication. The intrinsic material photophysics related to the generation of free charges, their dynamics and efficiency, however, remains to be understood. As fabrication techniques improve, larger crystal grain sizes have been shown to be a critical factor for improving both the optical and transport properties of the hybrid metal halide perovskites. In this work, we use pulses of multi-THz frequency light in the ultra-broadband 1 - 30 THz (4 - 125 meV) range to observe the ac conductivity in large single crystal CH₃NH₃PbI₃. Our spectra reveal the ultrafast dynamics and efficiencies of free charge creation and extremely high charge carrier mobility as high as 500 - 800 cm²/Vs. While quasi-equilibrium analysis of efficiencies through the Saha equation suggests a binding energy on the order of 49 meV, an observed reflectance feature appearing at high pump fluence occurs at 12 meV and is consistent with an orbital transition of the exciton, indicating a much lower Rydberg energy of 17 meV at room temperature. The signature of the exciton is found to vanish on a 1 ps time scale commensurate with the appearance of mobile carriers, consistent with thermal dissociation of the exciton to the continuum in the room temperature tetragonal phase.

5.2 Introduction

The impressive photovoltaic [201], water photolysis[202], and even lasing [203] properties of hybrid metal halide perovskites, combined with a composition of earth abundant elements, low fabrication cost and rapid energy payback time [204], shows great

5.2. Introduction

promise for next generation solution processable optoelectronic devices. The overall power conversion efficiency of organo-metal halide perovskite solar cells has climbed to 20.1% in a span of only three years [205, 206], the fastest rate of increase compared to all other solar cell technologies. This fast pace in device development has been matched by a flurry of spectroscopic investigations attempting to understand the intrinsic charge generation, recombination and transport properties of these materials [53, 71, 75–77, 79, 83, 207–217]. A key spectral region for these materials is 1 - 100 meV, encompassing the proposed exciton binding energy that determines the charge photogeneration efficiency [77, 78], carrier scattering rates governing charge transport, and lattice vibrations whose role in screening the exciton remains controversial [75, 81]. Time-resolved terahertz spectroscopy (TRTS) is a powerful technique to probe these low energy excitations immediately after photoexcitation on femtosecond time scales [134]. Previous THz studies on the trihalide and mixed halide perovskites have focused on frequencyaveraged THz absorption, probing energies below 10 meV [53, 71, 78]. These measurements on thin film samples have placed initial lower limits on the mobility, shown suppressed bi-molecular recombination, and indicated the role of the exciton binding energy in the generation of free charges on a ~ 2 ps time scale [53]. A very recent TRTS study performing full energy resolved spectroscopy on CH₃NH₃PbI₃ thin films over a relatively low 2 THz bandwidth observed a conductivity spectrum dominated by the disorder of the polycrystalline films and focused on the long time recombination dynamics occurring over several hundreds of picoseconds [217].

In this work, we concern ourselves with the intrinsic sub-picosecond dissociation dynamics of excitons and generation of charges in single crystal CH₃NH₃PbI₃. Only

recently have large single crystals of the hybrid metal halide perovskites become available, showing impressive charge transport characteristics including mobilities as high as 150 cm²/Vs and diffusion lengths over 100 μ m [50, 51, 54, 59, 218]. We perform complete energy and time-resolved ultra-broadband THz spectroscopy in the 4-125 meV spectral range (30 THz bandwidth) on a large single crystal of the hybrid metal halide perovskite CH₃NH₃PbI₃. Femtosecond photoexcitation at the band edge probes the kinetics of mobile charge generation via dissociation of excitons, without the influence of excess kinetic energy, with 40 fs temporal resolution. Our greatly enhanced bandwidth reveals the conductivity spectrum in the THz band is dominated completely by mobile charge screening of a large optically-active phonon, not considered in previous TRTS work. Accounting for the dispersion of the phonon, a simple Drude conductivity spectrum is revealed, permitting direct extraction of charge densities and mobilities in the absence of disorder. We observe remarkably high carrier mobilities for single crystals that reach 800 cm²/Vs on ultra-short time scales and analyze our results under the assumption of quasi-equilibrium to yield an exciton binding energy of 49 ± 3 meV. A more direct measurement of the exciton is found at high photoexcitation densities, where an orbital transition indicates a much lower binding energy of approximately 17 meV for the room temperature tetragonal phase [50]. We discuss this apparent discrepancy and point towards future work required to understand the nature of the exciton in this material.

5.3 Methods

5.3.1 Sample preparation

Single-crystals of CH₃NH₃PbI₃ suitable for characterization were grown from a solvent mixture comprising of aqueous HI (57% w/w, 5.1 mL) and aqueous H_3PO_2 (50% w/w, 1.7 mL). In a typical procedure, a 20 mL scintillation vial was charged with the colorless solvent mixture and heated to boiling (ca. 120° C). Addition of solid PbO (670 mg, 3 mmol) and CH₃NH₃Cl (202 mg, 3 mmol) led initially to the formation of a black precipitate which rapidly dissolved leading to a clear bright yellow solution. The boiling hot solution was then capped with several layers of parafilm tape to ensure that the composition of the vapors was maintained throughout the crystal growth process. Omission of this step leads to the crystallization of $CH_3NH_3PbI_3.H_2O$, instead. On standing, upon reaching ambient temperature a countable number (in the range of 10-100) of small CH₃NH₃PbI₃ crystals begin to form, which act as initial seeds for the subsequent crystal growth from the supersaturated supernatant solution. Well-formed, faceted crystals of rhombic dodecahedral crystal habit were obtained after 2 weeks with crystal sizes ranging from 1-4 mm among several batches, with the size of the crystals being inversely proportional to the number of the initial crystal seeds. The crystals were collected manually by decanting the mother liquor, pressed dry with a soft filtration paper and thoroughly dried under a stream of N_2 gas.

5.3.2 THz spectroscopy

Fig 5.1 shows the schematic of the optical pump – multi-THz probe measurement of the large, mm^3 sized single crystal of CH₃NH₃PbI₃, probing the (110) facet (in the cubic



FIGURE 5.1: (a) A schematic of the time-resolved multi-THz spectroscopy experiment is given, where a 40 fs, 1.56 eV pump pulse photoexcites the CH₃NH₃PbI₃ crystal at normal incidence, colinearly with a multi-THz probe pulse with Fourier spectral components spanning 1 - 30 THz (4 -125 meV). The sample is a single crystal CH₃NH₃PbI₃ approximately 1.5 x 1.5 mm in size with the (110) facet (indexed in the cubic setting) as the probed surface.

setting or (100) in the tetragonal setting) [50] of the crystal with image provided. The unit cell of the cubic phase is also shown, with the average position of the $CH_3NH_3^+$ cation indicated by the orange ball in the center of the unit cell. In these experiments, an optical pulse photoexcites the sample and the induced charge degrees of freedom are then probed by transmission or reflection of a phase-stable, single cycle electromagnetic transient with frequency components in the THz range, called a THz pulse. Charge carriers and excitons are excited in the sample by the pump beam resonant with the band edge at 1.56 eV to minimize initial excess energy, thereby suppressing direct exciton dissociation through this channel [6]. The penetration depth of the pump pulse is taken to be 1 μ m determined by thin film absorption [219], and it is assumed this is the same for a single crystal. Multi-THz pulses are generated via a two-colour laser plasma in dry air and the electric field is directly detected after normal incidence reflection off the crystal facet by an air-biased coherent detection scheme with 30 THz



FIGURE 5.2: In the absence of a photoexcitation, the incident (blue), transmitted (red) and reflected (black) multi-THz pulses after interaction with the crystal are shown.

bandwidth [134]. All measurements were performed under dry air environment and no evidence of oxidation was observed during the experiments.

5.4 Results

The incident THz pulse (E_{inc}), is shown in Fig. 5.2 along with the transmitted (E_{trans}) and reflected (E_{refl}) pulses in the absence of a photoexcitation. The ultra-broadband THz pulse E_{inc} (t) contains spectral components from 1 - 30 THz (4-125 meV or 33-1000 cm⁻¹), as shown in the corresponding Fourier amplitude spectrum in Fig 5.3. While the reflected pulse retains all incident Fourier components with noticeable dispersion, E_{trans} (t) is strongly chirped with no spectral components below 25 meV due to absorption and reflection arising from an infrared active phonon and dielectric relaxation of



FIGURE 5.3: Fourier amplitude spectra of the incident (black), transmitted (blue) and reflected (red) multi-THz pulses after interaction with the crystal in the absence of a photoexcitation. The amplitude of the pump-induced differential reflected field, $|\Delta E(\omega, 600 fs)|$, is also shown in green.

the CH₃NH₃⁺ cation [72]. The change of amplitude and phase of the THz pulse after transmission provides the complex dielectric function $\tilde{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ via inversion of the Fresnel equations, and is shown in Fig. 5.4. The spectra is dominated by an infrared-active Pb-I bond stretching mode at ~ 8 meV, previously observed in Raman and THz spectroscopy [83, 220] which happens to overlap with a breathing of the PbI₆ octahedra coupled with librational motion of the CH₃NH₃⁺ cation, as calculated recently in Ref. [221]. Higher frequency vibrational modes are observed at 112 meV and 155 meV, in agreement with Ref. [222] and associated with the C-N bond vibrations. In addition, a broad GHz dielectric contribution has also been identified from microwave measurements due to the relaxation of the CH₃NH₃⁺ cation [81]. The CH₃NH₃⁺ group is free to rotate and undergo librations in the room temperature tetragonal phase giving



FIGURE 5.4: The dark state dielectric function probing the (110) plane in transmission, with areas of no information indicated by the hatched regions.

a Debye contribution to the dielectric function with a picosecond relaxation time. As a result of these two lattice responses, the optical transmission is strongly suppressed for energies below 25 meV. The real dielectric function, $\epsilon_1(\omega)$, responsible for renormalizing the Coulomb interaction of injected electrons and holes and therefore the exciton binding energy E_B [79, 219], is nearly constant at 5.5 for 40 - 100 meV range. Below 40 meV near resonant with the exciton binding energy, however, $\epsilon_1(\omega)$ is quite dispersive. The dynamics of exciton-phonon coupling should therefore be considered when discussing the appropriate dielectric function [72].

We now turn to the time-resolved THz spectra after photoexcitation. The reference multi-THz waveform in the absence of optical pumping, $E_{ref}(t)$, is shown in Fig. 5.1 and Fig. 5.5(a) after normal incidence reflection from the (110) crystal facet, showing



FIGURE 5.5: (a) The reflected THz transient from the unexcited CH₃NH₃PbI₃ crystal (110) facet and (b) the two-dimensional $\Delta E(t,\tau_p) = E_{pump}(t,\tau_p) - E_{ref}(t)$ data set for pump-probe delay times $\tau_p < 1$ ps. (c) Selected cuts in the map along constant τ_p are shown, representing the buildup of photoconductivity in the crystal.

slight reshaping due to the dispersion of the crystal. The pump-induced change in the reflected THz electric field $\Delta E(t,\tau_p) = E_{pump}(t,\tau_p) - E_{ref}(t)$ at a given pump-probe delay time τ_p is measured at variable delays producing the two-dimensional time-domain data set shown in Fig. 5.5(b). Both $E_{ref}(t)$ and $\Delta E(t,\tau_p)$ are measured simultaneously through a double modulation scheme, required to eliminate the influence of systematic timing variations [166]. The Fourier amplitude of the modulated field in quasi-equilibrium is given in Fig. 5.3, showing spectral information is obtained between 8 -



FIGURE 5.6: (a) Amplitude and (b) phase of the differential multi-THz reflectance shifted by steps of 0.5 for clarity.

80 meV. The significant phase shift compared to the reference pulse indicates a strong change in the dispersion after charges are photo-injected into the crystal. This is a signature of injected mobile charges screening the lattice from the applied field, within the pump pulse penetration depth of 1 μ m in the crystal [219]. The amplitude of the $\Delta E(t,\tau_p)$ response, proportional to the pump-induced photoconductivity in the sample, reaches its maximum within 400 fs after photoexcitation as seen in the differential waveforms in Fig. 5.5(c) for variable τ_p . We note that this is 10 times the temporal resolution of our technique and thus mobile carriers are not generated instantaneously but rather through exciton dissociation [78].

The corresponding spectral amplitude and phase of the pump-induced change in THz reflectance, defined as $\Delta \tilde{r}(\omega, \tau_p) = \Delta \tilde{E}(\omega, \tau_p) / \tilde{E}_{ref}(\omega)$, are shown in Fig. 5.6(a) and (b), respectively for pump-probe times from 0 - 400 fs at a pump fluence of 80 μ J/cm². The data can be understood by the analytic formula[134]:



FIGURE 5.7: The model of the complex index of refraction of the unexcited crystal used to describe the substrate dispersion and extract the complex photoconductivity.

$$\Delta \tilde{r}(\omega, \tau_p) = -\left(\frac{1+\tilde{r}_0}{\tilde{r}_0}\right) \frac{Z_0 d\tilde{\sigma}(\omega, \tau_p)}{1+\tilde{n}(\omega) + Z_0 d\tilde{\sigma}(\omega, \tau_p)}$$
(5.1)

where $\tilde{\sigma} = \sigma_1 + i\sigma_2$ is the complex ac photoconductivity, $\tilde{n} = n + i\kappa$ is the complex crystal index of refraction and \tilde{r}_0 is the complex crystal reflection coefficient given by $\tilde{r}_0 = (1 - \tilde{n})/(1 + \tilde{n})$. In the absence of photoconductivity, $\Delta \tilde{r}(\omega) = 0$ as well as in the limit for a highly reflective crystal with $n \gg 1$ where $r_0 \rightarrow -1$. Fig. 5.7 shows the complex index of refraction of the crystal used to describe \tilde{r}_0 , composed of a picosecond Debye dielectric relaxation and Lorentzian response modelling the 8 meV infrared active phonon in agreement with Fig. 5.4. The background complex refractive index of the crystal $\tilde{n}(\omega) = \sqrt{\tilde{\epsilon}(\omega)}$ and the dielectric function $\tilde{\epsilon}(\omega)$ is given by the Lorentzian phonon and Debye components

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\gamma} + \frac{\epsilon_s}{1 - i\omega\tau_D}$$
(5.2)

The high frequency dielectric function $\epsilon_{\infty} = 5.5$ determined from transmission measurements in Fig. 5.4, the Pb-I bending mode $\omega_0/2\pi = 1.96$ THz and the Debye relaxation time $\tau_D = 2.5$ ps with a low energy limit from literature $\epsilon_s \approx 30$ [81]. The spectra were found to be relatively insensitive to the phonon relaxation rate, set to a reasonable $\gamma = 0.1$ THz. The corresponding reflectivity amplitude $|r_0|$ is shown in Fig. 5.7 exhibiting a sharp drop to a minimum just below 20 meV. Thus the screeening of the lattice by injected mobile charge carriers is responsible for the large Δr response observed in Fig. 5.6(a), and by Kramers-Kronig the corresponding phase change in Fig. 5.6(b). By inversion of Eq. 5.1, the complete $\tilde{\sigma}(\omega, \tau_p)$ spectra can be extracted in temporal slices following photoexcitation, revealing the underlying ultrafast charge transport characteristics.

An example of the $\tilde{\sigma}(\omega, \tau_p)$ spectrum recorded at $\tau_p = 1$ ps after excitation is shown in Fig. 5.8. The data is very well described by a simple Drude model $\tilde{\sigma}(\omega) = \frac{n_D e^2 \tau}{m^*} \frac{1}{1-i\omega\tau}$, where n_D is the mobile charge density and τ is the momentum scattering time determining the charge carrier mobility through the relation $\mu = e\tau/m^*$ with $m^* = 0.2m_e$ being the charge carrier effective mass [223]. The Drude response confirms the band nature of transport in the single crystal CH₃NH₃PbI₃ as opposed to charges in a disordered film where hopping conductivity occurs. The scattering time τ can be estimated simply by the crossing point of σ_1 and σ_2 , occurring at an energy $h/(2\pi\tau) \approx 10$ meV. This provides an estimate of $\tau \sim 70$ fs corresponding to a remarkably high $\mu \sim 620$ cm²/Vs for a solution processed semiconductor. This measurement represents the highest mobility observed in these materials to date although recent improvements in



FIGURE 5.8: The complex conductivity spectrum with Drude spectrum fits recorded at 1 ps following excitation.

grain size and large crystal fabrication have seen μ on the order of 150 cm²/Vs [54, 59]. Moreover, the amplitude of the photoconductivity directly yields the mobile carrier density $n_D \approx 3.3 \times 10^{17}$ cm⁻³, estimated by the Drude dc limit $\sigma_{dc} = n_D e\mu$. The mobile charge carrier generation efficiency is given by $x = n_D/n_{ph} \approx 12\%$ where $n_{ph} = 2.9 \times 10^{18}$ cm⁻³ is the absorbed photon density given the pump fluence of 80 μ J/cm² and the 10% reflection of the pump at 795 nm [224]. This result is consistent with the expected result of the Saha-Langmuir equation defined as [77]:

$$\frac{x^2}{1-x} = \frac{1}{n_{phot}} \left(\frac{2\pi m_{ex} k_B T}{h^2}\right)^{3/2} e^{-\frac{E_B}{k_B T}}$$
(5.3)

assuming an exciton binding energy $E_B = 50$ meV at 293 K using an exciton effective mass $m_{ex} = 0.11$ m_e [223].

The results of global fitting of the Drude model to the complete two-dimensional



FIGURE 5.9: The mobile charge carrier generation efficiency defined as the ratio of the charge density to the absorbed photon density, at pump fluences of 80 and 140 μ J/cm².

time-frequency $\tilde{\sigma}(\omega)$ maps, fitting both real and imaginary components simultaneously, are shown in Fig. 5.9 and Fig. 5.10. The dynamics of the mobile charge generation efficiency for two pump fluences is shown in Fig. 5.9, exhibiting a slight transient enhancement for $\tau_p < 10$ ps at the lower fluence. The Saha-Langmuir equation accounts for this behaviour predicting a decrease in efficiency to 10% for the elevated fluence due to the greater probability of electron-hole binding [77]. The remaining ~ 90% of excitations, however are bound excitons that are unable to screen the lattice directly due to their charge neutrality. If pump photons excite carriers above the band edge, however, exciton dissociation will be influenced by the initial excess kinetic energy, providing higher mobile charge yields. The goal of this study, however, is to probe the energetics of thermal dissociation governed solely by the exciton binding energy and so we leave this to future work. The mobility is also extracted through the Drude fits as $\mu = e\tau/m^*$ and



FIGURE 5.10: Charge carrier mobility derived from the 80 and 140 μ J/cm² data sets with global complex fits to the Drude model.

is found to be relatively fluence independent, as shown in Fig. 5.10. A $\approx 20\%$ decrease is observed in carrier mobility on a sub-picosecond time scale, which we conjecture could be due to the charging of trap states or some charge-mediated phonon scattering mechanism. Despite the slight reduction in the transient mobility, the steady-state mobility of 550 cm²/Vs is orders of magnitude higher than other solution processed semiconductors. Such a high intrinsic charge carrier mobility points towards future improvements in photovoltaic power conversion efficiencies.

The induced mobile charges, however, should also screen the exciton as discussed in a recent observation of band filling effects [210], and so one expects more efficient generation at very high carrier densities. The critical Mott density that defines the threshold for the efficiency of this screening, however, has been estimated at $n_{crit} \approx 1 \times$ 10^{18} cm⁻³, nearly an order of magnitude higher than densities in Fig. 5.6. To investigate



FIGURE 5.11: (a) The two-dimensional data set of the differential reflectance amplitude at a fluence of $810 \ \mu\text{J/cm}^2$, showing the early time region where a low energy transient peak appears at $\approx 12 \text{ meV}$. Vertical lines indicate cut regions shown in (b) at 12 meV and 20 meV corresponding to exciton and free charges, respectively. The dynamics of exciton dissociation are represented by the decay of the 12 meV peak concomitant with the 1 ps free charge density risetime.

the effects of charge screening of the exciton, a two-dimensional data set was taken at $F=810\mu$ J/cm² with the $|\Delta r(\omega)|$ map shown in Fig. 5.11(a). The response is not well described by a Drude model alone, as it exhibits a transient low energy peak at 12 meV, below the main reflection peak at 20 meV. The dynamics of this excitation are shown by the vertical cuts in the map along the τ_p axis for the two peaks and plotted in Fig. 5.11(b). The onset of the lattice screening occurs on a time scale of 0.5 - 1 ps, larger than the 40 fs temporal resolution of the measurement and indicating the charge generation is driven by exciton dissociation. The 12 meV exciton peak initially tracks the rise time of the free charge 20 meV peak, however decays to the noise level by the time the lattice response is fully screened at $\tau_p = 1$ ps. This indicates a coupling

between the two excitations and we conclude that the 12 meV peak is due to an intraexcitonic orbital transition given the binding energies for trap states have been recently estimated to be much larger, on the order of 100 - 400 meV from the band edge [225]. We note if excitation into trap states was the dominant photoexcitation at the band edge, one would not expect a Drude conductivity spectrum but rather a conductivity which is activated at a characteristic frequency. Even if the quantum efficiency reaches 4.5% predicted by the Saha-Langmuir equation at this elevated fluence, $n_D \approx 1.3 \times 10^{18} \text{ cm}^{-3}$ which exceeds n_{crit} . In this regime, one expects all excitons are dissociated forming an uncorrelated plasma. The disappearance of the 12 meV peak could be due to the dynamic screening of the injected exciton population as the density increases beyond the critical Mott density on a sub-picosecond time scale. In this case we would also expect a frequency shift of the peak to lower energies as the charge density increases, which we do not see. We note that previous THz work investigating the Mott criterion for silicon has not observed this softening either [226]. The non-instantaneous rise time of the excitonic peak can be explained by considering the bandwidth of the pump pulse resulting in a non-resonant excitation to the ground state and it taking time for the many-body Coulomb correlations to build, forming an exciton [6].

The 12 meV peak is likely connected with the transition with the largest dipole moment, or an 1s - 2p transition which is typically 70% of the exciton Rydberg energy. This would suggest an exciton binding energy of approximately 17 meV in the room temperature tetragonal phase, in agreement with recent magneto-absorption measurements for the low temperature orthorhombic phase [76]. This is inconsistent however with their expectation of a critical collapse of the binding energy at room temperature

5.5. Conclusions

to values on the order of 5 meV. A more detailed understanding of the broadband dielectric function in the THz range at low temperatures is required and will be the topic of future work. Finally, we note that our quasi-equilibrium analysis has yielded a value consistent with several previous works employing the Saha equation, yet is in disagreement with the more direct measurement of an orbital transition of the exciton. Miyata et al. in Ref. [76] partially explained this discrepancy between their findings and those of others who find $E_B \sim 50$ meV by assuming their films were much more crystalline. Our single crystal measurements, however, show this result is present even in the absence of disorder. One possible cause could be a more complicated internal energetic structure of the exciton given the near resonance with a strong lattice vibration [72]. A better understanding of these materials will clearly require a detailed mapping of the dielectric function over relevant excitonic energy scales and temperature spanning structural transitions.

5.5 Conclusions

In conclusion, we have performed optical pump - multi-THz spectroscopy on a single crystal lead halide perovskite in the 8 - 100 meV spectral region relevant to the exciton. Our spectra reveal the dynamic screening of infrared active phonons and the background Debye relaxation of the $CH_3NH_3^+$ cation by the photogenerated free charge population. The sub-picosecond conductivity spectra directly reveals free charge densities and remarkably high mobilities of ~ 800 cm²/Vs on sub-picosecond time scales. Charge generation proceeds via exciton dissociation which is complete after 1 ps, much longer than the 40 fs temporal resolution of the technique. Analysis of the quantum

yield of free charges using a quasi-equilibrium Saha equation predicts an exciton binding energy of 49 ± 3 meV, however a more direct signature of an orbital excitonic transition at 12 meV is observed that indicates a binding energy on the order of 17 meV. The disagreement between the two may lie in the assumption of quasi-equilibrium or in a more detailed energetic structure of the exciton due to interaction with a near resonant phonon. The signature of the exciton is observed at densities above the Mott criterion where the Coulomb interaction is dynamically screened and they dissociate into free carriers.

Chapter 6

Conclusions

A state of the art air-plasma based THz time-resolved spectrometer was designed and constructed to study photoconductivity dynamics in a variety of materials. This spectrometer, unique to Canada and existing in only a handful of laboratories worldwide, is capable of covering the entire THz spectral window with a temporal resolution of ~ 40 fs with a few GHz spectral resolution. Using the enhanced detection bandwidth, it was possible to identify a previously unknown narrowband THz emission at 10.6 THz from the most commonly used nonlinear crystal in femtosecond research, β -BBO. The capabilities of this spectrometer was benchmarked on well known and studied inorganic semiconductors such as silicon, and then used to study carrier dynamics in several novel materials, including the quintessential hybrid organometallic halide perovskite CH₃NH₃PbI₃ of great interest within the solar cell community, and Pb₂P₂Se₆ with applications as a next generation γ -ray detection material. The importance of this work is not only to show these systems as promising materials for practical applications but also addressed fundamental questions related to their intrinsic photophysical properties.

The emission properties of β -BBO crystal were investigated, observing a strong narrowband THz emission at 10.6 THz. The source for this narrowband emission was identified as an optical rectification process, confirmed by the azimuthal angular dependence and the pump power scaling. The narrowband emission is due to phase matching near a restrahlen band, with phase matching achieved only over a narrow frequency range. Although there are many broadband sources of THz light, there are relatively few narrowband optical rectification sources. This work essentially tells the reader that virtually every lab already possesses a narrowband THz source already, just that they cannot detect the emission as it is beyond the typical 7-8 THz upper detection frequency for a GaP crystal. Moreover, multi-cycle THz emission from β -BBO crystal has an important advantage over other THz emitters such as periodic poling crystals which requires sophisticated processing or quantum cascade lasers that besides need cryogenic temperatures for high efficiency.

Multi-THz spectroscopy photoconductivity measurements were performed on a single crystal Pb₂P₂Se₂, a prospective material for γ -ray detectors. The figure of merit for detection materials is governed by the high capture cross section, satisfied by this material's high mass density and charge number *Z*, but also the ability to collect charge which is governed by the mobility - lifetime product. Moreover, since most models assume a simple exponential decay of charges governed by a single decay time, it is important to know whether the dynamics of mobile charge decay indeed obeys this law. Transient multi-THz spectroscopy can answer both of these questions, and was used to study this new γ -ray detector material. Clear phonon signatures were found within the bandwidth of the THz pulse, complicating the analysis. The temporal dynamics of the photoexcited carriers were investigated, presenting a power law decay

consistent with dispersive transport, showing that the assumption of a single decay time is false in this material. An estimation of the carrier mobility yielded a value of $\sim 10 \text{ cm}^2 \text{ (Vs)}^{-1}$ based on frequency averaged response. Such a low mobility, combined with the observed dispersive transport, indicates a disordered potential landscape for charge carrier transport and implies that improvement of the crystal growth can lead to a better quality γ -ray detector material.

Finally, hybrid organometallic perovskites show impressive photophysical properties making them promising materials for future optoelectronic devices. Understanding the charge generation and transport mechanisms, among other intrinsic properties, is imperative to understand the limitations of device performance. The complex dielectric function in the THz spectral region was extracted for the first time in the range from 25-100 meV above the reststrahlen band for this material. The charge generation dynamics of hybrid metal-organic perovskite was studied by pulses of multi-THz frequency with an ultrabroadband range covering the major optical phonons corresponding to Pb-I vibrations and CH₃NH₃⁺ librations, free charge scattering rates and excitonic orbital transitions. The experimental evidence shows the dynamic screening of infrared active phonons and dielectric relaxation of CH₃NH₃⁺ cation occurs within 400 fs. Taking account of the background phonon dispersion, the THz conductivity spectrum was found to obey a simple free carrier Drude model in contrast to what has been observed in polycrystalline films where signs of disorder are present. Charge generation was extracted directly through the Drude plasma frequency, with an efficiency of approximately 11-13 % at these pump fluences, and appears only after ≈ 1 ps following photoexcitation. Simultaneously with the Drude spectrum, a small transient feature in the reflectivity is observed at 12 meV and assigned to an orbital exciton transition.

This feature is found to disappear on a 1 ps time scale, commensurate with the onset of free charges in the system, indicating that exciton dissociation is the mechanism for charge generation in this material. Assuming a Wannier exciton and a 1s-2p transition at 12 meV, the binding energy is estimated to be ≈ 17 meV at room temperature, comparable to thermal energies and consistent with an exciton dissociation picture. Finally, the picosecond conductivity shows a transient mobility as high as 800 cm² (Vs)⁻¹, the highest measured to date in a single crystal sample.

Future work towards a better understanding of the fundamental properties of perovskites would require to map the dielectric function in the THz range at room temperature in an angular dependence, given that the material is birefringent and will exhibit a different dielectric function. The mapping of the dielectric function in the THz range needs to be performed at low temperatures to characterize the low temperature charge carrier dynamics and understand the differences in the optical properties between the orthorhombic and tetragonal phases.

MAPbI₃ degrades in ambient air which could limit their use in solar cell devices, for this reason other perovskite materials are emerging that promise improved thermal and humidity stability [227], these new materials will require to use the same techniques along with the knowledge acquired to understand its specific properties. Ultimately, commercial solar cell devices will be made from films due to cost effective concerns. Once film processing methods improve to obtain high quality and large grain sizes, a study of the grain size dependence will be needed and could be compared with a benchmark of pure, single crystal metal halide perovskites to have an idea of the quality of the film and to know when the films are approaching the characteristics of a single crystal. When split-orbit coupling is included into the theoretical calculations, a Rashba band splitting nature emerges for these materials [65, 228]. The strong split-orbit coupling makes sense, given the presence of heavy atoms such as lead, and has been reported for CH₃NH₃PbBr₃ [229]. Treating the material as Rashba helps to understand the unusually long carrier lifetimes that the material exhibits: recombination in the material is similar to the one in an indirect bandgap semiconductor [228]. Undoubtedly the inclusion of Rashba will help to answer some of the open questions regarding the fundamental properties of metal halide perovskites.

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