HIGH FREQUENCY RESOLUTION TERAHERTZ TIME-DOMAIN SPECTROSCOPY

by

BAGVANTH REDDY SANGALA

DAVID HILTON, COMMITTEE CHAIR
PERRY GERAKINES
RENATO CAMATA
JAMES PATTERSON
ANGELA SPECK

A DISSERTATION
Submitted to the graduate faculty of The University of Alabama at Birmingham, in the partial fulfillment of the requirements for the degree of Doctor of Philosophy

BIRMINGHAM, ALABAMA

2013
HIGH FREQUENCY RESOLUTION TERAHERTZ TIME-DOMAIN SPECTROSCOPY

BAGVANTH REDDY SANGALA
DEPARTMENT OF PHYSICS

ABSTRACT

A new method for the high frequency resolution terahertz time-domain spectroscopy is developed based on the characteristic matrix method. This method is useful for studying planar samples or stack of planar samples. The terahertz radiation was generated by optical rectification in a ZnTe crystal and detected by another ZnTe crystal via electro-optic sampling method. In this new characteristic matrix based method, the spectra of the sample and reference waveforms will be modeled by using characteristic matrices. We applied this new method to measure the optical constants of air. The terahertz transmission through the layered systems air-Teflon-air-Quartz-air and Nitrogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas was modeled by the characteristic matrix method. A transmission coefficient is derived from these models which was optimized to fit the experimental transmission coefficient to extract the optical constants of air. The optimization of an error function involving the experimental complex transmission coefficient and the theoretical transmission coefficient was performed using patternsearch algorithm of MATLAB. Since this method takes account of the echo waveforms due to reflections in the layered samples, this method allows analysis of longer time-domain waveforms giving rise to very high frequency resolution in the frequency-domain. We have presented the high frequency resolution terahertz time-domain spectroscopy of air and compared the results with the literature values. We have also fitted the complex susceptibility of air to the Lorentzian and Gaussian functions to extract the linewidths.

Keywords: Terahertz, far infrared, Nitrogen ice, THz-TDS, Water vapor.
DEDICATION

“The human race is so puny compared to the universe that being disabled is not of much cosmic significance.”

Prof. Stephen Hawking

I dedicate this thesis to my parents and teachers.
ACKNOWLEDGEMENTS

First of all, I would like to thank my advisor, Dr. David Hilton for his kind support throughout my PhD. I would also like to thank my PhD committee members: Dr. Perry Gerakines, Dr. Renato Camata, Dr. James Patterson, and Dr. Angela Speck for their kind support during my dissertation research.

I would like to thank Dr. Yogesh Vohra and Dr. David Shealy for accepting my application for PhD at UAB and supporting me with a teaching assistantship between Aug, 2007 and May, 2009. I would like to thank the UAB Physics Department for offering me career enhancement award in 2007.

I would like to thank Dr. Renato Camata for his interactive teaching of the Classical Mechanics course. I would like to thank Dr. David Hilton for teaching me Electromagnetic Theory course with deeper understanding. I always thank Dr. Hilton for his kind explanation to the questions that I asked him during the course work. I would like to thank Dr. Yogesh Vohra for the fruitful discussions of the Solid State Physics topics during my preparation for the qualifier exams. I would also like to thank Dr. Yogesh Vohra for his encouragement and positive comments to prepare for writing all of the qualifiers in single attempt and pass them all. I would also like to thank Dr. Yogesh Vohra for his support while I was analyzing the XRD data of Holmium metal under high pressure. I would like to thank Dr. David Hilton for his support via research assistantship to work on my PhD project by his NASA grant NSPIRES 07-APRA07-NNX09AI28G.

I would like to thank the Physics Department office staff at UAB: Jerry McCurry, Amanda Dickinson, Amy Bain, and Mark Case. I would like to thank Jerry Sewell of work shop for his kind help and discussions on drawings and designs of the parts needed for building my experimental setup. I would like to thank Dr. Perry Gerakines for his help in setting up the cryostat and vacuum systems in my experimental setup. I would like to thank Dr. Gerakines for his discussions throughout my project and editing my papers and posters. I would like to thank Dr. Dough White and specially Dr. Christina Richey for their help in designing the sample gas line and
writing a user manual for the thin film deposition system in my experiment.

I would like to thank Andrew Stemshorn, Dr. Walter Uhoya and Dr. Gopi Samudrala for their help with XRDA and FIT2d softwares to analyze the Holmium XRD data. I would like to thank Jeremy Curtis, John Ptacek, Christopher Spradlin, Nathan Ridling, Pramesh Singh, Sonal Singh, Dr. Parimal Bapat, Dr. Sarah Thomas, Alan Marinez, Dr. Hadiyah Nicole Green, and Dr. Chun-Wei Wang for their moral support. I would like to thank Nate Brady and Jeremy Curtis for their help in maintaining the lasers in the lab.

I would like to thank my teachers Prof. A. K. Kapoor, Prof. C. S. Sunandana, Dr. Sunil Singh, Prof. Sheshubhai, Prof. D. Narayana Rao, and Prof. Surya P. Tewari of School of Physics of University of Hyderabad, India for inspiring and recommending me to do my PhD at UAB. I would like to thank my family members especially, my mother for letting me be away from her during my PhD. I would also like to thank my friend V. Srinivasa Reddy and my room mate Dr. Gopi Samudrala for their moral support throughout my PhD.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 BACKGROUND</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1 SPECTRAL RESOLUTION</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2 MOTIVATION FOR THE PROJECT</td>
<td>3</td>
</tr>
<tr>
<td>1.1.3 PRIOR METHODS</td>
<td>3</td>
</tr>
<tr>
<td>1.2 DETERMINATION OF LINESHAPE IN HIGH RESOLUTION THz-TIME-DOMAIN</td>
<td>5</td>
</tr>
<tr>
<td>1.2.1 PROPAGATION OF ELECTROMAGNETIC RADIATION THROUGH ST-RATIFIED MEDIA</td>
<td>5</td>
</tr>
<tr>
<td>1.2.2 MODELING OF TERAHERTZ PROPAGATION USING CHARACTERISTIC MATRICES</td>
<td>6</td>
</tr>
<tr>
<td>1.3 PRIOR OBSERVATIONS OF WATER VAPOR ABSORPTION</td>
<td>7</td>
</tr>
<tr>
<td>1.4 ABSORPTION LINE SHAPES</td>
<td>8</td>
</tr>
</tbody>
</table>
5.1.2 NEED FOR HIGH RESOLUTION TERAHertz SYSTEM . . . 42

5.2 HIGH RESOLUTION TERAHertz TIME-DOMAIN SPECTRO-SCOPY
OF AIR ........................................ 42

5.2.1 MODEL OF CHARACTERISTIC MATRICES OF THREE LAYER-
ERED SYSTEMS ................................ 43

5.2.2 MODEL OF CHARACTERISTIC MATRICES OF FIVE LAYER-
ERED SYSTEMS ................................ 46

5.2.3 PHYSICS OF THz ABSORPTION IN AIR ................. 50

5.2.4 FITTING OF COMPLEX SUSCEPTIBILITY BY LORENTZIAN
FUNCTIONS ........................................ 52

5.2.5 FITTING OF COMPLEX SUSCEPTIBILITY BY GAUSSIAN
FUNCTIONS ........................................ 53

5.2.6 COMPARISON OF GAUSSIAN FITTING PARAMETERS TO
LITERATURE VALUES ......................... 54

5.2.7 COMPARISON OF LORENTZIAN AND GAUSSIAN FITTINGS 55

6 SUMMARY AND CONCLUSIONS ............................. 64

6.1 SUMMARY ........................................ 64

6.2 NEW APPLICATIONS ................................... 65

6.3 FUTURE DIRECTIONS ................................. 67

BIBLIOGRAPHY ....................................... 68
LIST OF TABLES

Table                                       page

4.1 Absorption center frequencies in Nitrogen ice at various temperatures. 36

5.1 Extracted data by fitting complex susceptibility peaks of air to Gaussian models and comparison to literature values. 56

5.2 Extracted data by fitting complex susceptibility peaks of air to Lorentzian and Gaussian models. 62
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>THz time-domain spectroscopy experimental setup for studying Nitrogen ices</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>THz time-domain spectroscopy experimental setup for studying air</td>
<td>16</td>
</tr>
<tr>
<td>3.1</td>
<td>Electro-optic detection</td>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
<td>Propagation of radiation through a three layered sample and reference systems</td>
<td>23</td>
</tr>
<tr>
<td>3.3</td>
<td>Propagation of radiation through a five layered sample and reference systems</td>
<td>26</td>
</tr>
<tr>
<td>5.1</td>
<td>The THz waveforms and transmission coefficients of Nitrogen ice at various temperatures</td>
<td>41</td>
</tr>
<tr>
<td>5.2</td>
<td>THz waveforms for the reference (film stack: Nitrogen gas-Teflon-Nitrogen gas) and sample (film stack: Air-Teflon-Air)</td>
<td>44</td>
</tr>
<tr>
<td>5.3</td>
<td>Amplitude of THz spectra of sample and reference waveforms for the three layered systems</td>
<td>45</td>
</tr>
<tr>
<td>5.4</td>
<td>Amplitude of THz transmission coefficient for the three layered systems</td>
<td>46</td>
</tr>
<tr>
<td>5.5</td>
<td>Real and imaginary parts of refractive index of air from the three layer characteristic matrix analysis</td>
<td>47</td>
</tr>
</tbody>
</table>
5.6 THz waveforms for the reference (film stack: Nitrogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas) and sample (film stack: air-Teflon-air-Quartz-air). ........................................ 48

5.7 Amplitude of THz spectra of sample and reference waveforms for the five layered systems. ........................................ 48

5.8 Amplitude of THz transmission coefficient for the five layered systems. 49

5.9 Real and imaginary parts of refractive index of air from the five layer characteristic matrix analysis. ....................................................... 50

5.10 Real and imaginary parts of susceptibility of air. .......................... 52

5.11 Real and imaginary parts of susceptibility peak of air around 0.557 THz fitted to a Lorentzian. ......................................................... 53

5.12 Real and imaginary parts of susceptibility peak of air around 0.557 THz fitted to a Gaussian. ......................................................... 54

5.13 Real and imaginary parts of susceptibility peak of air around 0.753 THz fitted to a Lorentzian and a Gaussian. ................................. 57

5.14 Real and imaginary parts of susceptibility peak of air around 1.164 THz fitted to a Lorentzian and a Gaussian. ................................. 58

5.15 Real and imaginary parts of susceptibility peak of air around 1.209 THz fitted to a Lorentzian and a Gaussian. ................................. 59

5.16 Real and imaginary parts of susceptibility peak of air around 1.603 THz fitted to a Lorentzian and a Gaussian. ................................. 60

5.17 Real and imaginary parts of susceptibility peak of air around 1.797 THz fitted to a Lorentzian and a Gaussian. ................................. 61
CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The electromagnetic radiation with frequencies from 0.1 THz to 10 THz is defined as terahertz radiation (THz). Owing to the gated detection, terahertz time-domain spectroscopy and imaging have emerged as efficient techniques for sensing in THz frequencies [Mittleman (2002)]. Terahertz time-domain spectroscopy (THz-TDS) has applications in homeland security [Laman et al. (2008); Leahy-Hoppa et al. (2007); Federici et al. (2005)], biomedical sciences [Pickwell and Wallace (2006), Siegel (2004)], astrophysics [Groppi and Kawamura (2011), Siegel (2002), Siegel (2007)], and in understanding of fundamental physics in gases, liquids and solids [Mittleman et al. (1998), Theuer et al. (2011)]. We have constructed a THz-TDS system in which THz radiation was generated by optical rectification and detected by electro-optic sampling method in (110) oriented ZnTe crystals [Nahata et al. (1996)]. The tera-
hertz spectra with useful content in 0.2-2 THz were achieved with this spectrometer.

We have encountered the frequency resolution limitation while analyzing the THz absorption in Nitrogen ices and that lead us to the development of a new method for high frequency resolution THz-TDS. We have applied this technique to study air at ~12% RH. The material for the sample waveform is air-Teflon-air-Quartz-air and the material for the reference waveform is Nitrogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas. By using the characteristic matrix method to model the THz propagation through these systems, the optical constants of air were extracted. We fitted the complex susceptibility of air to Lorentzian and Gaussian functions to extract the center frequency and fullwidth at half maxima of the observed absorption features.

1.1.1 SPECTRAL RESOLUTION

The spectral resolution of a spectrometer is defined as the smallest linewidth that the spectrometer can measure without broadening it due to its design. In THz-TDS, the frequency resolution of the Fourier transform of a THz waveform is determined by the temporal length of the window[Goodman (2004)]. For higher frequency resolution, the longer duration time-domain waveforms are needed. Owing to the simplicity of the mathematical modeling, planar sample or stack of planar samples have been analyzed in THz-TDS[Ralph et al. (1994), Duvillaret et al. (1996), Dorney et al.
waveforms transmitted through planar samples have time delayed multiple reflections due to interfaces separating different media.

1.1.2 MOTIVATION FOR THE PROJECT

The frequency resolution in THz-TDS needs to be improved to resolve narrow linewidth absorption features in samples. We encountered the spectral resolution limits while studying THz absorption in Nitrogen ice samples. During the vapor deposition of ice films, ice films can grow on front and back side of a substrate making the waveform pass through ice-substrate-ice and vacuum-substrate-vacuum systems for sample and reference scans respectively. In this thesis, we develop a characteristic matrix method to model the THz transmission to do high frequency resolution spectroscopy in planar layered materials.

1.1.3 PRIOR METHODS

Fourier transform infrared (FTIR) spectroscopy is an efficient technique to study material in the infrared spectral region. In this technique, radiation from an incandescent bulb is split into two beams and made to interfere with each other. The measured interference intensity as a function of delay between the two beams is called an interferogram. The Fourier transformation of the interferogram is calculated to get
the spectrum of the incandescent bulb or any material in the path of the beams. FTIR can give very high resolution spectra because of the use of wedged optics but even in that, to do quantitative analysis, one has to model the transmission coefficient using characteristic matrix method. In the past, in an attempt to achieve high resolution THz-TDS, designing of thicker sources and detectors [(110) ZnTe on (100) ZnTe] and samples to push the echoes further in time was reported [Turchinovich and Dijkhuis (2007)]. High resolution THz-TDS was also achieved for a thick sample by coating the back side of the GaP electro-optic detection crystal [Kroell et al. (2004)]. The Duvillaret’s transmission coefficient [Duvillaret et al. (1996)] can give reliable high frequency resolution spectra for a thin sample but the transmission coefficient model does not properly model the time delayed reflections. Waveguide THz-TDS [Zhang and Grischkowsky (2004)] can also demonstrate high resolution technique, but it is not practical to use this method for studying ices grown on a substrate by vapor deposition. Very high resolution THz-TDS was achieved with asynchronous optical sampling method but it required use of two femtosecond lasers [Kim et al. (2009), Yasui et al. (2005)]. Our method involved only mathematical modeling of the transmission coefficient.
1.2 DETERMINATION OF LINESHAPE IN HIGH RESOLUTION THz-TIME-DOMAIN SPECTROSCOPY

We develop a transmission coefficient that can take into account the multiple reflections in all of the layers of the stack of thin films.

1.2.1 PROPAGATION OF ELECTROMAGNETIC RADIATION THROUGH ST-RATIFIED MEDIA

When a ray of light propagates through a stratified medium, the electric and magnetic fields before the medium and after the medium are related by a $2\times2$ matrix called characteristic matrix. Since the derivation of characteristic matrix starts from a monochromatic wave, field matching conditions, and Maxwell’s equations, it takes all of the reflections of the electric field wave inside the layer into account. For a multi-layered system, the total characteristic matrix can be taken as a product of characteristic matrices for individual layers in the propagation direction of the incident radiation.

If the electromagnetic fields of a TM-polarized oblique incident ray before and after a thin film are $[H_y(o), E_x(o)]$ and $[H_y(L), E_x(L)]$, the characteristic matrix ($C$)
of the film satisfies the equation\[\text{Born and Wolf (1999)}]\]

\[
\begin{bmatrix}
H_x(o) \\
E_y(o)
\end{bmatrix} = C
\begin{bmatrix}
H_x(L) \\
E_y(L)
\end{bmatrix} = \begin{bmatrix}
\cos \beta & \frac{-i}{q} \sin \beta \\
-iq \sin \beta & \cos \beta
\end{bmatrix}
\begin{bmatrix}
H_x(L) \\
E_y(L)
\end{bmatrix}.
\]

Here, $\beta = \frac{2\pi n L}{c} \cos \theta$, $q = \frac{1}{n} \cos \theta$, $\theta$ is angle made by the light rays with the normal in the film, $n$ is refractive index of the film, $L$ is thickness of the film, $c$ is the velocity of light in vacuum, and $\nu$ is the frequency of the field. The ratio of amplitudes of transmitted electric field $[E_y(L)]$ and incident electric field $[E_y(o)]$ is given by,

\[
t = \frac{E_y(L)}{E_y(o)} = \frac{2q_1}{(C_{11} + C_{12} q_1)q_1 + (C_{21} + C_{22} q_2)}.
\] (1.1)

Here, $q_t$ is the $q$ computed in the medium immediately after the thin film.

1.2.2 MODELING OF TERAHERTZ PROPAGATION USING CHARACTERISTIC MATRICES

For a multi-layer thin film system with layers labeled $k = 1, 2, \ldots$ with refractive indices $n_k$, thicknesses $L_k$, with $\beta_k$ and $q_k$ defined as in the previous section, the total characteristic matrix for the complete system is given by\[\text{Born and Wolf (1999)}]\].

\[
C = \begin{bmatrix}
\cos \beta_1 & \frac{-i}{q_1} \sin \beta_1 \\
-iq_1 \sin \beta_1 & \cos \beta_1
\end{bmatrix}
\begin{bmatrix}
\cos \beta_2 & \frac{-i}{q_2} \sin \beta_2 \\
-iq_2 \sin \beta_2 & \cos \beta_2
\end{bmatrix}
\ldots
\]
In THz-TDS, two waveforms are acquired: one is without the sample called a reference waveform and other is with the sample called sample waveforms. We wrote characteristic matrices for sample and reference waves in frequency domain and derived a formula for the transmission coefficient which is defined as the ratio of the electric fields transmitted through the sample and the reference. We optimized an error function involving this transmission coefficient and the experimental transmission coefficient to obtain the optical constants of air.

1.3 PRIOR OBSERVATIONS OF WATER VAPOR ABSORPTION

At standard pressure and temperature, the main contribution to THz absorption in air occurs due to rotational transitions of water vapor[Moller and Ruthschild (1971)]. The terahertz absorption by water vapor was observed in the grating based spectrometers[Moller and Ruthschild (1971)], in Fourier transform infrared spectroscopy [Moller and Ruthschild (1971); Hall and Dowling (1967); Kauppinen et al. (1978); Johns (1985)], and in tunable far infrared spectroscopy[ Matsushima et al. (1995)]. The pure rotational spectrum of water vapor was also studied by terahertz time domain spectroscopy [van Exter et al. (1989); Cheville and Grischkowsky (1998, 1999); Xin et al. (2006)]. Line broadening of water vapor in high temperature flames was reported by Cheville et al. [Cheville and Grischkowsky (1999)]. Pressure broaden-
ing due to atmospheric gases was reported by Gamache et al. and Gasster et al [Gasster et al. (1988); Gamache and Fischer (2003)]. Specific line broadening due to the presence of atmospheric gases at low pressures was studied recently by several groups [Podobedov et al. (2004); Cazzoli et al. (2008b); Golubiatnikov et al. (2008); Cazzoli et al. (2008a)]. Xin et al. [Xin et al. (2006)] have studied the water vapor using THz-TDS at different humidity levels.

1.4 ABSORPTION LINE SHAPES

The natural decay of population in an upper energy level down to a lower energy level can be modeled as an exponential decay which results the emission frequency line shape of a Lorentzian. The Lorentzian line shape also results when the collisions among the molecules in a gas are modeled as an exponential decay of population in upper level into lower level with a characteristic collisional time constant.

The Maxwell’s velocity distribution of molecules in a gas at a given temperature results a Gaussian profile to the Doppler shifted frequencies to the emitted photons. The natural broadening and collisional broadening are called homogeneous broadenings because the resultant spectral shape function is the same as the one for the individual molecules. Doppler broadening is also called inhomogeneous broadening. Since, in a gas at room temperature, all of the processes (homogeneous and inho-
mogeneous broadening) can happen, generally a convolution function (Voigt) of the Lorentzian and Gaussian is fitted to the absorption lines of a gas [McHale (1999); Hollas (2004)].

The chapter 3 has a detailed explanation on the physics behind the Lorenztian and Gaussian absorption line shapes of gases.
We built a terahertz time-domain spectroscopy setup and integrated that with a cryostat for ice growth to perform low frequency resolution THz-TDS of astrophysical interesting ices. We studied Nitrogen ice samples with this experimental setup. For a second experimental setup, we removed the cryostat from the experiment and used a Teflon block and a Quartz window in the path of THz. In this experiment we have used air at \( \sim 12\% \) RH as our sample and studied that using the new high frequency resolution spectroscopy method.

2.1 TERAHERTZ TIME-DOMAIN SPECTROSCOPY OF NITROGEN ICE

The experimental setup that we built for the terahertz time-domain spectroscopy (THz-TDS) of the astrophysical ices is shown in Figure 2.1.
We use 650 mW of our amplifier (Coherent Legend seeded by Coherent Micra-10) output with 3 W average power, 1 kHz repetition rate, 35 fs pulse width, and with wavelength centered at 800 nm to run our THz-TDS setup. A beam splitter splits the power so that 5% of the power (gate pulses) is used to detect the THz electric field and 95% of the power (pump pulses) is used to generate THz radiation inside a 1 mm thick (110) oriented ZnTe crystal. A teflon block after the ZnTe crystal blocks
the residual pump pulse and allows the THz radiation to pass through it. A pair of off-axis paraboloidal mirrors (OAPM) with appropriate effective focal lengths are used to collect THz radiation to a frequency-independent spot where a sample can be placed. A similar pair of OAPMs are used to collect the transmitted THz through the sample and to focus it onto a 1 mm thick, (110) oriented ZnTe crystal.

As the gate pulse and THz pulse co-propagate in the detecting ZnTe, the gate pulse polarization rotates due to the birefringence induced by the instantaneous THz field in the ZnTe. A quarter wave plate balances the intensities of orthogonal components of the gate pulse. Imbalance of the intensities occurs when the gate pulse interacts with the THz induced birefringence in ZnTe. The difference photocurrent measured by the diode pair due to the orthogonal light components of gate pulse is linearly proportional to the instantaneous THz electric field. The photocurrent is amplified (by a current pre-amplifier) and measured by a lock-in amplifier. By varying the stage position (delay between gate pulse and THz pulse) and recording the photocurrent at each position, the THz electric field, $E_{THz}(t)$, can be reconstructed. The entire setup is enclosed in a box and purged with dry Nitrogen gas to avoid THz absorption by atmospheric water vapor.
2.1.1 ADVANTAGES OF THz-TDS

- Signal-to-noise ratio (SNR) is better in THz-TDS due to gated detection when compared to a system with incoherent detector. Detector sees terahertz noise only for 50 fs (the width of the gate pulse) out of 1 ms (gate pulse repetition rate) resulting in a better SNR. In addition to this, the experiment is modulated at a fixed frequency and the signal is amplified by lock-in amplifier with the reference frequency same as the modulation frequency. This limits the noise to the components of frequency same as modulation frequency and eliminates the noise at other frequencies.

- This technique measures both the amplitude and phase of the broadband THz electric field. This allows us to model our transmission coefficient to determine complex optical constants of a sample over a broadband of THz frequencies.

- THz-TDS generates a well collimated and coherent THz beam for spectroscopy when compared to diffuse incoherent sources.

2.2 EXPERIMENTAL PROCEDURE

After reaching 4 $\mu$torr pressure in the cryostat, we start cooling the substrate. When the substrate reaches temperature 20 K, we record a reference THz scan. After completing reference scan, we release sample gas into cryostat to condense on the
substrate forming an ice film. We increase the temperature of this ice film to record THz scans at different temperatures.

The THz spectrometer, cryostat, and lock-in amplifier are controlled by a LabView program. The program controls the Lake Shore temperature controller to maintain a required temperature for a THz scan. A THz scan begins with ESP300 motion controller setting the delay stage to its zero position. At this position of the stage, the program takes data from the SR830 lock in Amplifier (data: voltage corresponding to the difference current signal), Vaisala HMT330 hygrometer (data: relative humidity in the box), LakeShore temperature controller (data: temperature of ice), and the ESP300 motion controller (data: stage position). After taking this data, the program asks the ESP300 to move the stage to a next position and take the data from the four instruments again. This process is repeated at each position of the delay stage. The stage moving step size (sampling rate, \( t_s \)), number of steps (scan window size, \( T \)), temperature range, and its step size are the inputs to the program given at the beginning of the experiment. The program plots the graphs of lock-in voltages, relative humidity in the box, and sample temperature as functions of the time delay and saves the data to a file. Once a THz scan at a temperature is taken, the program sets the temperature to a next value and starts a new scan. This is done for all of the desired temperatures.
During the growth of an ice film, we look at the interference signal of the transmitted 1342 nm wavelength cw laser through the ice. As the ice gets deposited, the path difference between the directly transmitted 1342 nm radiation and the echoed 1342 nm radiation increases giving rise to a varying transmitted radiation intensity with maxima and minima as the interference fringes. Each fringe maximum to next maximum corresponds to an ice thickness of $\frac{\lambda}{2n}$; using this, we can determine the thickness of the ice film by counting the number of fringes. When the ice is deposited at faster rate, it grows on front and back sides of the substrate resulting in a fast and slow fringes in the interference signal. For slower deposition it grows only on the front side showing almost constant period fringes.

2.3 TERAHERTZ TIME-DOMAIN SPECTROSCOPY OF AIR

A schematic of the experimental setup used for studying air is shown in FIGURE 2.2. In this, the Newport delay stage MFA-CC was replaced by the Newport delay stage IMS500MVTP, the cryostat is replaced by a quartz window, instead of Nitrogen ice, water vapor in the purge box at 12% RH was used as the sample and rest of the components and procedures are the same as in the earlier experimental setup. Sample and reference scans of 200 ps long were acquired with 1 sec lock-in time constant at a gate delay time step of 50 fs. For the sample scan, the relative humidity of the
water vapor was maintained at $12 \pm 0.5 \%$ RH and for reference scan at $0.8 \pm 0.2 \%$ RH by controlling the Nitrogen gas flow to the purge box manually.
3.1 TERAHERTZ GENERATION BY OPTICAL RECTIFICATION

In our spectrometer, THz radiation is generated by optical rectification (OR) in a Zinc Telluride (ZnTe) crystal. The frequency components present in the incident femtosecond pump pulse mix in a 1 mm thick (110) oriented ZnTe creating a macroscopic polarization \( \tilde{P}(t) \), that oscillates at frequencies between zero and a few THz (presently 2 THz). This polarization is the source for the generation of THz radiation. In nonlinear optics, this polarization (\( \tilde{P} \)) can be expanded into a power series of pump pulse electric field(\( \vec{E} \)) as in equations (3.1)-(3.4).

\[
\tilde{P}(r,t) = \tilde{P}^{(1)} + \tilde{P}^{(2)} + \tilde{P}^{(3)} + \ldots
\]

(3.1)

\[
P_{i}^{(1)} = \tilde{\chi}_{ij}^{(1)} E_{j}
\]

(3.2)
\[ P^{(2)}_i = \bar{\chi}^{(2)}_{ijkl} E_j E_k \quad (3.3) \]
\[ P^{(3)}_i = \bar{\chi}^{(3)}_{ijkl} E_j E_k E_l \quad (3.4) \]

Here, \( \chi^{(n)} \) is an \( n^{th} \) order nonlinear susceptibility tensor and \( i,j,k \) represent components along the Cartesian axes (X, Y, Z). Optical rectification is a \( \bar{\chi}^{(2)} \) process that mixes the frequencies of an ultrafast pump pulse to generate a THz pulse by equation (3.3).

The incident pump pulse is given by equation (3.5).

\[ \vec{E}(t) = \int_0^\infty \vec{E}(\omega) \exp[-i\omega t]d\omega + \text{c.c.} \quad (3.5) \]

Here, c.c. stands for complex conjugate of the integral before the + sign. Plugging equation (3.5) into equation (3.3), the component of the polarization that results in optical rectification is:

\[ P^{(2)}_i(t) = 2\bar{\chi}^{(2)}_{ijkl} \int_0^\infty \int_0^\infty E_j(\omega_1) E_k(\omega_2) \exp[-i(\omega_1 - \omega_2)t]d\omega_1 d\omega_2 + \text{c.c.} \quad (3.6) \]

In the far field, the radiated electric field (\( \vec{E}_r \)) is:

\[ \vec{E}_r \propto \frac{\partial^2}{\partial t^2} \vec{P}^{(2)}_{OR}(t). \quad (3.7) \]

Here, \( \vec{P}^{(2)}_{OR}(t) = P^{(2)}_{1}(t)\hat{i} + P^{(2)}_{j}(t)\hat{j} + P^{(2)}_{k}(t)\hat{k} \). As \( \vec{P}^{(2)}_{OR}(t) \) oscillates at THz fre-
quencies, the emitted radiation has THz frequencies.

In our case, linearly polarized picosecond THz pulses containing frequencies from 0.1 to 2.5 THz are generated with peak electric field of approximately 10 V/cm. The amplitude (and phase) of the emitted THz waveform depend on the size of the nonlinear tensor element \(\bar{\chi}^{(2)}\), the relative orientation \(\theta\) of the generating ZnTe crystal, length of the ZnTe crystal, and the phase matching between the generated THz field and the pump field \(E_o\), as shown in equation (3.8). The generated THz electric field is proportional to the intensity of the pump pulse \(E_o^2\)[Chen et al. (2001)].

\[
|E_{THz}| \propto |\bar{\chi}^{(2)}| E_o^2 \sin^2 \theta (1 + 3 \cos^2 \theta) \frac{1}{2}
\]

(3.8)

The bandwidth of the emitted THz is limited by the temporal pulse width of the pump beam and thickness of the ZnTe crystal. The narrower the temporal width of the optical pulse, the broader is its frequency content. This enables a broadband difference frequency generation in ZnTe. We define coherence length \(l_c\) as the distance over which the pump field and generated THz field acquire a phase delay of 180\(^\circ\) (at which the perfectly destructive interference resulting in a reduced THz conversion happens). For 800 nm wavelength of pump field, the coherence length in ZnTe is given by:

\[
l_c = \frac{\pi c}{\omega_{THz} [3.22 - n_{THz}]}
\]

(3.9)
where $c$ is speed of light in vacuum, $\omega_{THz}$ is THz angular frequency, $n_{THz}$ is the phase index of ZnTe at THz frequencies, and 3.22 is the group refractive index of ZnTe at 800 nm [Nahata et al. (1996)]. Equation (3.9) shows that the coherence length decreases with increasing THz frequency. This creates an upper cutoff frequency for thicker crystals. When thickness of crystal ($d$) is less than $l_c$, the phase mismatch between pump and THz fields is less and efficient broadband conversion of radiation will happen. Therefore, to have a broadband emission, using optical rectification, we need a thinner crystal of ZnTe.

3.2 TERAHERTZ DETECTION BY ELECTRO-OPTIC SAMPLING

We will use electro-optic sampling (EOS) to detect the broadband THz pulses. This offers amplitude and phase sensitive measurement of THz electric field. A femtosecond optical gate pulse undergoes a polarization rotation due to the birefringence induced by a picosecond THz pulse in a ZnTe crystal. This birefringence is proportional to the instantaneous THz electric field [Chen et al. (2001)]. We detect the change to the polarization state of the gate pulse using a balanced detector. By varying the time delay between the THz pulse and the gate pulse, we can reconstruct the entire THz electric field. A monochromatic component of the gate pulse has an
Here, the axes X, Y are chosen to align with principal refractive index axes of ZnTe. Z is direction of the plane wave propagation into the plane of the paper.

The electric field given by:

$$\vec{E}_g = (E_x \hat{i} + E_y \hat{j}) \cos(kz - \omega t).$$  \hspace{1cm} (3.10)

Its plane of polarization makes an angle $\phi$ with X-axis where $\phi = \arctan \left( \frac{E_y}{E_x} \right)$ (see Figure 3.1). After propagating through the ZnTe crystal in which THz pulse created an instantaneous birefringence, the gate pulse acquires a phase shift:

$$\vec{E}_{gf} = E_x \hat{i} \cos \left( kz + \frac{2\pi}{\lambda} n_e d - \omega t \right) + E_y \hat{j} \cos \left( kz + \frac{2\pi}{\lambda} n_o d - \omega t \right).$$  \hspace{1cm} (3.11)
Here, $n_e$ and $n_o$ are refractive indices of ZnTe along X and Y axes respectively. The angle made by the plane of polarization of this wave with x-axis is given by,

$$\phi_f = \arctan\left(\frac{\tan(\phi) \cos(kz + \frac{2\pi}{\lambda} n_o d - \omega t)}{\cos(kz + \frac{2\pi}{\lambda} n_e d - \omega t)}\right) \neq \phi. \quad (3.12)$$

Therefore, the gate pulse polarization rotates after propagating through ZnTe.

The intensities measured by the diode pair are, therefore:

$$I_x = E_x^2 \cos^2\left(kz + \frac{2\pi}{\lambda} n_e d - \omega t\right), \quad (3.13)$$

$$I_y = E_y^2 \cos^2\left(kz + \frac{2\pi}{\lambda} n_o d - \omega t\right). \quad (3.14)$$

With an appropriate optical bias, the balanced detectors record:

$$I_x - I_y \approx \frac{E_x^2\pi(n_e - n_o)}{\lambda} d. \quad (3.15)$$

Here, the birefringence is proportional to the THz field, $n_e - n_o \propto E_{THz}$. As a result, the difference current measured by the diode pair is proportional to the THz electric field. By varying the delay between THz pulse($\approx 1\text{ps}$) and gate pulse($<50\text{ fs}$) and measuring the intensity difference of orthogonal field components of gate pulse, we can reconstruct the time-dependent THz electric field.
3.3 CHARACTERISTIC MATRICES FOR THREE LAYERED SYSTEMS

An equation for the transmission coefficient for the propagation of sample and reference waves respectively through the air-Teflon-air and Nitrogen gas-Teflon-Nitrogen gas systems is derived in this section.

Figure 3.2: Modeling of the THz transmission through the three layered systems. a) For the case of reference waveform. b) For the case of sample waveform. Here, $n_1$, $n_2$, and $n$ are refractive indices of Nitrogen, Teflon and air respectively, $L_2$, $L_1$, and $L_3$ are thicknesses of Teflon, air columns before and after the Teflon substrate respectively.

Figure 3.2 shows the schematic of an electromagnetic wave propagation through a Nitrogen-Teflon-Nitrogen system (reference wave) and air-Teflon-air system (sample wave).
wave) for normal incidence. The characteristic matrix method [Born and Wolf (1999)] allows us to write characteristic matrices for reference wave and sample wave cases that relate amplitude of electric fields before (at point A in Figure 3.2) and after (at point B in Figure 3.2) the systems.

The characteristic matrix for the reference wave is given by \( O \).

\[
O = \begin{bmatrix}
\cos \beta_1 & \frac{i}{q_1} \sin \beta_1 \\
-iq_1 \sin \beta_1 & \cos \beta_1
\end{bmatrix}
\begin{bmatrix}
\cos \beta_2 & \frac{i}{q_2} \sin \beta_2 \\
-iq_2 \sin \beta_2 & \cos \beta_2
\end{bmatrix}
\begin{bmatrix}
\cos \beta_3 & \frac{i}{q_3} \sin \beta_3 \\
-iq_3 \sin \beta_3 & \cos \beta_3
\end{bmatrix}
\]

(3.16)

Here, \( \beta_i = \frac{2\pi \nu n_i L_i}{c} \), \( q_i = \frac{1}{n_i} \) for \( i = 1, 2, 3 \). Here, \( n_1 = n_3 \) and \( n_2 \) are refractive indices of Nitrogen and Teflon respectively. Also, \( L_2, L_1, \) and \( L_3 \) are thicknesses of Teflon, front side air column, and backside air column respectively, \( c \) is velocity of light in vacuum, and \( \nu \) is THz frequency.

The ratio of amplitudes of transmitted electric field \( (E_r \text{ at B}) \) and incident electric field \( (E_i \text{ at A}) \) is given by,

\[
t_r(\nu) = \frac{E_r}{E_i} = \frac{2q_1}{(O_{11} + O_{12}q_1)q_1 + (O_{21} + O_{22}q_1)}
\]

(3.17)

Here, \( q_l \) is defined as \( q \) in the medium after the three layered system which can be taken as Nitrogen gas.
The characteristic matrix for the sample wave is given by $P$.

\[
P = \begin{bmatrix}
\cos \beta_4 & \frac{q_4}{q_6} \sin \beta_4 \\
-iq_4 \sin \beta_4 & \cos \beta_1
\end{bmatrix}
\begin{bmatrix}
\cos \beta_5 & \frac{q_5}{q_6} \sin \beta_5 \\
-iq_5 \sin \beta_5 & \cos \beta_5
\end{bmatrix}
\begin{bmatrix}
\cos \beta_6 & \frac{q_6}{q_6} \sin \beta_6 \\
-iq_6 \sin \beta_6 & \cos \beta_6
\end{bmatrix}
\]
(3.18)

Here, $\beta_i = \frac{2\pi n_i L_i}{c}$, $q_i = \frac{1}{n_i}$ for $i = 4, 5, 6$ with $L_4 = L_1, L_5 = L_2, L_6 = L_3, n_4 = n, n_5 = n_2, n_6 = n$. The ratio of amplitudes of transmitted electric field ($E_s$ at B) and incident electric field ($E_i$ at A) is given by,

\[
t_s(\nu) = \frac{E_s}{E_i} = \frac{2q_1}{(P_{11} + P_{12}q_1)(P_{21} + P_{22}q_1)}
\]
(3.19)

From equations (3.17), (3.19), the ratio of amplitudes of electric fields transmitted through sample ($E_s$) and reference ($E_r$) is given by,

\[
T_3(\nu) = \frac{E_s}{E_r} = \frac{(O_{11} + O_{12}q_1)q_1 + (O_{21} + O_{22}q_1)}{(P_{11} + P_{12}q_1)(P_{21} + P_{22}q_1)}
\]
(3.20)

3.4 CHARACTERISTIC MATRICES FOR FIVE LAYERED SYSTEMS

An equation for the transmission coefficient for the propagation of sample and reference waves respectively through the air-Teflon-air-Quartz-air and Nitrogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas systems is derived in this section.
Figure 3.3: Modeling of the THz transmission through the five layered systems. a) For the case of reference waveform. b) For the case of sample waveform. Here, \( n_1, n_2, n, n_3 \) are refractive indices of Nitrogen gas, Teflon, Air and Quartz respectively, \( L_2, L_4, L_1, L_3, \) and \( L_5 \) are thicknesses of Teflon, Quartz and Air column 1, Air column 2 and Air column 3 respectively.

Figure 3.3 shows the schematic of an electromagnetic wave propagation through a Nirogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas system (reference wave) and air-Teflon-air-Quartz-air system (sample wave) for the normal incidence. The characteristic matrix method [Born and Wolf (1999)] allows us to write characteristic matrices for reference wave and sample wave cases that relate amplitude of electric fields before (at point A in Figure 3.3) and after (at point B in Figure 3.3) the systems.

The characteristic matrix for the reference wave is given by \( \cdot \).
Here, $\beta_i = \frac{2\pi n_i L_i}{c}$, $q_i = \frac{1}{n_i}$ for $i = 1, 2, 3, 4,$ and $5$. Here, $n_1 = n_3 = n_5, n_2,$ and $n_4$ are refractive indices of Nitrogen, Teflon, and Quartz respectively. Also, $L_2, L_4, L_1, L_3, L_5,$ are thicknesses of Teflon, Quartz, air column 1, air column 2, and air column 3 respectively, $c$ is velocity of light in vacuum, and $\nu$ is THz frequency.

The ratio of amplitudes of transmitted electric field ($E_r$ at B) and incident electric field ($E_i$ at A) is given by,

$$t_r(\nu) = \frac{E_r}{E_i} = \frac{2q_1}{(\mathbb{Q}_{11} + \mathbb{Q}_{12}q_1)q_1 + (\mathbb{Q}_{21} + \mathbb{Q}_{22}q_1)}$$

(3.22)

Here also, $q_i$ is taken the $q$ in the medium after the fifth layer which was Nitrogen gas.

The characteristic matrix for the sample wave is given by $\mathbb{P}$. 

$\mathbb{Q} = \begin{bmatrix}
\cos \beta_1 & \frac{-q_1}{q_2}i \sin \beta_1 \\
-q_1 \sin \beta_1 & \cos \beta_1
\end{bmatrix}
\begin{bmatrix}
\cos \beta_2 & \frac{-q_2}{q_3}i \sin \beta_2 \\
-q_2 \sin \beta_2 & \cos \beta_2
\end{bmatrix}
\begin{bmatrix}
\cos \beta_3 & \frac{-q_3}{q_4}i \sin \beta_3 \\
-q_3 \sin \beta_3 & \cos \beta_3
\end{bmatrix}
\begin{bmatrix}
\cos \beta_4 & \frac{-q_4}{q_5}i \sin \beta_4 \\
-q_4 \sin \beta_4 & \cos \beta_4
\end{bmatrix}
\begin{bmatrix}
\cos \beta_5 & \frac{-q_5}{q_6}i \sin \beta_5 \\
-q_5 \sin \beta_5 & \cos \beta_5
\end{bmatrix}$

(3.21)
\[
\mathbb{P} = \begin{bmatrix}
\cos \beta_6 & \frac{-i}{q_6} \sin \beta_6 \\
-iq_6 \sin \beta_6 & \cos \beta_6
\end{bmatrix}
\begin{bmatrix}
\cos \beta_7 & \frac{-i}{q_7} \sin \beta_7 \\
-iq_7 \sin \beta_7 & \cos \beta_7
\end{bmatrix}
\begin{bmatrix}
\cos \beta_8 & \frac{-i}{q_8} \sin \beta_8 \\
-iq_8 \sin \beta_8 & \cos \beta_8
\end{bmatrix}
\begin{bmatrix}
\cos \beta_9 & \frac{-i}{q_9} \sin \beta_9 \\
-iq_9 \sin \beta_9 & \cos \beta_9
\end{bmatrix}
\begin{bmatrix}
\cos \beta_{10} & \frac{-i}{q_{10}} \sin \beta_{10} \\
-iq_{10} \sin \beta_{10} & \cos \beta_{10}
\end{bmatrix}
\]

Here, \( \beta_i = \frac{2\pi \nu n_i L_i}{c} \), \( q_i = \frac{1}{n_i} \) for \( i = 6, 7, 8, 9, \) and 10. Here, \( n_6 = n_8 = n_{10} = n, n_7 = n_2, \) and \( n_9 = n_9 \) are refractive indices of air, Teflon, and Quartz respectively. Also, \( L_7 = L_2, L_9 = L_4, L_6 = L_1, L_8 = L_3, L_{10} = L_5, \) are thicknesses of Teflon, Quartz, air column1, air column 2, and air column 3 respectively, \( c \) is velocity of light in vacuum, and \( \nu \) is THz frequency.

\[
t_s(\nu) = \frac{E_s}{E_i} = \frac{2q_1}{(P_{11} + P_{12}q_1)q_1 + (P_{21} + P_{22}q_1)}
\]

From equations (3.22), (3.24), the ratio of amplitudes of electric fields transmitted through sample \( (E_s) \) and reference \( (E_r) \) is given by,

\[
T_s(\nu) = \frac{E_s}{E_r} = \frac{(O_{11} + O_{12}q_1)q_1 + (O_{21} + O_{22}q_1)}{(P_{11} + P_{12}q_1)q_1 + (P_{21} + P_{22}q_1)}
\]
3.5 PURE ROTATIONAL SPECTRUM OF WATER VAPOR

In 0.2-2 THz part of the terahertz spectrum, there are about seventeen absorption lines that have been previously studied and result from quantized rotations of water vapor molecules. The relevant Hamiltonian used in the literature [Matsushima et al. (1995)] to calculate the rotational transition frequencies to match the experimental values is given in equation (3.26). The Hamiltonian is essentially a power series expansion of Hamiltonian of a rigid rotor up to 12th power of angular momentum taken to include the centrifugal effects of rotating water molecules. The fitting parameters with which the discrepancy between observed and calculated frequencies less than 1 MHz can be found in Matsushima et al.[Matsushima et al. (1995)].

\[
H = \frac{(B + C)}{2} J^2 + \{(A - (B + C)/2\} J_z^2 + \frac{(B - C)}{2} J_{xy}^2 - \Delta J (J^2)^2 - \Delta J K J^2 J_z^2
- \Delta K J_z^4 - 2 \delta_J J_z^2 J_{xy}^2 - \delta_K \{J_z^2, J_{xy}^2\} + H_J (J^2)^3 + H_{JK} (J^2)^2 J_z^2 + H_{KJ} J_z^2 J_{xy}^4 + H_K J_z^6
+ 2 h_J (J^2)^2 J_{xy}^2 + h_{JK} J_z^2 \{J_z^2, J_{xy}^2\} + h_K \{J_z^4, J_{xy}^2\} + L_J (J^2)^4 + L_{JK} (J^2)^3 J_z^2 + L_{KJ} (J^2)^2 J_z^4
+ L_{KK} J_z^6 + L_K J_z^8 + 2 l_J (J^2)^3 J_{xy}^2 + l_{JK} (J^2)^2 \{J_z^2, J_{xy}^2\} + l_{KJ} J_z^2 \{J_z^4, J_{xy}^2\}
+ l_K \{J_z^6, J_{xy}^2\} + P_J (J^2)^5 + P_{JK} (J^2)^4 J_z^2 + P_{KJ} (J^2)^3 J_z^4 + P_{KK} (J^2)^2 J_z^6 + P_{KJ} J_z^2 J_z^8
+ P_{KK} J_z^4 + P_{JK} J_z^2 \{J_z^6, J_{xy}^2\} + P_{KK} J_z^2 \{J_z^6, J_{xy}^2\} + P_K \{J_z^8, J_{xy}^2\} + T_J J_z^{12}.
\]

(3.26)
Here, $J_{xy}^2 = J_x^2 - J_y^2$ and $\{A, B\} = AB - BA$. The values of the fitting parameters $A, B, C, \Delta J, \Delta JK, \Delta K, \delta J, \delta K, H_J, H_{JK}, H_K, h_J, h_{JK}, h_K$, and etc and the quantum numbers that give rise to experimentally observed frequencies are shown in the references [Matsushima et al. (1995); Johns (1985)].

3.6 PHYSICAL MODELS FOR SUSCEPTIBILITY OF VARIOUS LINE SHAPES

3.6.1 LORENTZIAN SHAPED LINEAR SUSCEPTIBILITY

In a gas, a Lorentzian absorption line shape results when an ensemble of identical two-level resonators (isolated or colliding at constant rate) interact with radiation. The derivation of the Lorentzian profile linear susceptibility by the density matrix formulation is given in Boyd’s book [Boyd (2003)]. In the density matrix ($\rho$) formulation, the average of dipole moment ($\hat{\mu}$) of a two level system is given by,

$$\langle \hat{\mu} \rangle = \text{trace}(\rho \hat{\mu}). \quad (3.27)$$

The density matrix equation of motion with the phenomenological inclusion of damping is given by,

$$\dot{\rho}_{nm} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}]_{nm} - \gamma_{nm}(\rho_{nm} - \rho_{nm}^{eq}). \quad (3.28)$$
Here, \( \hat{H} \) is the total Hamiltonian of the two level system, \( \gamma_{nm} \) is the phenomenological decay constant, and \( n \) & \( m \) are the row and column indices of the \( 2 \times 2 \) matrix (operator) elements. Seeking the solution of \( \rho \) in the form of a perturbation expansion, assuming the applied field as sum of plane waves, and taking the macroscopic polarization as sum of the dipole moments of all \textit{identical two level systems}, the linear susceptibility can be expressed as follows,

\[
\chi^{(1)} = \frac{N}{\hbar} \frac{\mu^2}{(\omega_o - \omega_p) - i\gamma_L}.
\]

Here, \( N \) is the atomic number density, \( \omega_p \) is the radial frequency of the applied electric field, \( \omega_o \) is the resonance radial frequency for a two level system, \( \mu \) is the dipole moment, and \( \gamma_L (= \gamma_{nm}) \) is also called the dephasing life time [Boyd (2003)].

A similar expression can also be obtained from the consideration of the natural decay of an excited state where the population decays like an exponential. Since the Fourier transformation of an exponential decay is a Lorentzian, this gives rise to a \textit{naturally broadened} Lorentzian in the frequency domain.

\[
\frac{d}{dt} N = -\frac{1}{\tau} N \implies N(t) = N_o \exp \left( \frac{-|t|}{\tau} \right)
\]

Here, \( N_o \) is the initial population of the upper energy level, \( N(t) \) is population at
time $t$, and $\tau$ is the time constant of decay.

Fourier transform of $N(t)$ is,

$$
N(\omega) = \int_{-\infty}^{\infty} N(t) \exp(-i\omega t) dt = \frac{N_o}{(\frac{1}{\tau} + i\omega)} 
$$

(3.31)

The Lorentzian line shape also results for identical collisional probability in a gas. In this case, the population is decayed due to the collisional encounter with molecules in a gas. Since the decay is exponential for first order decay process in time-domain, it results in a Lorentzian shape in frequency-domain. This broadening is called *collisional broadening or pressure broadening*. Both the natural broadening and the collisional broadening are called *homogeneous broadening*.

3.6.2 GAUSSIAN SHAPED LINEAR SUSCEPTIBILITY

In a gas, the interaction of light with non-identical resonators can give rise to absorption profiles other than Lorentzian shape[for example: Montecchi et al. (2004)]. Montecchi et al. have considered an ensemble of not identical absorbing centers as composed of sub-ensembles of identical replicas having resonant radial frequency $\omega'_{\text{abs}}$ with susceptibility described as Lorentzian. If the frequency of these sub-ensembles be distributed according to a Gaussian function centered around the most probable resonant radial frequency $\omega_o$, the susceptibility of the whole system can be taken as,
\[ \chi_{inh}(\omega_p) = \frac{\mu^2 \Delta N_0}{\epsilon_o} \int_{-\infty}^{\infty} \frac{P_G(\omega'_{abs})}{\omega'_{abs} - \omega_p - i \gamma_L} d\omega'_{abs} \quad (3.32) \]

with \( P_G(\omega'_{abs}) = \frac{1}{\Delta \omega_G} \sqrt{\frac{\ln 2}{\pi}} \exp \left[ -(\ln 2) \left( \frac{\omega'_{abs} - \omega_o}{\Delta \omega_G} \right)^2 \right] \). This kind of distribution to the resonant frequencies can occur because of Doppler shift of light frequency due to light interaction with molecules having velocities distributed as Maxwell’s distribution.

In the limit of \( \gamma_L \rightarrow 0 \), and using the definition of Abramowitz and Stegun’s error function, the equation (3.32) becomes,

\[ \chi_G(\omega_p) = -i \frac{\mu^2 N \hbar}{\epsilon_0 \Delta \omega_G} \sqrt{\ln 2} \exp \left[ -(\ln 2) \left( \frac{\omega_p - \omega_o}{\Delta \omega_G} \right)^2 \right] \times \left[ 1 - \text{erf} \left( i \sqrt{\ln 2} \frac{\omega_p - \omega_o}{\Delta \omega_G} \right) \right]. \quad (3.33) \]

Here, \( \mu \) is the dipole moment, \( N \) is the number density of the absorbers, \( \omega_G \) is the half width at half maxima of the absorption line, \( \omega_o \) is the center radial frequency of the absorption line, and \( \omega_p \) is the radial frequency of the perturbation field, \( \hbar \) is the reduced Planck’s constant, and \( \epsilon_0 \) is the permittivity of the free space. If the complex susceptibility of an absorption line profile fits well to the Gaussian profile given above, we can say that the gas has a distribution of two level systems with resonant frequencies following a Gaussian distribution [Montecchi et al. (2004)].
A simplified explanation for the Gaussian line profile can be given by considering the Doppler effect of light and Maxwell’s velocity distribution of molecules of a gas. A blue shifted photon frequency due to velocity \( v_x \) of an emitting molecule is given by,

\[
\nu = \nu_o + \frac{v_x}{c}.
\]  

(3.34)

For consideration of one dimensional motion, Maxwell’s distribution gives the probability of having a molecule with velocity \( v_x \) as

\[
f(v_x) = C \exp \left( -\frac{m v_x^2}{2 k_B T} \right).
\]  

(3.35)

Here, \( C \) is normalization constant. By the substitution of equation (3.34) in (3.35), we can see the probability of having a photon with shifted frequency will be a Gaussian. Therefore, we get a Gaussian line profile as a result of Doppler effect of light interacting with a gas with Maxwell’s velocity distribution.
4.1 TERAHERTZ SPECTROSCOPY OF NITROGEN ICE

A reference THz scan was taken before depositing the ice at 20 K. Nitrogen ice was grown on the sapphire substrate at 20 K. The ice temperature was maintained at 10 K, 15 K, 20 K, 22 K, 25 K, 27 K, and 30 K for sample scans. All the waveforms were 22 ps long and acquired with a lock-in time constant of 3 sec and the gate delay step size of 0.1 ps. The spectra of reference and sample waveforms were calculated by using a MATLAB code. Since the waveforms of 22 ps long were used for calculation of spectra, the frequency resolution was 46 GHz.

We have defined the ratio of the sample spectrum to the reference spectrum as the transmission coefficient. The transmission coefficient data shows an absorption around 1.45 THz. We found that the absorption center frequency was shifting to smaller values as the temperature of the ice was increased. We have plotted the
Our Experiment

<table>
<thead>
<tr>
<th>T[K]</th>
<th>$\nu_o$[THz]</th>
<th>T[K]</th>
<th>$\nu_o$[THz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.465</td>
<td>8</td>
<td>1.472</td>
</tr>
<tr>
<td>15</td>
<td>1.61</td>
<td>13</td>
<td>1.464</td>
</tr>
<tr>
<td>20</td>
<td>1.445</td>
<td>18</td>
<td>1.456</td>
</tr>
<tr>
<td>22</td>
<td>1.444</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1.437</td>
<td>25</td>
<td>1.440</td>
</tr>
<tr>
<td>27</td>
<td>1.430</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.426</td>
<td>31.5</td>
<td>1.426</td>
</tr>
</tbody>
</table>

Table 4.1: Absorption center frequencies in Nitrogen ice at various temperatures.

4.2 HIGH FREQUENCY RESOLUTION OPTICAL CONSTANTS OF AIR

We have obtained two sets of data for the high frequency resolution spectroscopy of air. In the first set, only a Teflon block was placed in the path of THz beam and in the second set, a Teflon block and a Quartz substrate were placed at a separation. For the analysis of the first set of data, characteristic matrices involving three matrices were used for both the sample waveform and reference waveform. For analysis of the second set of the data, characteristic matrices involving five matrices were used for both the sample waveform and reference waveforms. For the reference waveform scans, a relative humidity of $0.8\pm0.2\%$ was maintained and for the sample waveform scans it
was maintained at 12 ± 0.5%. For acquiring both the data sets, lock-in integration
time of 1 sec, sampling rate of 50 fs, total waveform length of 200 ps were used. The
inverse Fourier transformations of the waveforms were calculated using a MATLAB
code with zero padding the waveforms up to $2^{14}$ data points.

4.2.1 THREE LAYERED SYSTEMS

We optimize the error function[Duvillaret et al. (1996)] shown below to extract opti-
tical constants of air by using thicknesses of the various layers.

\[
\left[ \log |T_3| - \log |T_e| \right]^2 + \left[ \text{Arg} (T_3) - \text{Arg} (T_e) \right]^2
\]

(4.1)

Here, $T_e = \frac{F_{E_s(t)}}{F_{E_r(t)}}$ is experimental transmission coefficient, which is the ratio of
inverse Fourier transform of sample and reference waveforms, $T_3$ is given by equation
(3.20), and $|T|$, and $\text{Arg} (T)$ stand for modulus, and argument of $T$ respectively.

The optimization is done by patternsearch function of MATLAB. We have measured
the thicknesses of the layers as $L_1 = 24$ mm, $L_2 = 4.82$ mm, $L_3 = 996$ mm and
used these together with the refractive indices $n_1 = 1$ and $n_2 = 1.44 + i 0.0024$ in the
analysis. The Teflon block thickness was measured with a digital calipers and other
lengths were measured with a ruler.
4.2.2 FIVE LAYERED SYSTEMS

We optimize the error function\[Duvillaret et al. (1996)] shown below to extract optical constants of air by using thicknesses of the various layers.

\[
\left[ \log|\mathcal{T}_5| - \log|\mathcal{T}_e| \right]^2 + \left[ \text{Arg}(\mathcal{T}_5) - \text{Arg}(\mathcal{T}_e) \right]^2 \tag{4.2}
\]

Here, $\mathcal{T}_e = \frac{F[E_e(t)]}{F[E_r(t)]}$ is experimental transmission coefficient, which is the ratio of inverse Fourier transform of sample and reference waveforms, $\mathcal{T}_5$ is given by equation (3.25), and $|\mathcal{T}|$, and $\text{Arg}(\mathcal{T})$ stand for modulus, and argument of $\mathcal{T}$ respectively. The optimization is done by \textit{patternsearch} function of MATLAB. We measured the thicknesses of the layers as $L_1 = 24$ mm, $L_2 = 4.82$ mm, $L_3 = 489$ mm, $L_4 = 2$ mm, $L_5 = 464$ mm and used these together with refractive indices $n_1 = 1$, $n_2 = 1.44 + i 0.0024$, and $n_3 = 2.16 + i 0.0024$ in the analysis. The thicknesses of the Teflon block and the Quartz window were measured with a digital calipers and other lengths were measured with a ruler.

4.3 FITTING OF ABSORPTION LINES

Each of the observed lines in the susceptibility data was fitted around the peak to Lorentzian and Gaussian profile functions that are given below.
4.3.1 LORENTZIAN MODEL

The homogeneous line broadening susceptibility function as given in [Boyd (2003)] is,

\[ \chi_L = y_o + \frac{A}{(2\pi\nu_o - 2\pi\nu) - i\gamma}. \]  (4.3)

Full width at half maxima in linear frequency units is \( \frac{2\gamma}{\pi} \). Fitness function = \( \Sigma_i\{[\angle\chi_L(i) - \angle\chi_e(i)]^2 + [||\chi_L(i)| - |\chi_e(i)||]^2\} \) was minimized by using \textit{patternsearch} algorithm. Here \( \chi_e \) is experimental susceptibility, \( \chi_L \) is theoretical susceptibility.

4.3.2 GAUSSIAN MODEL

The inhomogeneous line broadening susceptibility functions for the case of pure Doppler broadening [Montecchi et al. (2004)] are given by \( \chi_G \) with,

\[ \text{Re}(\chi_G) = -A \exp \left[ -(\ln 2) \left( \frac{\nu - \nu_o}{g} \right)^2 \right] \text{erfi} \left( \sqrt{\ln 2} \frac{\nu - \nu_o}{g} \right), \]  (4.4a)

\[ \text{Im}(\chi_G) = -A \exp \left[ -(\ln 2) \left( \frac{\nu - \nu_o}{g} \right)^2 \right]. \]  (4.4b)

Full width at half maxima in linear frequency units is \( 2g \).

Fitting of \( \tilde{\chi}_G = y_o + \text{Re}(\chi_G) - i\text{Im}(\chi_G) \) was done using \textit{patternsearch} algorithm. Fitness function for this case is \( \Sigma_i\{[\angle\chi_G(i) - \angle\chi_e(i)]^2 + [||\chi_G(i)| - |\chi_e(i)||]^2\} \). Here \( \chi_e \) is experimental susceptibility, \( \chi_G \) is theoretical susceptibility.
CHAPTER 5

RESULTS

5.1 THz SPECTROSCOPY OF NITROGEN ICE

A reference terahertz waveform was taken at 20 K before growing the Nitrogen ice. The ice was grown on sapphire substrate at 20 K for 2 hours. The thickness of the ice measured from the fringe counting method due to interference of 1342 nm laser during ice deposition was about 0.720 mm. Sample terahertz waveforms were acquired with Nitrogen ice at 10 K, 15 K, 20 K, 22 K, 25 K, 27 K, and 30 K. The Nitrogen ice started sublimating around 35 K preventing the higher temperature measurements.

5.1.1 THz WAVEFORMS AND TRANSMISSION THROUGH N$_2$ ICE

The reference waveform and all the sample waveforms and the transmission coefficients for the data at all of the temperatures of Nitrogen ice are plotted in Figure
Figure 5.1: The terahertz waveforms and transmission coefficients of Nitrogen ice at various temperatures. Waveforms are shifted vertically up for clarity of view. The delay time is shown only 0-14 ps but actually, 22 ps long waveforms were used in the analysis. The amplitude of transmission coefficient also zoomed in around the 1.45 THz feature. We can see the absorption center frequency shifting to smaller values as the ice temperature is increased.

For clarity of the plots, only waveforms of first 14 ps long are shown here but in the actual analysis 22 ps long waveforms were used. The amplitude of transmission coefficient also plotted only around the 1.45 THz feature. We can see the absorption center frequency shifting to smaller values as the ice temperature is increased.
5.1.2 NEED FOR HIGH RESOLUTION TERAHERTZ SYSTEM

The Nitrogen ice data were spectral limited. This means the full width at half maxima of the observed feature around 1.45 THz could be less than 46 GHz but it is showing as 46 GHz because we were not able to analyze the longer waveforms due to limitations in the mathematical modeling of the transmission coefficient. To overcome this limitation, we have made use of the characteristic matrix method which can take care of multiple reflections in the waveforms due to propagation of THz waveform through a stack of films. We tested this for the case of air as multiple layers forming more layers with Teflon and Quartz.

5.2 HIGH RESOLUTION TERAHERTZ TIME-DOMAIN SPECTROSCOPY OF AIR

Two sets of data were acquired for the high frequency resolution time-domain spectroscopy of air. In the first set of data, there was only a Teflon block in the terahertz beam path dividing the path between the generating and detecting ZnTe crystals into two. The THz transmission through the reference i.e., “Nitrogen gas-Teflon-Nitrogen gas” and through the sample i.e., “air-Teflon-air” was modeled using the characteristic matrices involving three in each one. In the second set of data, there were a Teflon block and a Quartz substrate in the path of THz beam making a five
layered system between the generating and detecting ZnTe crystals. In this case, the reference wave i.e., THz propagation through a “Nitrogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas” and the sample wave propagating through “air-Teflon-air-Quartz-air” was modeled using characteristic matrices involving five in each one. In the analysis of both the data sets, an error function involving the experimental and theoretical transmission coefficient was optimized to obtain the optical constants of air. Using the complex refractive index \( n \), the complex susceptibility \( \chi \) was calculated (as \( \chi = n^2 - 1 \)). The complex susceptibility was fitted to Lorentzian and Gaussian models to obtain the center frequency and fullwidth at half maxima of the observed absorption lines.

5.2.1 MODEL OF CHARACTERISTIC MATRICES OF THREE LAYERED SYSTEMS

The waveforms transmitted through the reference system i.e., Nitrogen gas-Teflon-Nitrogen gas and sample system i.e., air-Teflon-air are shown in Figure 5.2. The waveforms of 200 ps length were acquired at a delay step size of 0.05 ps and 1 sec lock-in integration time constant. The relative humidity of 0.8±0.2 % for the reference waveform and 12±0.5% for sample waveform were maintained.

In Figure 5.2, both in reference waveform and sample waveform, we can see the echo waveforms due to the 4.82 mm thick Teflon block(measured with a digital
Figure 5.2: THz waveforms for the reference (film stack: Nitrogen gas-Teflon-Nitrogen gas) and sample (film stack: air-Teflon-air). The sample waveform was shifted up by 0.05 for clarity of view. The arrows show the echo pulses due to the Teflon block and also the space between the first ZnTe and Teflon block.

calipers) with a refractive index of 1.44 at THz frequencies and also another echo because of Nitrogen column in reference waveform and due to air column in sample waveform between the first ZnTe crystal and Teflon. We have computed the inverse Fourier transforms of these waveforms with a MATLAB code. Figure 5.3 shows the amplitude of the reference and sample spectra. We can see a small absorption in reference waveform due to the presence of water vapor at 0.8±0.2 % Relative humidity.

The transmission coefficient was calculated by taking the ratio of the sample spectrum to the reference spectrum. Figure 5.4 shows the amplitude of the transmission coefficient as a function of frequency. We can observe about seventeen absorption
Figure 5.3: Amplitude of THz spectra of sample and reference waveforms. We can see interference fringes due to the presence of echoes in the waveforms. The sample spectrum has absorption dips due to water vapor.

lines between 0.2 THz and 2 THz. The optical constants of air were calculated by optimizing an error function involving the experimental transmission coefficient and a transmission coefficient modeled based on characteristic matrices. The optimization was done using patternsearch algorithm of MATLAB. Figure 5.5 shows the real and imaginary parts of the extracted complex refractive index.
Figure 5.4: Amplitude of THz transmission coefficient which was defined as the ratio of sample and reference spectra.

5.2.2 MODEL OF CHARACTERISTIC MATRICES OF FIVE LAYERED SYSTEMS

The waveforms transmitted through the reference system i.e., Nitrogen gas-Teflon-Nitrogen gas-Quartz-Nitrogen gas and sample system i.e., air-Teflon-air-Quartz-air are shown in Figure 5.6. The waveforms of 200 ps length were acquired at a delay step size of 0.05 ps and 1 sec lock-in integration time constant. The relative humidity of 0.8±0.2 % for the reference waveform and 12±0.5% for sample waveform were maintained.

In Figure 5.6, both in reference and sample waveforms, we can see the echo waveforms due to the 4.82 mm thick teflon block (measured with a digital calipers) with a
Figure 5.5: Real and imaginary parts of refractive index of air from the three layer characteristic matrix analysis.

Refractive index of 1.44 at THz frequencies and also another echo because of Nitrogen column in reference waveform and due to air column in sample waveform between the first ZnTe and Teflon, and one more echo because of the Quartz substrate. We have computed their inverse Fourier transform with a MATLAB code. Figure 5.7 shows the amplitude of the reference and sample spectra. We can see a small absorption in reference waveform due to the presence of water vapor at 0.8±0.2 % Relative humidity.
Figure 5.6: THz waveforms for the reference (film stack: Nitrogen gas-Teflon-nitrogen gas-Quartz-Nitrogen gas) and sample (film stack: air-Teflon-air-Quartz-air). The sample waveform was shifted up by 0.05 for clarity of view. The arrows show the echo pulses due to Teflon block, Quartz substrate, and the space between the first ZnTe and Teflon.

Figure 5.7: Amplitude of THz spectra of sample and reference waveforms. We can see interference fringes due to the presence of echoes in the waveforms. The sample spectrum has absorption dips due to water vapor.
Figure 5.8: Amplitude of THz transmission coefficient which was defined as the ratio of sample and reference spectra.

The transmission coefficient was calculated by taking the ratio of the sample spectrum to the reference spectrum. Figure 5.8 shows the amplitude of the transmission coefficient as a function of frequency. We can observe about seventeen absorption lines between 0.2 THz and 2 THz. The optical constants of air were calculated by optimizing an error function involving the experimental transmission coefficient and a transmission coefficient modeled based on characteristic matrices. The optimization was done using patternsearch algorithm of MATLAB. Figure 5.9 shows the real and imaginary parts of the complex refractive index obtained.
Figure 5.9: Real and imaginary parts of refractive index of air from the five layer characteristic matrix analysis.

5.2.3 Physics of THz Absorption in Air

The observed peak frequencies of terahertz absorption in H₂O vapor were compatible with the calculations based on a Hamiltonian for the pure quantized rotational spectrum [Johns (1985); Matsushima et al. (1995)]. The Hamiltonian is a power series expansion of Hamiltonian of a rigid rotor up to 12th power of angular momentum taken to include the centrifugal effects of rotating water molecules. The form
of the Hamiltonian and the fitting parameters with which the discrepancy between observed and calculated frequencies less than 1MHz can be found in Fusakazu et al.[Matsushima et al. (1995)]. Xin et al.[Xin et al. (2006)] were able to distinguish the absorption lines between the ortho and para water vapor that have the ratio of total nuclear spin of two hydrogen molecules of 1:3. Pure rotational transitions in the ground and first excited state of vibrational states of water vapor were observed in hot samples of water vapor[Cheville and Grischkowsky (1998, 1999)]. As presented in Table 5.1, our measured absorption center frequencies and the full width at half maxima are compatible with the pure rotational lines of water vapor in air.

Cheville et al.[Cheville and Grischkowsky (1998, 1999)] suggested that the observed linewidths are due to the temperature broadening of the states and the collisions among the water vapor and other molecules in the sample gas. They have introduced a dephasing time which is the inverse of the FWHM and verified that when inverse of the total dephasing time was taken as sum of inverses of individual major species contribution along with their concentration in the sample gas, the calculated FWHM were agreeing with the experimental FWHM. They also compared the FWHMs of lines at 1490 K and at 300 K and showed that there is a power law dependence between FWHMs at 1490 K and at 300 K.
5.2.4 Fitting of Complex Susceptibility by Lorentzian Functions

Fitting of the absorption lines around the peaks was done only for the second set of data which involved the five layered systems. The complex susceptibility was calculated by using the formula $\chi = n^2 - 1$. Figure 5.10 shows both the real and imaginary parts of the susceptibility from the experiment for the five layered model.

We have fitted the complex susceptibility by a Lorentzian function to all of the lines around the absorption centers. We have fitted a double Lorentzian for a doublet...
Figure 5.11: Real and imaginary parts of susceptibility peak of air around 0.557 THz fitted to a Lorentzian.

peak. Figure 5.11 shows fitting of the Lorentzian function to a feature around 0.557 THz.

5.2.5 FITTING OF COMPLEX SUSCEPTIBILITY BY GAUSSIAN FUNCTIONS

We have fitted the complex susceptibility by a Gaussian function to all of the lines around absorption centers. We have fitted a double Gaussian for a doublet peak. Figure 5.12 shows fitting of a Gaussian line to a feature around 0.557 THz.
5.2.6 COMPARISON OF GAUSSIAN FITTING PARAMETERS TO LITERATURE VALUES

Table 5.1 shows the absorption line centers from our experiment (column1), line centers measured by Matsushima et al. [Matsushima et al. (1995)] (column2), full width at half maxima ($\Delta$) obtained from our data (column3), $\Delta$ measured by Gasster et al. [Gasster et al. (1988)] (column4), and $\Delta$ calculated from the data of Gamache et al. [Gamache and Fischer (2003)] (column5), $\Delta$ calculated from the data of Hoshina et al. [Hoshina et al. (1988)] (column6). We can see that the absorption center fre-
frequencies measured by us are in agreement with the high frequency resolution data measured by Matushima et al. The fullwidth at half maxima data obtained by fitting the Gaussian model to the complex susceptibility of air are also in agreement with the reported data in the literature. For the columns 5 and 6, the pressure broadening parameters due to the atmospheric gases Nitrogen ($\gamma^{N_2}$) and and Oxygen ($\gamma^{O_2}$) were taken in 0.79:0.21 ratio to calculate the fullwidth at half maxima of water vapor lines in air from the data given in Hoshina et al. [Hoshina et al. (1988)] and Gamache et al. [Gamache and Fischer (2003)].

5.2.7 COMPARISON OF LORENTZIAN AND GAUSSIAN FITTINGS

The fittings of both the Lorentzian and a Gaussian functions to the lines were compared for all of the lines. Here, we present comparison of some of the lines in Figures 5.13, 5.14, 5.15, 5.16, and 5.17.

Table 5.2 shows absorption center frequencies, full width at half maxima, fitness function values and whether a line fits well to a Gaussian (G) or Lorentzian (L). Here, some of the peaks fit best to Gaussian and some to Lorentzian.
Table 5.1: Extracted data by fitting complex susceptibility peaks of air to Gaussian models and comparison to literature values.

<table>
<thead>
<tr>
<th>Our $\nu_o$ [THz]</th>
<th>$\nu_o$ [THz]$^a$</th>
<th>Our $\Delta$ [GHz]</th>
<th>$\Delta$ [GHz]$^b$</th>
<th>$\Delta$ [GHz]$^c$</th>
<th>$\Delta$ [GHz]$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.557</td>
<td>0.557</td>
<td>6.7</td>
<td>-</td>
<td>6.5</td>
<td>6.0</td>
</tr>
<tr>
<td>0.753</td>
<td>0.752</td>
<td>6.8</td>
<td>5.9</td>
<td>6.4</td>
<td>6.0</td>
</tr>
<tr>
<td>0.989</td>
<td>0.988</td>
<td>6.2</td>
<td>6.0</td>
<td>6.2</td>
<td>6.0</td>
</tr>
<tr>
<td>1.099</td>
<td>1.098</td>
<td>6.8</td>
<td>6.3</td>
<td>6.0</td>
<td>5.8</td>
</tr>
<tr>
<td>1.113</td>
<td>1.113</td>
<td>6.8</td>
<td>5.4</td>
<td>5.9</td>
<td>6.2</td>
</tr>
<tr>
<td>1.164</td>
<td>1.163</td>
<td>6.8</td>
<td>6.0</td>
<td>5.8</td>
<td>4.9</td>
</tr>
<tr>
<td>1.209</td>
<td>1.208</td>
<td>6.8</td>
<td>5.5</td>
<td>5.8</td>
<td>5.6</td>
</tr>
<tr>
<td>1.23</td>
<td>1.23</td>
<td>6.8</td>
<td>6.0</td>
<td>-</td>
<td>5.7</td>
</tr>
<tr>
<td>1.412</td>
<td>1.410</td>
<td>6.8</td>
<td>6.0</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td>1.603</td>
<td>1.602</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
<td>5.7</td>
</tr>
<tr>
<td>1.664</td>
<td>1.661</td>
<td>11.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.671</td>
<td>1.670</td>
<td>8.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.719</td>
<td>1.717</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>1.764</td>
<td>1.762</td>
<td>11.9</td>
<td>-</td>
<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td>1.797</td>
<td>1.797</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.869</td>
<td>1.868</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
<td>4.4</td>
</tr>
<tr>
<td>1.920</td>
<td>1.920</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*a. $\nu_o$ reported in Matsushima et al. (1995)*

*b. $\Delta$ was reported as $0.79\gamma_{N_2} + 0.21\gamma_{O_2}$ from the data Gasster et al. (1988)*

*c. $\Delta$ was calculated by taking $0.79\gamma_{N_2} + 0.21\gamma_{O_2}$ from the data of Gamache and Fischer (2003)*

*d. $\Delta$ was calculated by taking $0.79\gamma_{N_2} + 0.21\gamma_{O_2}$ from the data of Hoshina et al. (1988)*
Figure 5.13: Real and imaginary parts of susceptibility peak of air around 0.753 THz fitted to a Lorentzian and a Gaussian.
Figure 5.14: Real and imaginary parts of susceptibility peak of air around 1.164 THz fitted to a Lorentzian and a Gaussian.
Figure 5.15: Real and imaginary parts of susceptibility peak of air around 1.209 THz fitted to a Lorentzian and a Gaussian.
Figure 5.16: Real and imaginary parts of susceptibility peak of air around 1.603 THz fitted to a Lorentzian and a Gaussian.
Figure 5.17: Real and imaginary parts of susceptibility peak of air around 1.797 THz fitted to a Lorentzian and a Gaussian.
<table>
<thead>
<tr>
<th>$\nu_0$[THz]</th>
<th>FWHM[GHz]</th>
<th>Fitness ($\Sigma F_i$)</th>
<th>$\nu_0$[THz]</th>
<th>FWHM[GHz]</th>
<th>Fitness ($\Sigma F_i$)</th>
<th>Best Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.577</td>
<td>6.4</td>
<td>0.43</td>
<td>0.557</td>
<td>6.7</td>
<td>0.03</td>
<td>G</td>
</tr>
<tr>
<td>0.753</td>
<td>6.4</td>
<td>0.17</td>
<td>0.753</td>
<td>6.8</td>
<td>0.29</td>
<td>L</td>
</tr>
<tr>
<td>0.989</td>
<td>6.4</td>
<td>4.27</td>
<td>0.989</td>
<td>6.2</td>
<td>5.58</td>
<td>L</td>
</tr>
<tr>
<td>1.099</td>
<td>6.4</td>
<td>2.38</td>
<td>1.099</td>
<td>6.8</td>
<td>10.07</td>
<td>L</td>
</tr>
<tr>
<td>1.113</td>
<td>6.6</td>
<td>2.08</td>
<td>1.113</td>
<td>6.8</td>
<td>1.65</td>
<td>L</td>
</tr>
<tr>
<td>1.164</td>
<td>7.7</td>
<td>0.23</td>
<td>1.164</td>
<td>6.8</td>
<td>0.16</td>
<td>G</td>
</tr>
<tr>
<td>1.209</td>
<td>6.1</td>
<td>1.04</td>
<td>1.209</td>
<td>6.8</td>
<td>0.69</td>
<td>G</td>
</tr>
<tr>
<td>1.23</td>
<td>8.9</td>
<td>5.54</td>
<td>1.23</td>
<td>6.8</td>
<td>6.0</td>
<td>L</td>
</tr>
<tr>
<td>1.412</td>
<td>7.9</td>
<td>0.17</td>
<td>1.412</td>
<td>6.8</td>
<td>0.07</td>
<td>G</td>
</tr>
<tr>
<td>1.603</td>
<td>7.8</td>
<td>0.17</td>
<td>1.603</td>
<td>6.8</td>
<td>0.40</td>
<td>L</td>
</tr>
<tr>
<td>1.664*</td>
<td>9.5</td>
<td>5.0</td>
<td>1.664*</td>
<td>11.9</td>
<td>19.79</td>
<td>L</td>
</tr>
<tr>
<td>1.671*</td>
<td>7.3</td>
<td>5.0</td>
<td>1.671*</td>
<td>8.9</td>
<td>19.79</td>
<td>L</td>
</tr>
<tr>
<td>1.718</td>
<td>8.2</td>
<td>1.78</td>
<td>1.719</td>
<td>6.8</td>
<td>3.26</td>
<td>L</td>
</tr>
<tr>
<td>1.764</td>
<td>10.3</td>
<td>9.95</td>
<td>1.764</td>
<td>11.9</td>
<td>8.67</td>
<td>G</td>
</tr>
<tr>
<td>1.797</td>
<td>7.4</td>
<td>8.52</td>
<td>1.797</td>
<td>8.0</td>
<td>8.50</td>
<td>G</td>
</tr>
<tr>
<td>1.869</td>
<td>9.4</td>
<td>1.20</td>
<td>1.869</td>
<td>7.2</td>
<td>0.78</td>
<td>G</td>
</tr>
<tr>
<td>1.921</td>
<td>4.9</td>
<td>2.47</td>
<td>1.920</td>
<td>7.9</td>
<td>1.53</td>
<td>G</td>
</tr>
</tbody>
</table>

Table 5.2: Extracted data by fitting complex susceptibility peaks of air to Lorentzian and Gaussian models.
The ones with * are doublet peaks. The Fitness function is defined as
\[ \sum_i \{\left[ \angle \chi_t(i) - \angle \chi_e(i) \right]^2 + \left[ |\chi_t(i)| - |\chi_e(i)| \right]^2 \}. \]
Here, \( \chi_e \) is experimental susceptibility and \( \chi_t \) is theoretical susceptibility.
6.1 SUMMARY

There is a need for terahertz absorption data of astrophysical ices because of the new missions Hershel, SOFIAL, and ALMA. We built a terahertz time-domain spectroscopy experimental setup and integrated it with a cryostat in which we could grow the ices by the vapor deposition technique. The ices of Nitrogen were studied in the temperature range of 10 K to 30 K. The system was limited by the spectral bandwidth and also spectral resolution. By the characteristic matrix method, we were able to do high frequency resolution spectroscopy of air making a multi-layered thin film system. We have modeled the THz transmission through the sample and reference systems using the characteristic matrix method. We have derived an expression for the transmission coefficient which was the ratio of electric field transmitted through the sample and the electric field transmitted through a reference. We have mini-
mized a function involving the theoretical transmission coefficient and experimental transmission coefficient to extract the optical constants of air. We have computed the linear susceptibility of air. The absorption features in these data were fitted with Lorentzian and Gaussian profiles to extract the absorption center frequencies and widths. *The new knowledge contained in this thesis is, the use of characteristic matrix method to model the THz transmission and inversion of a transmission coefficient to obtain optical constants with absorptions of any line shape. Earlier, only Ralph et al. have used characteristic matrix method but they assumed a line shape for fitting the transmission coefficient manually but in this thesis, there is no limitation on the line shape of absorption features present in the transmission coefficient. Moreover, in this thesis, the optical constants are extracted by an optimization process using a computer code instead of manual fitting of transmission coefficient.*

6.2 NEW APPLICATIONS

Using the high frequency resolution terahertz time-domain spectroscopy method demonstrated in this thesis together with an efficient way of growing good quality ice films and measurement of ice thickness, we can study ices interesting to astrophysical community. Since the sample and reference waveforms can be modeled as ice-substrate-ice and vacuum-substrate-vacuum respectively, a transmission coeffi-
cient can be derived from the characteristic matrix method and optimized to match the experimental one to get optical constants of ices.

As demonstrated in this thesis, a multilayer planar solid system, liquid system, gas system or a any combination of these three can be studied with this new high frequency resolution terahertz time-domain spectroscopy method. In the literature, integration of graphene with Boron Nitride was demonstrated as a high performance system for electronics [Bresnehan et al. (2012)], hetero-layered materials with tunable direct band gaps were demonstrated [H. et al. (2013)], multilayer thin films system as a THz bolometer was demonstrated [Zhou et al. (2008)], and multilayered materials for components in the THz frequency range were fabricated [Hosako (2005)]. Thin films as transistors and quantum well hetero-structures as THz amplifiers [Tredicucci and Calro (2009)] were also demonstrated, stacks of metamaterials were demonstrated as THz bandpass filters [Zhu et al. (2012)], and liquid crystals were demonstrated as THz quarter waveplates [Hsich et al. (2006)]. In the further study of all these materials, our new high frequency resolution terahertz time-domain spectroscopy system can be used. Since these sample systems are planar multilayered, to resolve any narrow absorption lines in these material, the ideal THz analysis method would be the one demonstrated in this thesis.
6.3 FUTURE DIRECTIONS

The new high frequency resolution terahertz time-domain spectroscopy method can be extended to the measurement of astrophysical ices. Currently, the spectral bandwidth is limited by the thickness of the ZnTe crystals. Though the THz absorption data of astrophysical ices in 0.1-1THz is useful for the Hershel, for the analysis of data from other astrophysical telescopes, we need broadband THz laboratory data of astrophysical ices. The spectral bandwidth of the spectrometer has to be increased. It may be achieved by the plasma assisted generation of THz radiation. This might help in studying many ices and ice mixtures. The ice thickness measurement system has to be changed because for some ices (example: mixtures of N₂ and CO₂), the thickness measurement 1342 nm light damages the ices even for the lowest possible power. A new system based on the reflective geometry methods may be implemented for this. Also, to avoid the issues of Nitrogen ice sublimation, a sample cell for growing ices might be needed.


