

NMR INSTRUMENTATION AND STUDIES IN  
AMMONIUM AND METHYL SUBSTITUTED  
AMMONIUM COMPOUNDS

**A Thesis**

**Submitted for the award of the Degree of**

**Doctor of Philosophy**

*in the Faculty of Science*

By

**K. J. MALLIKARJUNAIAH**

**[kjmarjun@gmail.com](mailto:kjmarjun@gmail.com)**



Department of Physics  
Bangalore University  
Bangalore - 560 056 (INDIA)

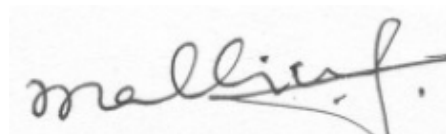
**August 2007**

Dedicated to

My beloved parents

## DECLARATION

I hereby declare that the work presented in this thesis is entirely original and has been carried out by me independently in the Department of Physics, Bangalore University, Bangalore - 560 056, under the guidance and supervision of **Dr. Ramakrishna Damle**, Reader, Department of Physics, Bangalore University, Bangalore-560 056. Further, this work has not been submitted in part or full to any University or Institute for the award of any degree, diploma, fellowship, associateship or similar title.



Date: August 20, 2007

**(K.J. MALLIKARJUNIAH)**

Research Scholar  
Department of Physics  
Bangalore University  
Bangalore - 560 056.

## CERTIFICATE

This is to certify that the thesis entitled '**NMR Instrumentation and Studies in Ammonium and Methyl substituted Ammonium compounds**' submitted by Sri **K.J. Mallikarjunaiah**, for the award of the degree of Doctor of Philosophy in the Faculty of Science, Bangalore University, Bangalore, is based on the work carried out by him under my guidance and supervision. Further, to the best of my knowledge, this work has not been submitted in part or full to any University or Institute for the award of any degree, diploma, fellowship, associateship or similar title.

Date: August 20, 2007

(Dr. RAMAKRISHNA DAMLE)

Research Supervisor  
Department of Physics  
Bangalore University  
Bangalore-560 056.

## List of Publications

### Journals

1. “Study of molecular reorientation and quantum rotational tunneling in tetramethylammonium selenate by  $^1\text{H}$  NMR”.  
[K. J. Mallikarjunaiah](#), K. C. Paramita, K. P. Ramesh and R. Damle  
*Solid State Nuclear Magnetic Resonance* **32(1)**, 11-15 (2007).  
[doi:10.1016/j.ssnmr.2007.07.003](https://doi.org/10.1016/j.ssnmr.2007.07.003)
2. “Study of molecular dynamics and phase transitions in trimethylammonium trichlorogermanate using  $^1\text{H}$  NMR and DSC measurements”.  
[K.J. Mallikarjunaiah](#), K.P. Ramesh and R. Damle  
*Physica Status Solidi – b* **244 (10)**, 3809-3816 (2007).  
**Doi:10.1002/pssb.200743104**  
[doi:10.1002/pssb.200743104](https://doi.org/10.1002/pssb.200743104)
3. “ $^1\text{H}$  NMR study of internal motions and quantum rotational tunneling in  $(\text{CH}_3)_4\text{NGeCl}_3$ ”  
[K.J. Mallikarjunaiah](#), K. Jugeshwar Singh, K.P. Ramesh and R. Damle  
*Magnetic Resonance in Chemistry* – **46(2)**, 110-114 (2008)..  
[doi:10.1002/mrc.2097](https://doi.org/10.1002/mrc.2097)
4. “Conditioning and automation of NMR signal acquisition”  
[K. J. Mallikarjunaiah](#) and R. Damle  
*Vignanabharathi*, **17(1)**, 50 (2005).
5. “Modulation schemes of wide-line NMR signal absorption”  
N. Sasidhar, [K. J. Mallikarjunaiah](#) and R. Damle  
*Journal of Instrumentation Society of India*, **32(1)**, 1-8 (2002).  
[www.isoi.in/Journal/BackIssues/32\(1\).pdf](http://www.isoi.in/Journal/BackIssues/32(1).pdf)
6. “ $^1\text{H}$  and  $^{19}\text{F}$  NMR study of molecular dynamics in tetramethylammonium hexafluorophosphate”  
[K.J. Mallikarjunaiah](#), K.P. Ramesh and R. Damle  
*Solid State Nuclear Magnetic Resonance* **34(3)**, 180-185 (2008).  
[doi:10.1016/j.ssnmr.2008.08.002](https://doi.org/10.1016/j.ssnmr.2008.08.002)
7. “ $^1\text{H}$  and  $^{19}\text{F}$  NMR relaxation time studies in  $(\text{NH}_4)_2\text{ZrF}_6$  superionic Conductor”  
[K.J. Mallikarjunaiah](#), K.P. Ramesh and R. Damle  
*Applied Magnetic Resonance* **35 (3)**, 449-458 (2008).

## Conferences

8. <sup>1</sup>H and <sup>19</sup>F NMR study in tetramethylammonium hexafluorophosphate (CH<sub>3</sub>)<sub>4</sub>NPF<sub>6</sub>”  
**K.J. Mallikarjunaiah**, K.P. Ramesh and R. Damle  
“**NMRS-2008**” INMAS, Delhi (India), Jan. 16-19, **2008**, p.
9. “NMR instrumentation and studies in Ammonium and methyl substituted Ammonium compounds”  
**K.J. Mallikarjunaiah**  
**DAE-SSPS-2007**, Mysore Uni., Mysore (India), Dec. 27-31, 2007, [PPT Poster](#)  
Proceedings of *DAE Solid State Physics Symposium-2007*, **52**, [1229](#) (**2007**).
11. “<sup>1</sup>H and <sup>19</sup>F NMR relaxation time studies in (NH<sub>4</sub>)<sub>2</sub>ZrF<sub>6</sub> superionic conductor”  
**K.J. Mallikarjunaiah**, K.P. Ramesh and R. Damle  
**International Conference** on "*Modern Development of Magnetic Resonance*" (**Zavoisky100**), Kazan, Russian Federation, Sept. 24-29, **2007**, **pp 195**.  
[www.kfti.knc.ru/zavoisky100](http://www.kfti.knc.ru/zavoisky100)
12. “<sup>1</sup>H NMR study of molecular dynamics in trimethylammonium trichlorogermanate (CH<sub>3</sub>)<sub>3</sub>NHGeCl<sub>3</sub>”  
**K.J. Mallikarjunaiah**, K. Jugeshwar Singh, K.P. Ramesh and R. Damle  
“**NMRS-2007**” NCL, Pune (India), Feb. 05-08, **2007**, **pp 136**.  
[http://www.ncl-india.org/nmrs2007/cam/NMRS\\_poster\\_papers.pdf](http://www.ncl-india.org/nmrs2007/cam/NMRS_poster_papers.pdf)
13. “<sup>1</sup>H NMR study on Tetramethylammonium selenate ((CH<sub>3</sub>)<sub>4</sub>N)<sub>2</sub>SeO<sub>4</sub>”  
**K.J. Mallikarjunaiah**, K.C. Paramita, K.P. Ramesh and R. Damle,  
“**DAE-SSPS –2006**” Bharkatulla Uni., Bhopal (India), Dec. 26-30, 2006.  
Proceedings of *DAE Solid State Physics Symposium-2006*, **51**, 133 (**2006**).
14. “Computer Controlled programmable pulse generator for Pulsed NMR measurements”  
**K. J. Mallikarjunaiah**, J. T. Devaraju and R. Damle  
*National symposium on Instrumentation (NSI-27)*, Bharathiyar Uni., Coimbatore (India), Nov 27-29, **2002**. **pp 35**.

## Acknowledgements

---

I am greatly indebted to my research guide [Dr. Ramakrishna Damle](#), Reader, Department of Physics, Bangalore University Bangalore, for not only introducing me to the field of “Nuclear Magnetic Resonance” but also for open atmosphere in the lab, with the prophetic and timely advice, guidance and constant encouragement throughout my association with him. Right from my M.Sc days, I was always fascinated about him and I have often felt to be fortunate enough to work under his able supervision and cope up with his pitch. His faith and confidence in me has always boosted my morale, particularly in difficult times. Like a true friend he was always there with me in the thick and thin of research. I am also grateful to him for his valuable and consistent guidance towards the completion of my research work. I have thoroughly enjoyed every academic discussion that I had with him.

I have been fortunate enough to work with [Dr. K.P. Ramesh](#), Principal Research Scientist, Department of Physics, Indian Institute of Science, Bangalore. I am greatly indebted to him for allowing me to work in his laboratory. He gave me full freedom, took keen interest and showed maximum concern about my research work. I gratefully acknowledge every academic help rendered by him during my research period. My association with him and his students did make me to learn many finer aspects of research in general and NMR in particular. I am immensely benefited as well by his vast literature knowledge in the area of NMR/NQR. At the same time, I would like to acknowledge his lab members Mr. Ramanuja, Dr. Sutirtha Mukhopadyay (presently at North Western University, Illinois, USA), Dr. Chakradhar (presently at CGCRI, Kolkata), Mr. Jugeshwar Singh, Mr. Subramanyam (presently at Eindhoven University of Technology, Netherlands) and Mr. S. Sunil Kumar for their kind concern and cooperation throughout my stay in IISc. I would like to take this opportunity to convey my special

thanks to Mrs. Paramita Kar Choudhury for her great help while doing the experiments, especially for giving a small but appropriate break in the early morning hours. I thank Central facility (Physics) for material characterization experiments, Mr. Samuel (Inorganic and Physical Chemistry, IISc) for timely help in sealing the samples and Centre for Cryogenic Technology timely supply of coolant for my experiments without which I would have not reached this page.

I would like to take this opportunity to express my heartfelt gratitude to Dr. J.T. Devaraju, Lecturer, Department of Electronic sciences, Bangalore University, for teaching me the basics of programming for PPG. In addition, I take this moment to thank Prof. Rajan Anavekar, Dr. Meera, Dr. Sharath Ananthamurthy, Prof R. Chandramani, Prof. Hanumanthappa (Rtd.) and all the staff members of the Department of Physics, Bangalore University for their great concern about my research progress and timely encouragement during the course of my stay at Bangalore University, Bangalore.

I take this opportunity to thank **Prof. Ramani**, Chairperson, Department of Physics, Bangalore University, Bangalore, for her kind concern, encouragement and support. I also gratefully remember and acknowledge the encouragement and concern shown by the previous Chairpersons of our Department. Further, I also extend my heartiest thanks to every faculty in the Department of Physics, Bangalore University Bangalore for their kind cooperation.

I really enjoyed the best possible company of Mr. P.N. Kulkarni, Dr. S.R. Kulkarni, Mr. Madhu and Mr. Praveen in our NMR lab at Department of Physics, Bangalore University. Their presence has made me to rediscover a way of looking at the problem and appropriate simple solutions.

Thanks to Dr. Veeranna Gowda, Anand, Satyajith, Raghu, Shivaprasad and new research scholars gang at the Department of Physics, Bangalore University.

I acknowledge my heartfelt thanks to Board of Research in Nuclear Science (BRNS), Department of Atomic Energy, India, for financial assistance. I would also like to acknowledge my sincere gratitude for Dr. Chandrachoodan (BARC, Mumbai) and Mr. Gopal Joshi (BARC, Mumbai) for their timely help.

At last but definitely not the least, I owe a lot to my father, mother, brothers, sister, sister in laws and specially for my brother in law for their patience, understanding, love, trust..... the list could go on. My association with Miss Anthony Saleena, Miss Lilly Grace and Mrs. Chaitra of Sri Krishna Institute of Technology, Bangalore, really gave me a homely atmosphere and I am indebted for their great and timely concern about me and my research progress.

## Preface

---

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most powerful tools in modern science to study structure and dynamics of molecules. Basic research regarding phase transition, quantum tunneling, molecular dynamics and structure has been carried out using this spectroscopic technique. The application of NMR to modern day science has extended from the study of chemical dynamics to functional group analysis, medical diagnosis, bonding connectivity and orientation, molecular conformations and even to 3D imaging to resolutions of the order 1 mm.

Though commercial high-resolution NMR spectrometers are available, they are very expensive not only to procure but also to maintain them. However, low-resolution NMR spectrometers are sufficient for NMR second moment and relaxation time measurements. Thus, for those interested in time domain experiments, it is appropriate to develop their own NMR spectrometers. In a few laboratories in India and abroad too, the NMR study of molecular dynamics and phase transitions are being carried out using home made spectrometers.

This thesis describes the assembling and development of wide line and pulsed NMR spectrometer (with high temperature and low temperature cryostat assembly) and Proton (and Fluorine) NMR investigations in a few ammonium and methyl substituted ammonium metal halides. Proton NMR line widths have been measured in these systems using a homemade wide line NMR spectrometer operating at 7-15 MHz. Proton NMR spin-lattice relaxation time ( $T_1$ ) have been measured in the temperature range 400 K – 4.2 K.

Inorganic salts containing symmetrical molecular groups like  $\text{NH}_4$  and  $\text{CH}_3$  are known to have wide spectrum of technological applications such as in medicine, energy and agriculture. Apart from applications, these compounds are of academic interest also.

Ammonium and methyl substituted ammonium metal halides have shown to exhibit not only complex reorientational dynamics but also interesting features like diffusion and spin rotation at higher temperatures ( $> 300\text{K}$ ) and structural phase transitions in the temperature range  $50 - 400\text{ K}$ . At lower temperatures, some of them have revealed the presence of tunnelling reorientations also. Many of these systems are also known to be good ionic conductors. However, there is rather little NMR data on inorganic compounds with low activation barrier. This thesis describes the NMR study of molecular dynamics in Diammonium hexafluorozirconate  $[(\text{NH}_4)_2\text{ZrF}_6]$ , Tetramethylammonium hexafluorophosphate  $[(\text{N}(\text{CH}_3)_4)\text{PF}_6]$ , Tetramethylammonium selenate  $[(\text{N}(\text{CH}_3)_4)_2\text{SeO}_4]$ , Trimethylammonium trichlorogermanate  $[\text{NH}(\text{CH}_3)_3\text{GeCl}_3]$  and Tetramethylammonium trichlorogermanate  $[\text{N}(\text{CH}_3)_4\text{GeCl}_3]$ . The first two of these compounds are commercially procured while the rest of the compounds have been synthesized and characterized in the laboratory. Powder x-ray diffraction and Differential Scanning Calorimetry (DSC) have been employed for the characterization of the compounds.

The thesis is presented in 5 Chapters. [Chapter 1](#) starts with a brief introduction to the relevant basic theoretical aspects of NMR spectroscopy required for the present investigations. Different relaxation mechanisms, such as dipole-dipole, translational diffusion and quantum rotational tunnelling etc., the effect of molecular motions on second moment and spin-lattice relaxation time have been discussed in the Chapter 1, with a special attention to unlike spin interaction. This Chapter also discusses the second moment and spin lattice relaxation measurement techniques used in the present investigations.

[Chapter 2](#) describes the assembling and testing of a home-made wide-line and pulsed NMR spectrometer. The wide-line NMR spectrometer basically consists of an electromagnet (Bruker B-MIN C5S), a marginal rf oscillator (operating in the frequency range  $5\text{-}15\text{ MHz}$ ), modulation and detection systems. NMR absorption signal is acquired on to a computer using a 12-bit ADC interface card. The automation of the NMR signal acquisition is found to be not only efficient and cost effective, but it provides a on-line calibration of the magnetic field for on-screen measurement of the line width of the NMR

signal. The pulsed NMR spectrometer consists of an rf transmitter capable of delivering short and powerful rf pulses, a high gain and low noise receiver amplifier and a matching network to couple the rf pulses to the sample coil and the sample coil to the receiver. A home built computer controlled Programmable Pulsed Generator (PPG) has been used to generate the required pulse sequences. Assembling and testing of the pulsed NMR spectrometer operating in the frequency range 10-30 MHz is described. The fabrication of a low temperature gas flow cryostat as well as high temperature assembly is also described.

[Chapter 3](#) describes the NMR spin-lattice relaxation time ( $T_1$ ) studies carried out in Diammonium hexafluorozirconate  $[(\text{NH}_4)_2\text{ZrF}_6]$ . Both  $^1\text{H}$  and  $^{19}\text{F}$  NMR  $T_1$  measurements have been made at 21.337 MHz as a function of temperature in the range 410 to 11 K.  $T_1$  shows a broad maximum around room temperature. On increasing the temperature,  $T_1$  starts decreasing up to 395 K above which it reduces sharply to less than a millisecond. In the same temperature region, FID duration also has been monitored for both the nuclei. For  $^1\text{H}$ , FID duration increases several times as the temperature is increased from 388 K to 410 K, while for  $^{19}\text{F}$ , it increases a few times in the same temperature region. Both decrease in  $T_1$  and narrowing of the NMR signal are attributed to diffusion of both  $\text{NH}_4$  and F ions through the lattice. Reported high ionic conductivity above 400 K also supports this.  $^1\text{H}$  NMR line width above 400 K, as reported, reaches a limit of modulation width indicating the diffusion of ammonium ions. Sublattice movement of F ions is also reported above 400 K. The observed maximum in  $T_1$  in the present study around room temperature is attributed to the competition between diffusion and reorientational motion of the  $\text{NH}_4$  ion. On decreasing the temperature below room temperature, both  $^1\text{H}$  and  $^{19}\text{F}$   $T_1$  gives rise to minimum around 160 K, which is attributed to  $\text{NH}_4$  ion motion. The  $T_1$  behaviour is analyzed based on the cross relaxation between proton and fluorine. At lower temperatures,  $T_1$  remains almost constant up to 50 K. However, on further cooling the sample,  $T_1$  increases for both the nuclei. Further,  $^1\text{H}$   $T_1$  exhibits a shallow minimum around 21 K, which may be attributed to quantum rotational tunneling of  $\text{NH}_4$  ions, which is in agreement with reported line shape analysis in the same compound.

The present investigation reveals that, in Ammonium zirconate, ammonium ion plays a major role in relaxation mechanism in the temperature range of study. At higher temperature, compound shows a diffusion of both ammonium and fluorine sublattice. Sharp increase of FID duration and sudden increase of relaxation rate around 395 K, is supported by wide-line NMR line shape and second moment analysis as well as the conductivity studies. Further, this investigation reveals the reorientational motion of the ammonium ion is responsible for fluorine relaxation also. Another important observation is that even at low temperatures the fluorine nuclei are being relaxed due to quantum rotational tunneling of the ammonium ion. Superionic conductivity in the sample is interpreted as due to the diffusion of  $\text{NH}_4$  ion and fluorine sublattice motion.

[Chapter 4](#) describes the NMR studies in tetramethylammonium salts.  $T_1$  studies (at 21.34 MHz) in Tetramethylammonium selenate  $(\text{N}(\text{CH}_3)_4)_2\text{SeO}_4$  and Second moment (at 7 MHz) as well as  $T_1$  (at 21.34 MHz) measurements in Tetramethylammonium hexafluorophosphate  $\text{N}(\text{CH}_3)_4\text{PF}_6$  have been carried out.

A broad  $T_1$  minimum observed in Tetramethylammonium selenate around 280 K is attributed to the simultaneous motions of  $\text{CH}_3$  and  $(\text{CH}_3)_4\text{N}$  groups. Lower activation energy obtained from the  $T_1$  analysis as well as powder XRD measurements confirm that, the present compound crystallizes in cubic form and not in tetragonal. Magnetization recovery is found to be stretched exponential below 72 K with varying stretched exponent. Low temperature  $T_1$  results show the quantum rotational tunneling of methyl groups and the observed  $T_1$  is the resultant of relaxation of all spin systems.

In  $(\text{N}(\text{CH}_3)_4)\text{PF}_6$ ,  $^1\text{H}$   $T_1$  measurements have been carried out at three Larmor frequencies (11.4, 16.1 and 21.34 MHz). At all frequencies, the observed single asymmetric minimum is attributed to simultaneous reorientations of both  $\text{CH}_3$  and  $(\text{CH}_3)_4\text{N}$  groups. Second moment measurements made at 7 MHz also supports this.  $^{19}\text{F}$  NMR  $T_1$  measurements have been carried out at 21.34 MHz and 16.1 MHz in the

temperature range 350 - 77 K. Cross correlation between proton and fluorine has been invoked to account for the observed  $^{19}\text{F}$  T1 data.

In [Chapter 5](#),  $^1\text{H}$  NMR T1 studies in Trimethylammonium trichlorogermanate  $[\text{NH}(\text{CH}_3)_3\text{GeCl}_3]$  and  $^1\text{H}$  NMR T1 as well as second moment studies in Tetramethylammonium trichlorogermanate  $[\text{N}(\text{CH}_3)_4\text{GeCl}_3]$  are presented. In Trimethylammonium trichlorogermanate  $[\text{NH}(\text{CH}_3)_3\text{GeCl}_3]$ ,  $^1\text{H}$  T1 measurements have been made as a function of temperature in the range 391 – 5.2 K at 20.53 MHz. The T1 data are analyzed in three parts: the High Temperature region (391 - 272 K), the Intermediate Temperature region (272-100 K) and the Low Temperature region (100 – 5.2 K). The Trimethylammonium trichlorogermanate undergoes several phase transitions (at 388, 323, 272, 100 and 57 K) along with thermally activated reorientations of the trimethylammonium and methyl groups. The observed phase transitions are attributed to the chloride ion diffusion (at higher temperatures) and changes in the symmetry of the  $\text{GeCl}_3$  ions (at lower temperatures), which may have indirect effect on proton spin lattice relaxation time. The observed two minima in intermediate temperature region are attributed to reorientation of  $\text{NH}(\text{CH}_3)_3$  and  $\text{CH}_3$  symmetric groups and corresponding motional parameters are evaluated. The observation of the decrease of activation energy of the TriMA/methyl groups with decrease in metal ion radius, in TriMABCl<sub>3</sub> complexes, may be due to the increased volume (higher metal ion (B) radius). At lower temperatures, T1 results show quantum rotational tunneling of the methyl group.

In Tetramethylammonium trichlorogermanate  $[\text{N}(\text{CH}_3)_4\text{GeCl}_3]$ ,  $^1\text{H}$  NMR second moment ( $M_2$ ) measurements are carried out, as a function of temperature in the temperature range 300 – 77 K at 7 MHz.  $^1\text{H}$  NMR spin lattice relaxation time (T1) measurements are carried out, as a function of temperature, at two Larmor frequencies 26 MHz and 11.4 MHz in the temperature range 270-17 K TMA-Germanate exhibits thermally activated reorientations of the Tetramethylammonium and methyl groups. In this compound, second moment results show only one plateau region and T1 results show a single asymmetric minimum than expected two plateau regions in the second moment

and two minima in the T<sub>1</sub> studies. This observation is explained by inferring that both the CH<sub>3</sub> and TMA groups in TMA – Germanate are reorienting with the same (order of magnitude) correlation times. It is also noticed that the decrease of activation energy of the TMA/methyl groups with decrease in metal ion radius, in TMABCl<sub>3</sub> complexes, may be due to the increased volume (higher metal ion (B) radius). Present investigations have not revealed any change in the magnetization recovery profile even below 170 K. Hence it is concluded that the TMA ion surrounding remains unaltered. At lower temperatures, T<sub>1</sub> results suggest the existence of the inequivalent methyl groups undergoing quantum rotational tunneling.

All the compounds investigated have given very useful information on the dynamics of the reorienting groups and the influence of the anion dynamics on the activation energy of the reorienting groups. The signatures of unlike nuclear interactions affecting the relaxation of a particular nucleus is seen in the T<sub>1</sub> data. The activation energies of the reorienting groups are found to lie in the range 8 - 30 kJ/mol. The low activation energy for the molecular reorientation in these systems make them good candidates for basic studies as well as potential possible applications.

**Most of the results of the present investigations are published in reputed International Journals.**

# Contents

---

<b>List of publications</b>	<b>i</b>
<b>Acknowledgements</b>	<b>iii</b>
<b>Preface</b>	<b>vi</b>
<b>1. <a href="#">NMR: Basic theory</a></b>	<b>1 - 31</b>
1.1 Nuclear Spins in a Static Magnetic field .....	1
1.2 The Classical Picture of Motion .....	5
1.3 Quantum mechanical Picture- Spin Hamiltonian .....	6
1.3.1 The dipolar Hamiltonian .....	7
1.3.2 Method of moments .....	9
1.4 Effects of molecular Motions .....	12
1.4.1 Line Narrowing .....	12
1.4.2 Relaxation.....	13
1.4.2.1 Dipole- dipole interaction.....	13
1.4.2.2 Translational diffusion .....	19
1.4.2.3 Tunneling reorientation .....	22
1.5 Free induction Decay.....	24
1.6 Measurement of $M_2$ and $T_1$ .....	26
1.6.1 Second moment ( $M_2$ ).....	26
1.6.2 Spin lattice relaxation ( $T_1$ ) .....	26
1.6.2.1 Inversion Recovery Method ( $\pi$ - $\tau$ - $\pi/2$ ) .....	26
1.6.2.2 Saturation Burst method.....	28
References.....	30
<b>2. <a href="#">NMR Instrumentation and Experimental techniques</a></b>	<b>32 - 64</b>
2.1 Introduction.....	32
2.2 Wide-line NMR spectrometer.....	32
2.2.1 Electromagnet .....	33
2.2.2 Oscillator .....	34
2.2.3 Modulation and lock in detection .....	35
2.2.4 Signal acquisition and Automation.....	42
2.3 Pulsed NMR spectrometer.....	47
2.3.1 PC controlled programmable pulse generator.....	48
2.3.2 Transmitter .....	52
2.3.2.1 RF unit.....	52
2.3.2.2 Medium power amplifier.....	52

2.3.2.3	High power amplifier .....	54
2.3.3	The NMR Probe Circuit .....	55
2.3.3.1	Series resonant circuit .....	56
2.3.3.2	Parallel resonant circuit .....	57
2.3.4	Receiver .....	58
2.4	Temperature variation setup .....	59
2.4.1	High temperature assembly .....	59
2.4.2	Liquid Nitrogen Assembly .....	60
2.4.3	Liquid Helium Assembly .....	61
	References .....	63
<b>3.</b>	<b><u>NMR Studies in Diammonium hexafluorozirconate</u></b> .....	<b>65-82</b>
3.1	Introduction .....	65
3.2	Earlier studies .....	67
3.3	Results and discussion .....	69
3.3.1	Analysis of $^1\text{H}$ NMR $T_1$ .....	69
3.3.3.1	High Temperature (HT) region (410-240 K) .....	70
3.3.3.2	Intermediate temperature range (240- 146 K) .....	73
3.3.3.3	Low Temperature (LT) region (146 – 11 K) .....	74
3.3.2	Analysis of $^{19}\text{F}$ NMR $T_1$ .....	77
3.3.2.1	High Temperature (HT) region (410-240 K) .....	78
3.3.2.2	Intermediate temperature range (200- 106 K) .....	78
3.3.2.3	Low temperature range (106-20 K) .....	79
3.4	Conclusion .....	79
	References .....	80
<b>4.</b>	<b><u>NMR Studies in Tetramethylammonium (TMA) Salts</u></b> .....	<b>83-116</b>
4.1	Tetramethylammonium Selenate $((\text{CH}_3)_4\text{N})_2\text{SeO}_4$ .....	84
4.1.1	Introduction .....	84
4.1.2	Earlier studies .....	84
4.1.3	Sample preparation and characterization .....	87
4.1.4	Results and discussion .....	87
4.1.4.1	High temperature region (389-170 K) .....	87
4.1.4.2	Low temperature region (72 - 6.6 K) .....	92
4.1.5	Conclusions .....	97
4.2	Tetramethylammonium Hexafluorophosphate $(\text{CH}_3)_4\text{NPF}_6$ .....	97
4.2.1	Introduction .....	97
4.2.2	Earlier studies .....	99
4.2.3	Results and discussion .....	99

4.2.3.1	Second moment.....	101
4.2.3.2	Spin lattice relaxation time.....	102
4.2.4	Conclusions.....	112
	References.....	113
<b>5.</b>	<b><u>NMR Studies in Trichlorogermanates</u></b>	<b>117-148</b>
5.1	Introduction.....	117
5.2	Trimethylammonium Trichlorogermanate ((CH <sub>3</sub> ) <sub>3</sub> NHGeCl <sub>3</sub> ).....	119
5.2.1	Earlier studies .....	119
5.2.2	Sample preparation and characterization.....	120
5.2.3	Results and discussion .....	121
5.2.3.1	High temperature region (391-272 K).....	122
5.2.3.2	Inter mediate temperature region (272 - 100 K) .....	124
5.2.3.3	Low temperature region (100 –5.2 K).....	127
5.2.4	Conclusions.....	130
5.3	Tetramethylammonium Trichlorogermanate ((CH <sub>3</sub> ) <sub>4</sub> NGeCl <sub>3</sub> ).....	131
5.3.1	Earlier studies .....	131
5.3.2	Sample preparation and characterization.....	132
5.3.3	Results and discussion .....	134
5.3.3.1	Second moment .....	134
5.3.3.2	Spin lattice relaxation time.....	136
5.3.4	Conclusions.....	144
	References.....	145
	Appendix - I .....	149
	Appendix-II.....	150