PREFACE

Nuclear Magnetic Resonance has come a long way from the time of its inception in becoming a powerful and versatile experimental tool for Physicists, Chemists, and Biologists alike to probe structure at a microscopic level, and more rewardingly, to report on different molecular dynamic processes. The advent of FT-NMR techniques has opened new areas of investigations which were hitherto not quite amenable to experimental techniques. NMR Imaging has become an important application of a basic idea developed in physics in the recent times. Measurements on different spin relaxation rates, which can be carried out even with simpler experimental methodologies (using pulsed NMR instruments, for example) are one of the most powerful methods of investigation, especially of solids, to throw valuable light on the dynamic processes, often important in our understanding of many other physical phenomena, structural phase transitions in solids being one of them. The spin-lattice relaxation time \( T_1 \) of a probe nucleus depends not only on the configuration of the molecular group in which this probe is situated and the crystal structure of the solid, but also, even more sensitively, on the motional state of these groups. The existence and its relative importance of a given type of motion, like reorientation or vibration, of a given molecular group is in turn dependent on the temperature as well as on the potential barriers such a group experiences in its surroundings due to the inter molecular interactions in the solid. Owing to this delicate coupling of the spin probe with its dynamic environment, investigation of relaxation rates as a function of temperature and resonance (Larmor) frequency can be profitably used to distinguish and report on the type of the different
inequivalence, correlation times, and activation energies with the help of appropriate molecular dynamic models. On the other hand, linewidth and second moment \( (M_2) \) measurements provide complementing and confirmatory information on these processes, which crucially helps to check the validity of the microscopic model proposed on the basis of the relaxation information.

The systems investigated in the present study, **tris(alkylammonium) halogeno bismuthates**, belong to a family of solids with the general formula \([\text{(CH}_3\text{)}_n\text{N}]\text{M}_2\text{X}_n\), where \( n \) varies from 0 to 4, \( M \) is a metal atom belonging to the Group V elements, but predominantly Sb and Bi, and \( X \) is a halogen atom like Cl, Br or I. These complex solids are formed by an infinite network of the \( \text{M}_2\text{X} \) anions and **alkylammonium** cations are situated in cavities within these layers, undergoing reorientational motions. These solids exhibit order-disorder type structural phase transitions, and due to the sensitive dependence of the dynamics of the cation on the structural and dynamic properties of the solid, such a phase transition will observably affect the dynamic state of the cations. Therefore to investigate the dynamic properties of these cations it is ideal to use proton as the NMR probe and manifestation of such transitions are then expected to be reflected as subtle and characteristic changes in resonance and relaxation parameters of the spin probe. With these objectives a systematic study of both Antimony and Bismuth substituted solids of above family was undertaken using proton magnetic resonance measurements in this laboratory. The work presented in this thesis concerns the spin-lattice relaxation time \( (T_1) \) and second moment \( (M_2) \) measurements on **tris(alkylammonium) halogeno bismuthates** with proton as the NMR probe, the measurements being made as a function of temperature and Larmor frequency. Since results on the Antimony
substituted compounds were readily available, this thesis presents a comparative picture of both Bi and Sb substituted compounds where ever possible apart from a discussion on Bismuth substituted compounds themselves. The measurements were made on a home-made automated pulsed-NMR spectrometer with the necessary supporting instrumentation having been developed as a part of this research project.

The thesis consists of three sections A, B and C. Section-A is dedicated to the discussion of the necessary theoretical ideas to interpret the results being presented later. A detailed discussion of Bloembergen-Purcell-Pound theory (BPP, in short) is provided. Further, outline of the general method of deriving the appropriate expression for the spin-lattice relaxation rate taking into account the relevant dynamic processes of a given cationic group is presented, the detailed models appropriate to the different cations being presented in later sections along with the results of measurements on each compound.

Section-B concerns the experimental details and is divided into three parts. Sub-section B-1 describes the methodology of pulsed NMR experiments, and of measurements of spin lattice relaxation time (T₁), spin-spin relaxation relaxation time (T₂) and second moment of resonance absorption line (M₂). Sub-section B-2 includes a brief description of the pulsed NMR spectrometer used. The author's contribution towards the upgradation of this instrument forms the content of sub-section B-3, and this includes a description of a microprocessor based pulse programmer which was developed as part of such an upgradation, the hardware and software details of the effort to automate the experiments by interfacing with a personal computer in the GPIB and RS-232-C environments, as well as the instrumentation effort to make the spectrometer compatible to
carry out other interesting measurements (like translational diffusion using spin echoes under pulsed field gradients).

In Section-C the results of investigations on *tris(alkylammonium)* halogeno bismuthates are presented, and these results are analyzed based on suitable theoretical models. This section begins with a brief survey of the properties of \( A M \_X \) family of compounds (sub-section C-1). The geometrical and bonding considerations which lead to the unique structures of these compounds are discussed in some detail, and is followed by a brief overview of the results of measurements by various physical techniques on *tris(alkylammonium)* halogeno metallates. The utility and relevance of a NMR study on these systems, in the light of the information presented, is then highlighted.

Sub-section (C-2) contains the results of \( T \) and \( M \) measurements on the compounds \( \left[ \left( CH \_3 \_4 \_N \right)_3 Bi \_2 Cl \_9 \right] \) and \( \left[ \left( CH \_3 \_4 \_N \right)_3 Bi \_2 Br \_9 \right] \). \( T \_1 \) data show the presence of structural phase transitions at 151K and 183K, respectively, in these compounds as confirmed by other physical measurements. Formation of \( T \) minima due to the isotropic reorientation of the tetramethylammonium cation is seen in both these compounds, and also, \( T \) minima due to the reorientation of the methyl groups about their \( C \) axes are also observed. To analyze the \( T \) data the theoretical model of Albert et al., (1972) is discussed in detail. Analysis of data in these compounds show the presence of dynamically inequivalent methyl groups and such a presence is a reflection of the considerable amount of structural disorder present in these compounds. Second moment measurement on these compounds as a function of temperature corroborates the model used to analyze \( T \) data but there is no signature of the phase transitions on \( M \_\_ \) data on these compounds. Further, analysis of \( T \) data strongly suggests
the possibility of additional structural phase transitions at about 91K in \([\text{(CH}_3\text{)}_4\text{N}]_3\text{Bi}_2\text{Cl}_9\) and 120K in \([\text{(CH}_3\text{)}_4\text{N}]_3\text{Bi}_2\text{Br}_9\).

Results of T and M measurements on \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) and \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) and their analysis form sub-section (C-3). These compounds contain cations which are more asymmetric than above, and they have preferred triad and diad axes of rotation. T data on \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) show the effect of isotropic reorientation of the dimethylammonium cation in the form of a minimum around 400 K but such a minimum is not seen below 400 K in the case of \([\text{(CH}_3\text{)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\), even though its presence is suggested by the T data. \([\text{(CH}_3\text{)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) shows the possibility of a structural phase transition at 300K whereas \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) shows a discontinuity in the T data at 152K, suggesting a structural phase transition. In both these compounds the signature of a structural phase transition at lower temperatures (around 100K) is detected by the NMR measurements (125 K in \([\text{(CH}_3\text{)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) and 78 K in \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\)). Theoretical models taking into account the triad and diad axis reorientations as well as the internal motions (methyl group dynamics) of these cations are presented in this section, and the T. data are thus analyzed for trimethylammonium and dimethylammonium group dynamics. The compound \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) exhibits an increased degree of structural inequivalence as evidenced by the observed dynamic inequivalence of trimethylammonium cations as well as the methyl groups. On the other hand, analysis of T data in \([\text{(CH)}_3\text{NH}]_3\text{Bi}_2\text{Cl}_9\) shows the presence dynamic inequivalence only among the methyl groups but not in dimethylammonium groups.

Sub-section (C-4) is devoted to the discussion of T. and M. measurements on the compound \((\text{CH NH})_3\text{Bi}_2\text{Cl}_9\). M data at the highest
temperature of measurement (≈ 400 K) in this compound show the presence of isotropic reorientation among all the cations. Four structural phase transitions are reported in this system using other physical techniques (385K, 349K, 247K and 200K) and M data show the signature of all the four transitions. At 385K M shows a slight increase which suggests an increase in the interproton distance in this compound. Around 349K, 249K and 200K, M data show stepwise increase as we go down the temperature from 385K and the values of the different plateaus suggest that there are three dynamically inequivalent methylammonium cations. It appears that the isotropic reorientation of each of one of them gets frozen by NMR line width time scales at 349K, 249K and 200K, respectively and the reorientation of these ions about their 3-fold C-N axis finally becomes dominant. The magnetization recovery in this compound shows marked non-exponential behaviour and is therefore fitted to a two exponential model and the corresponding relaxation times are calculated (T₁ and T₂).  

T₁ data show discontinuities at the respective transition temperatures and below 150K the non-exponentiality of the magnetization recovery disappears. T values seem to decrease monotonically with decreasing temperature below 150K, and the activation energy estimated from this portion suggests that the methylammonium cations may be undergoing uncorrelated C reorientations about their C-N axis.

(NH₄)₃Bi₂Cl₉ and (NH₄)BiBr are two of the ammonium substituted compounds of this family which provide interesting contrast with the other compounds as there are no internal dynamics possible with these cations. M measurements on (NH₄)₃Bi₂Cl₉ show that the cations are undergoing rather fast reorientations and T data show a maximum like structure. Interestingly, above 250K T values at 8 MHz are smaller than those at 5 MHz. Analysis of the data shows that such a non-BPP type
behaviour may be caused by the cross relaxation of the protons through the quadrupolar levels of Cl nucleus in this compound. (NH.)\textsubscript{3} Bi\textsubscript{4} Br shows an entirely different picture where T data show the formation of an usually expected minimum due to the isotropic reorientation of the NH cations, and at 250K a structural phase transition is observed as a slope change in the T data. The activation energy above this temperature is found to be about 7 kJ/mole, whereas below this temperature it is close to 18 kJ/mole, thereby showing the increased amount of hindrance to the cation dynamics. These discussions form sub-section (C-5).

It has been observed that Bismuth has a tendency to cluster with other atoms or halogens to form large clusters leading to compounds with novel anions having reasonable amount of free space for the cations to undergo reorientations. One such system is \([(C\textsubscript{8}H\textsubscript{14})\textsubscript{5}N] \text{Bi}_2\text{Cl}_{30}\) having the anion Bi Cl\textsubscript{30}, and this provides an interesting contrast to all the others discussed above. Sub-section (C-6) describes the results of T and M\textsubscript{2} measurements on this compound and includes a discussion on suitable theoretical model taking into account the dynamics of the tetraethylammonium cation. A phase transition is reported at 241 K and near this temperature both T and M\textsubscript{2} data show its signature. Analysis of T data shows the presence of a wide distribution of correlation times of the methyl group reorientations, and the analysis of T data in the observed range of temperature shows the presence of at least four dynamically inequivalent methyl groups.

Sub-section (C-7) provides a comprehensive survey of the results we have obtained from these investigations on tris(alkylammonium) halogeno bismuthates, and also a comparison with those of the Antimony substituted compounds of this family. The discussion brings out the role of Bismuth
in causing an increased amount of structural inequivalence (structural disorder) in these compounds as reflected by the presence of increased amount of inequivalence among the different groups, in comparison with the Antimony substituted compounds. A comparison of dynamic parameters above and below the phase transitions in the tetramethy lammonium substituted compounds shows that at their respective transition temperatures the correlation times of these motions reach, rather curiously, a particular value. Conclusions based on the present investigations on these compounds are summarized as the last part of this section.

Appendix - I of the thesis provides the listing of some of the assembly level programmes which are used for generation of different pulse sequences using the microprocessor based pulse programmer. Appendix - II gives programmes specific to the present work which are developed to automate the spectrometer in the GPIB and RS-232-C environment. Finally, Appendix - III provides the list of programmes which are developed in different programming languages (BASICA and ASYST) for analysis and display of data and graphics and a sample listing of some of the important programmes.