

Molecular Dynamics in Tetramethyl Ammonium Hexabromo Selenate $[\text{N}(\text{CH}_3)_4]_2\text{SeBr}_6$. A Proton NMR Study

B. V. S. Murthy, K. P. Ramesh, and J. Ramakrishna

Department of Physics, Indian Institute of Science, Bangalore 560 012, India

Z. Naturforsch. **48a**, 868–870 (1993); received February 22, 1993

^1H spin-lattice relaxation time T_1 and second moment M_2 have been studied as a function of temperature over the temperature range 445 to 77 K. A discontinuous change in T_1 at 365 K, indicates the presence of a phase transition, while the slope change at 152 K, is attributed to a change in the TMA ion dynamics from tumbling to torsion. The T_1 results could be explained in terms of inequivalent TMA ions and their small angle torsional oscillations. A second moment (M_2) transition occurs around 160 K and is ascribed to the freezing of TMA tumbling and CH_3 reorientation.

Key words: Molecular dynamics; Second moment; NMR; Spin-lattice relaxation time.

Introduction

Tetramethyl ammonium (TMA) ion dynamics in salts has been investigated, using ^1H NMR, by many workers [1–3]. Generally, the activation energy for the motion of the cation was found to be smaller in $(\text{TMA})\text{MX}_3$, $(\text{TMA})_2\text{MX}_4$ and $(\text{TMA})_2\text{MX}_6$ type complexes than in simple salts. In $(\text{TMA})_2\text{MCl}_6$ ($\text{M} = \text{Pt}, \text{Sn}, \text{Te}, \text{Zr}, \text{U}$) phase transitions have been found around 350 K and 150 K [4, 5–7, 8–10]. We have now investigated ^1H NMR in $(\text{TMA})_2\text{SeBr}_6$ and report on the results here.

The compound was prepared following the procedure of Gütber and Engeroff [11] and was checked by x-ray diffraction [8–10], melting temperature, specific gravity [12], IR frequencies [13] and elemental analysis. The proton T_1 measurements were carried out using a home built pulsed NMR spectrometer working at 10 MHz. The second moments were calculated from the Fourier transformed FID signals. The temperature of the sample was varied using a gas flow cryostat.

Results and Discussion

Tetramethyl ammonium ion, being tetrahedral, has 3 two-fold and 4 three-fold symmetry axes. The dom-

inant motions are the tumbling of the TMA ion and the three-fold reorientation of the methyl groups. In the model used to explain the ^1H spin-lattice relaxation [1], the intra-methyl and inter-methyl dipole-dipole interactions are considered to be modulated by these motions.

(i) Relaxation

The temperature variation of the relaxation time (T_1) measured from 445 to 77 K is shown in Figure 1. T_1 decreases from 425 K down to 365 K, where a small discontinuous decrease is observed. Above 425 K the relaxation time starts decreasing rapidly due to melting. In the temperature range 365 K to 152 K, T_1 exhibits a BPP behaviour and shows a minimum of 5.4 msec at 193 K. A small change in the slope of the T_1 plot is observed at 152 K. Between 130 K and 77 K, T_1 follows a BPP behaviour showing a low temperature minimum of 6.3 msec at 97 K.

The small discontinuous decrease of T_1 at 365 K indicates a phase transition. The activation energies above and below 365 K are found to be the same (13.8 kJ/mole). Similar phase transitions observed in $(\text{TMA})_2\text{MBr}_6$ ($\text{M} = \text{Pt}, \text{Te}, \text{Sn}$) at slightly higher temperatures (~ 400 K) have been identified as the $\text{Fd}3\text{c}$ to $\text{Fm}3\text{m}$ transitions [3]. The observed T_1 minimum of 5.4 msec at 193 K is much shorter than the expected T_1 value of 9.8 msec (10 MHz) for TMA tumbling. The observed T_1 behaviour could be explained by assuming an equal number of two inequivalent TMA ions (Type a and b) and equivalent methyl groups [14]. The

Reprint requests to Prof. J. Ramakrishna, Department of Physics, Indian Institute of Science, Bangalore 560 012, India.

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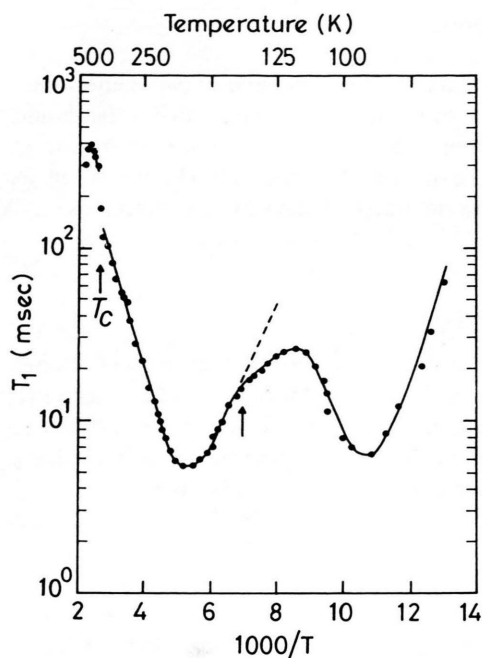


Fig. 1. Plot of relaxation time (T_1) vs. $1000/T$ in tetramethyl ammonium hexabromo selenate.

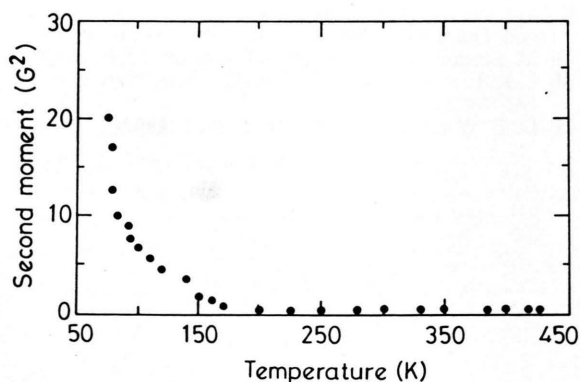


Fig. 2. Temperature variation of second moment in tetramethyl ammonium hexabromo selenate.

activation energies and the pre-exponential factors for the tumbling motion of the a and b type TMA ions are 13.8 and 12.6 kJ/mole with 1.5×10^{-12} and 7.8×10^{-12} sec, respectively. These activation energies are much smaller than the corresponding values in simple compounds like TMA halides [1], indicating a large freedom for the TMA ions in the present compounds. The slope change observed at 152 K is ascribed to changes in TMA dynamics from tumbling to small angle tor-

Table 1. Activation energies and phase transition temperatures (T_c) in tetramethyl ammonium hexabromo metallates.

$(TMA)_2MBr_6$	Activation energy (kJ/mole)	Motional mode	Phase transition temperatures T_c (K)	Ref.
PtBr ₆	18.4	CH ₃ reorientation	367, 123, 97	[3]
	18.7	Over all tumbling		
	8.5	Small angle CH ₃ torsion		
TeBr ₆	17.8	CH ₃ reorientation	362, 84	[3]
	19.2	Over all tumbling		
	7.7	Small angle CH ₃ torsion		
SnBr ₆	15.4	CH ₃ reorientation	371, 90	[3]
	23.2	Over all tumbling		
	9.4	Small angle CH ₃ torsion		
SeBr ₆	11.3	CH ₃ reorientation	365	present work
	13.8(a)	Over all tumbling of a ion		
	12.6(b)	Over all tumbling of b ion		
	3.8	Small angle TMA torsion		

sional oscillation (as the slope change occurs at a higher temperature than the methyl T_1 minimum, it can not be due to small angle torsion of the methyl groups). Following Woessner [15] the amplitude of the torsional oscillations (θ), the correlation time τ_0 and the activation energy are obtained as 12° , 1.2×10^{-12} sec and 3.8 kJ/mole, respectively. The second minimum of 6.3 msec, observed at 92.5 K, is ascribed to TMA torsional oscillations and C_3 reorientation of the methyl groups with corresponding activation energy and pre-exponential factor of 11.3 kJ/mole and 5.5×10^{-15} sec, respectively. A comparison of motional parameters and phase transition temperatures T_c with other members of the $(TMA)_2MBr_6$ group is given in Table 1.

(ii) Second Moment

The temperature variation of the second moment in $(TMA)_2SeBr_6$ is shown in Figure 2. The second moment remains nearly constant at a value of 0.45 G^2 from 430 K to 160 K. Below 160 K it steadily increases and reaches 23 G^2 at 77 K. The small second moment of 0.45 G^2 observed above 160 K can be explained in terms of TMA and CH_3 reorientations.

Since only a single step M_2 transition is observed, it appears that TMA and the CH_3 reorientations become effective in line narrowing around the same temperature. This is reasonable in view of the comparable activation energies for the two types of motions as seen from the T_1 data. Below this temperature, the slowing down of the TMA and CH_3 motions gives rise to a steady increase of the second moment.

Similar M_2 behaviour (0.6 G^2 above 150 K, and 24 G^2 around 77 K) has been observed in $(\text{TMA})_2\text{MX}_6$ ($\text{M} = \text{Pt}, \text{Te}, \text{Sn}$; $\text{X} = \text{Cl}, \text{Br}$) by Prabhumirashi *et al.* [2], and by Sato *et al.* [3]. They have also explained the M_2 behaviour (above 160 K) in terms of the isotropic reorientation of the cation and the CH_3 groups while that around 77 K as due to the freezing of the TMA and methyl groups.

Conclusions

The T_1 data show the presence of two inequivalent tumbling TMA ions, TMA small angle torsion and methyl group reorientation. The phase transition at 365 K, appears to be the $\text{Fd}3\text{c}$ to $\text{Fm}3\text{m}$ transition, as reported in the other $(\text{TMA})_2\text{MX}_6$ compounds.

Acknowledgements

The financial support from Department of Atomic energy, Government of India is gratefully acknowledged. One of the authors (B.V.S.M.) would like to thank S. J. College of Engineering, Mysore for leave of absence under the QIP Programme.

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