# Study of molecular reorientation and quantum rotational tunneling in tetramethylammonium selenate by $^1$H NMR ☆

K.J. Mallikarjunaiah[a], K.C. Paramita[b], K.P. Ramesh[b], R. Damle[a],*

[a]Department of Physics, Bangalore University, Bangalore 560 056, India
[b]Department of Physics, Indian Institute of Science, Bangalore 560 012, India

## Abstract

$^1$H NMR spin–lattice relaxation time measurements have been carried out in $[(CH_3)_4N]_2SeO_4$ in the temperature range 389–6.6 K to understand the possible phase transitions, internal motions and quantum rotational tunneling. A broad $T_1$ minimum observed around 280 K is attributed to the simultaneous motions of $CH_3$ and $(CH_3)_4N$ groups. Magnetization recovery is found to be stretched exponential below 72 K with varying stretched exponent. Low-temperature $T_1$ behavior is interpreted in terms of methyl groups undergoing quantum rotational tunneling.
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## 1. Introduction

$A_2BX_4$ compounds are generally interesting to study, as they exhibit incommensurate–commensurate phase transitions, ferroelectric properties and complex reorientational dynamics [1]. Successive replacement of hydrogen by $CH_3$ groups in ammonium ion according to the formula $(CH_3)_xNH_{4-x}$ ($x = 1, \ldots, 4$), leads to a cation with a larger ionic radius, which may result in strong phase transitions due to changes in symmetry as well as the tolerance factor [2]. Substitution of the $CH_3$ leads to additional symmetry elements and hence increased reorientation motions [3]. Tetramethylammonium (TMA) metal salts are known to exhibit phase transitions, hindered reorientational motion of the symmetry groups like $CH_3$ as well as whole cation $(CH_3)_4N$ and quantum rotational tunneling of the $CH_3$ groups. Moreover, TMA salts are of general interest in preparative chemistry. Their enhanced solubility in aprotic solvents in comparison to the corresponding alkali metal salts as well as their increased

reactivity, which is due to a lower degree of solvation of their anions in solutions of non-polar solvents, make them powerful and versatile synthetic reagents [4]. Among them, tetramethylammonium selenate (TMA-Selenate) is particularly interesting to study, not only for its interesting molecular reorientational dynamics but also for its use in preparative chemistry [4].

Sato et al. [5] have claimed that they have prepared the title compound TMA-Selenate and reported it as a tetragonal lattice system with $a = 13.95\,\text{Å}$ and $c = 12.90\,\text{Å}$ from the powdered XRD pattern. They have also observed three heat anomalies at 127, 279 and 290 K through DTA. Malchus and Jansen [4] also have synthesized the same compound by adopting a different preparation method and carried out the temperature-dependent single-crystal XRD measurements and they found a disagreement with that of Sato et al. According to the XRD analysis of Malchus and Jansen, the compound crystallizes in cubic lattice (Fm3m) with $a = 11.12\,\text{Å}$ and the complex ions are packed in an $Li_2O_2$-type arrangement. Further, in contrast to Sato et al., they have not reported any phase change in the temperature range 130–300 K. IR and Raman studies by the same authors [4] have proved that the $N(CH_3)_4^+$ tetrahedron is regular and in a fixed orientation, while the selenate ion,

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☆ $^1$H NMR study in TMA-Selenate.
*Corresponding author. Fax: +91 080 2321 1012.
E-mail address: damleraju@yahoo.com (R. Damle).

however, is orientationally disordered. Malchus and Jansen have carried out powder XRD study after exposing their compound to moisture and found that it compares well with the powdered XRD pattern reported by Sato et al. Hence they have concluded that Sato et al. might have studied the sample which was exposed to atmosphere and hence it might be the hydrate of TMA-Selenate and not the $[(CH_3)_4N]_2SeO_4$ [4]. Thus, these studies led to a controversy regarding the structure of this compound [4,5]. In the present study, we have made an attempt to resolve this.

## 2. Experimental

TMA-Selenate is synthesized by mixing TMA hydroxide (Aldrich, 33,163-5) and selenic acid (Aldrich, 30,843-9) in stoichiometric proportions [5]. Cylindrical crystals formed upon slow evaporation of the solvent, over a few months, are dried under vacuum before using them for further studies because of their hygroscopic nature. The powder XRD measurements are carried out at room temperature using the Panalytical diffractometer and our XRD pattern compares well with that of Malchus and Jansen [4]. The compound is finely powdered and vacuum-sealed into glass ampoules of 5 mm diameter in helium atmosphere for NMR studies.

^{1}H NMR spin–lattice relaxation time ($T_1$) measurements are carried out, as a function of temperature in the range 389–6.6 K, at 21.34 MHz using a home-made pulsed NMR spectrometer described earlier [6]. Inversion recovery pulse sequence is used for the measurement of $T_1$. The $T_1$ measurements in the high-temperature region (300–389 K)

are made using modified high-temperature set up. The temperature of the sample is varied from 300 to 6.6 K with the help of a continuous gas flow helium cryostat (CF200 Oxford Instruments Cryosystem) and controlled to an accuracy of $\pm 0.5$ K with the aid of ITC-503 (Oxford Instruments Intelligent Temperature Controller). Temperature at the sample is measured using a Pt 100 sensor for temperatures down to about 75 K and below which a germanium sensor is used.

## 3. Results and discusssion

A plot of $T_1$ versus $1000/T$ is shown in Fig. 1. Initially $T_1$ decreases with decrease in temperature from 389 K giving rise to a broad minimum of about 9 ms centered around 280 K. On further decrease in temperature, $T_1$ increases with a decrease in signal intensity and hence we could make measurements only up to 170 K and the signal vanishes completely around 150 K. On cooling the sample much below 150 K, the signal reappears at about 85 K and the signal intensity builds up enabling $T_1$ measurements from 72 down to 6.6 K, which is the lowest temperature of measurement in the present study.

### 3.1. High-temperature region (389–170 K)

Sato et al. [5] have made $T_1$ measurements at 20 MHz in the temperature range 400–200 K. They have observed two minima: a shallow one (19 ms around 400 K) and a deep one (11 ms around 280 K), which are attributed to TMA and $CH_3$ group reorientations, respectively. A theoretical
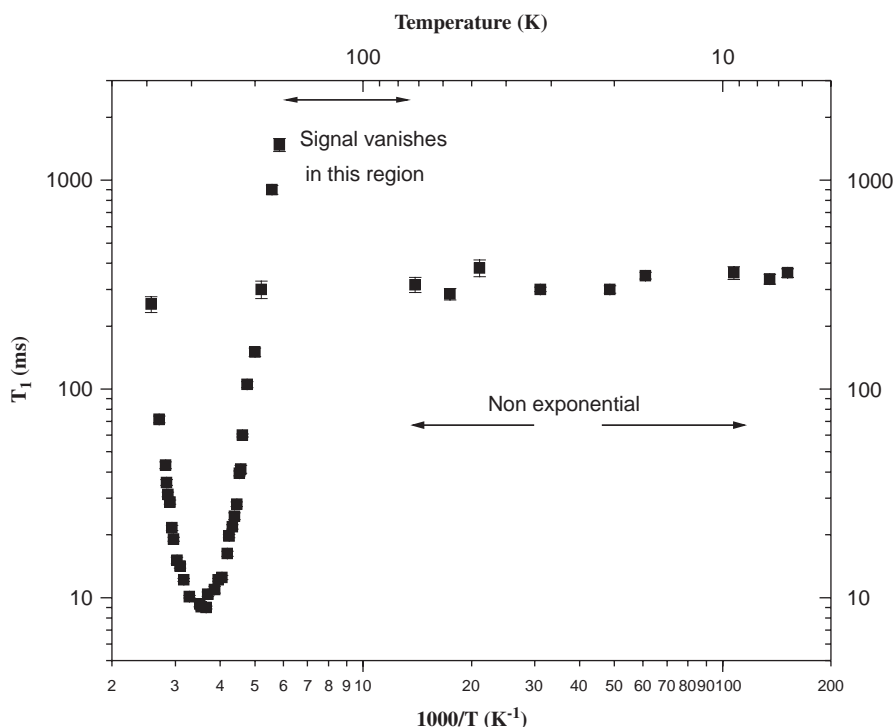


Fig. 1. Variation of $T_1$ as a function of inverse temperature at 21.34 MHz for $(TMA)_2SeO_4$ over the entire temperature region.

fit of $T_1$ was extrapolated above 400 K to emphasize the shallow minimum. On the contrary, our measurements [7] reveal only one broad minimum of about 9 ms around 280 K and on high-temperature side of the minimum, $T_1$ increases monotonically up to 250 ms at 389 K. The high-temperature (389–170 K) $T_1$ data can be explained using BPP model modified for the TMA group by Albert et al. [8].

### 3.1.1. Theory

The $T_1$ behavior in TMA compounds can be explained using a modified Bloembergen–Purcell–Pound [9] approach, as given by Albert et al. Albert et al. have studied the $^1H$ $T_1$ in several TMA halides and the experimental results have been analyzed by considering the TMA ion and methyl group reorientations about their $C_3$ axes. In TMA compounds, the two motions that mainly contribute to the relaxation are: (a) random reorientation of the $CH_3$ groups with correlation time $\tau_c$ and (b) isotropic tumbling of the TMA ion (whole cation) with a correlation time $\tau_{c1}$. They modulate the intra-methyl and inter-methyl dipole–dipole interactions and facilitate the spin–lattice relaxation.

Albert et al. have assumed that the observed $T_1$ data could be described by two superimposed BPP curves and the effective relaxation rate is the sum of the relaxation rates due to the intra-methyl and inter-methyl contributions and hence can be written as

$$T_1^{-1} = Af(\tau_{c2}) + Bf(\tau_{c1}), \tag{1a}$$

where

$$\tau_{c2}^{-1} = \tau_c^{-1} + \tau_{c1}^{-1}, \tag{1b}$$

$$A = \frac{9}{20}\frac{\gamma^4\hbar^2}{r^6} \tag{1c}$$

and

$$B = \frac{3}{20}\frac{\gamma^4\hbar^2}{r^6} + \frac{27}{10}\frac{\gamma^4\hbar^2}{R^6}. \tag{1d}$$

The notations used in Eqs. (1b)–(1d) have their usual meaning as in Albert et al. [8] and the function $f(\tau)$ is given by

$$f(\tau) = \tau(1 + \omega^2\tau^2)^{-1} + 4\tau(1 + 4\omega^2\tau^2)^{-1}, \tag{2}$$

where '$\tau$' represents a correlation time of the motion and is assumed to obey the Arrhenius equation given by

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right), \tag{3}$$

where $\tau_0$ and $E_a$ are called pre-exponential factor and activation energy of the corresponding motion, respectively.

The $T_1$ results of the fit are shown Fig. 2. The best-fit parameters for $CH_3$ and TMA cation motions are given in Table 1.

The observed activation energies for both $CH_3$ and $(CH_3)_4$ ions obtained from the present study are, respec-
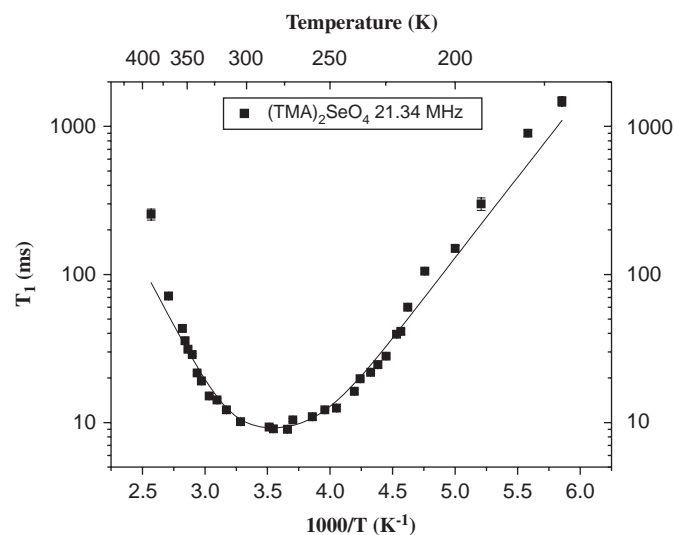


Fig. 2. Theoretical fit of $T_1$ to Eq. (1a) in the temperature region 389–170 K.

Table 1
Motional parameters for TMA-Selenate in the temperature region (389–170 K)

| Symmetric group | Activation energy (kJ/mol) | Pre-exponential factor ($10^{-14}$ s) |
|---|---|---|
| Methyl | 20.4 (0.1) | 0.9 (0.1) |
| TMA | 33.5 (0.5) | 53 (5) |

The values given in parentheses represent the errors.

tively, lesser than that of Sato et al. [5] for the same compound (27 and 41 kJ/mol) as well as in $[(CH_3)_4N]_2SO_4$ (28 and 45 kJ/mol) and $(CH_3)_4NX$ ($X$ = Cl, Br and I) (23–28 and 37–54 kJ/mol) [8]. However, they are in good agreement with the values reported in the compound $TMAClO_4$ (21.2 and 32.9 kJ/mol) [10]. The $CH_3$ group activation energy is slightly greater than 15–17 kJ/mol and the $(CH_3)_4$ group activation energy compares well with the reported value of 30–37 kJ/mol, determined for the room temperature phase of $[(CH_3)_4N]_2MX_4$ (M = Pb and Pt; X = Cl and Br) [11]. This shows an increased volume for reorientation of the groups as compared to pure salts. On comparing the activation energies of the $CH_3$ and $(CH_3)_4N$ groups in $[(CH_3)_4N]_2SeO_4$ with that of $[(CH_3)_4N]_2SO_4$, it must be noticed that the activation energy of the methyl group is less in $[(CH_3)_4N]_2SeO_4$ because of larger radius of the selenium atom and its increased cell volume [5].

The observed asymmetric broad $T_1$ minimum of 9 ms at 21.34 MHz in our study is neither in agreement with that of expected minimum of 11.74 ms for $CH_3$ group nor of 20.27 ms for $N(CH_3)_4$ group [8]. Similar broad minimum has been observed in $TMAClO_4$ also [10]. The occurrence of this broad minimum could be due to the fact that the reorientation rates of both methyl and TMA ions are of the same order. As discussed earlier, our powder XRD data do not agree with that of Sato et al., but agree quite well with

those reported by Malchus and Jansen, which confirms the crystal structure as cubic. Further, it is also worth noting that the lower activation energies obtained from the present study, with respect to Sato et al., also suggest that the symmetric groups are less hindered in the TMA-Selenate, as expected for a cubic system compared to a tetragonal system. Therefore, both our NMR and powder XRD results support the argument of Malchus and Jansen. Hence, we can conclude that the compound used in the present study is in the cubic space group in agreement with that of Malchus and Jansen [4] and not the hydrated TMA-Selenate as reported by Sato et al. [5].

The increase of $T_1$ on the low-temperature side of the $T_1$ minimum and a decrease of signal intensity beyond measurements and subsequent disappearance of the signal indicates that the compound reaches rigid lattice limit.

### 3.2. Low-temperature region (72–6.6 K)

On cooling the sample much below 150 K, the signal reappears at about 85 K and the signal intensity builds up enabling $T_1$ measurements from 72 to 6.6 K. The $T_1$ shows almost temperature-independent behavior in the temperature region 72–6.6 K and the magnetization recovery is found to be stretched exponential. Further, the exponent factor is found to vary with temperature. Value of the exponent factor is about 0.5 when the signal reappears and it remains the same within experimental errors till about 30 K. Below 30 K, the stretched exponent value increases monotonically and reaches unity as the temperature approaches 6.6 K.

The effects of rotational tunneling of $CH_3$ and $NH_4$ groups on proton spin–lattice relaxation have been discussed by several authors [12–18] to explain the non-exponential magnetization recovery and multiple $T_1$ minima at low temperatures.

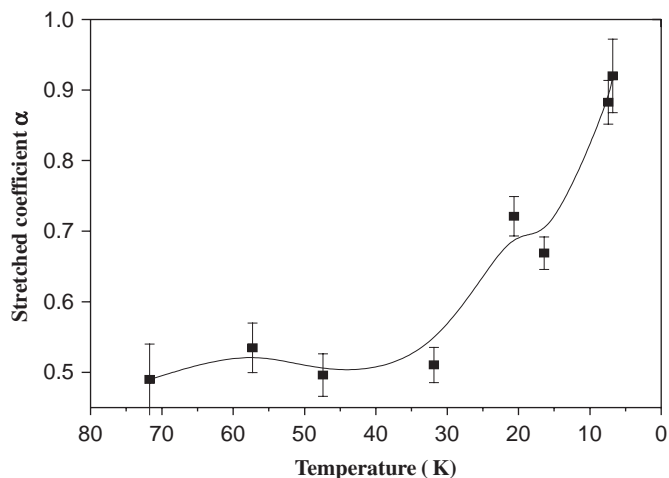The variation of the stretched exponent (Fig. 3) can be explained in the following way: in certain systems, the presence of inequivalent $CH_3$ groups may lead to different spin temperatures and each set of spins relaxing with its own relaxation time constant. Hence the bulk magnetization recovery follows a stretched exponential behavior. This is true when inequivalent $CH_3$ groups are present and if the spin diffusion becomes weaker in a certain range of temperatures. However, when the temperature is lowered, the stretched exponent approaches unity, suggesting that the methyl groups start attaining a common spin temperature. On further cooling the sample, the bulk magnetization recovery becomes single exponential.

In the present case, $T_1$ shows almost temperature-independent behavior and we have tried to fit our $T_1$ results using the model proposed by Köksal et al. [19] who also have observed similar behavior in certain metal acetates. According to the model proposed by them, $T_1$ shows temperature-independent behavior when only ground state of the tunnel splitting levels is occupied.

#### 3.2.1. Theory

Köksal et al. have studied a number of metal acetates by ^{1}H NMR $T_1$ measurements and explained their experimental results by considering temperature dependence of tunnel splitting. At low temperatures, it is assumed that only the torsional ground state ($n = 0$) of the methyl group is occupied. The relaxation occurs when spin-flips are connected with the tunnel splittings. When the tunneling frequency is larger than the Larmor frequency, one can write the expression for the relaxation rate by considering only the intra-methyl interaction and temperature dependence of the tunnel frequency, as

$$\frac{1}{T_{AE}} = C_{AE} \sum_{m=-2}^{2} \frac{m^2 \tau_{c0}^T}{1 + \langle \varpi_T^0 \rangle^2 (\tau_{c0}^T)^2}, \tag{4a}$$



Fig. 3. Variation of stretched exponent factor (α) with temperature. (The line drawn is a guide to eye.)
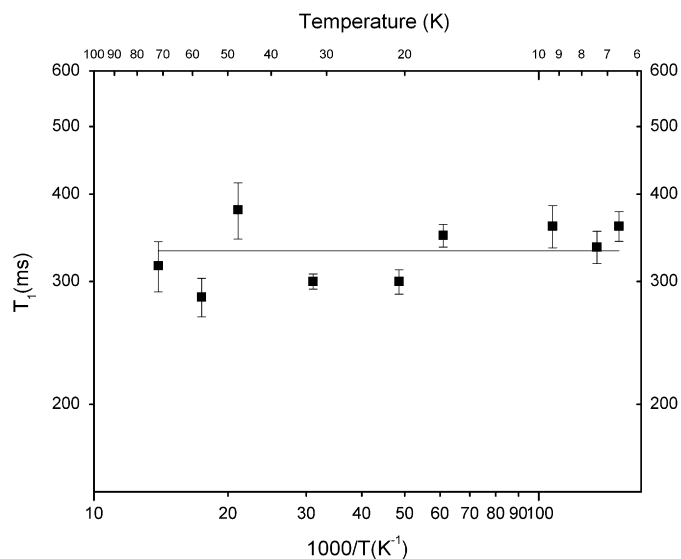


Fig. 4. Low-temperature (72–6.6 K) data fit to Eq. (4a). The solid line represents the fit to Eq. (4a).

Table 2
Motional parameters evaluated (72–6.6 K) using the Köksal model

| Parameters | Estimated values |
| --- | --- |
| $\tau_{c0}^{T}$ | $5.26 \times 10^{-11}\,\mathrm{s}$ |
| $C_{AE}$ | $6.25 \times 10^{9}\,\mathrm{s}^{-2}$ |
| $\varpi_{T}^{0}$ | $5.70 \times 10^{9}\,\mathrm{s}^{-1}$ |

where $\varpi_{T}^{0}$ is the tunnel frequency in the ground state and

$$C_{AE} = \frac{9}{20}\frac{\gamma^4 \hbar^2}{r^6}d_0^2. \tag{4b}$$

The notations used in Eqs. (4a) and (4b) have their usual meaning as in Köksal et al. [19].

We have tried to fit the $T_1$ data between 72 and 6.6 K to the model used by Köksal et al. as shown in Fig. 4. The motional parameters obtained are given in Table 2 which are comparable with those reported earlier [19,20].

Though the magnetization follows stretched exponential in this temperature region, the observed correlation time can be considered as the effective correlation time of the all spin systems.

### Acknowledgment

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