Proton magnetic relaxation in $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$

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Abstract. Internal motions of the protonic groups have been studied in polycrystalline $[(CH_3)_4N]_2HgBr_4$ and $[(CH_3)_4N]_2HgI_4$ from the temperature dependence of proton spin relaxation time (T_1) and the data analysed according to the spin lattice relaxation model due to Albert and coworkers. The temperature dependence of T_1 in the above compounds is compared with that in $(TMA)_2HgCl_4$ and $(TMA)_2ZnCl_4$.

1. Introduction

Interesting motional effects due to the methyl group and tetramethylammonium (TMA) ion reorientations studied by magnetic relaxation have been reported in several TMA halides (Dufourcq and Lemanceau 1970; Albert *et al* 1972; Gibson and Raab 1972; Polack and Sheinblatt 1973; Tsuneyoshi *et al* 1977; Koksal 1979). The substitution of Cd by Hg in TMA $CdCl_3$ and of Cl by Br and I in $TMAHgCl_3$ was found to have profound influence on the internal motions of the TMA ion and the methyl group (Sarma and Ramakrishna 1984a). $(TMA)_2ZnCl_4$ which belongs to the A_2BX_4 type of compounds is reported to be ferro-electric (Sawada *et al* 1978). Magnetic resonance and relaxation study (Blinc *et al* 1979) in $(TMA)_2ZnCl_4$ revealed reorientational motion of the methyl group and the TMA ion, even at 120 K. Niemela and Heinila (1981) inferred from the temperature dependence of the proton spin lattice relaxation time (T_1) in $(TMA)_2ZnCl_4$ that there are two inequivalent TMA ions in this compound. The motional effects in $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ investigated by proton magnetic relaxation technique are reported in this paper and the results are compared with the motional effects in $(TMA)_2HgCl_4$ reported earlier (Sarma and Ramakrishna 1984b).

2. Experimental

$(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ were prepared and characterized following the methods reported by Hooper and James (1971). The polycrystalline samples were ground to fine powder, packed and sealed under vacuum in Corning glass tubes (10 mm diameter and about 12 mm length) so that the sample is confined to the RF coil in the spectrometer probe. The samples were recrystallized (3 to 4 times) till the T_1 values did

not change any more on further recrystallization. Proton spin lattice relaxation times in the laboratory frame were measured using a laboratory-made pulse spectrometer operating at 10 MHz (Shenoy *et al* 1980). T_1 values, shorter than 500 msec, were measured by inversion recovery method using a π-t-$\pi/2$ pulse sequence and longer relaxation times were measured using a saturation burst sequence of $n\pi/2$-t-$\pi/2$ pulses. The FID signals have been measured using a box-car integrator (Shenoy *et al* 1979) with digital read-out and a single exponential decay in the temperature range of the experiments. The temperature of the sample could be varied over the range 77 to 500 K using a laboratory-made variable temperature assembly consisting of a gas-flow cryostat and a heater (Shenoy 1979). The temperature stability of the arrangement is better than $\pm$ 1 K. The observations were reproducible during the cooling and heating cycles, as well as when the sample was subjected to slow and rapid cooling.

3. Results and discussion

The temperature dependence of T_1 observed in $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ is presented in figure 1. The observed variation in T_1 with temperature is due to the motion of the protonic groups against the hindering potential barriers. These hindered motions are random functions of time and modulate the inter-proton dipolar interactions, which give rise to fluctuating magnetic field at a nucleus (proton), leading to the spin lattice relaxation (SLR). The SLR model proposed by Albert *et al* (1972) explains the occurrence of two T_1 minima in the T_1 versus $10^3/T$ curves of TMA halides. A shallow $T_{1\,\mathrm{min}}$ occurring in the high temperature region is generally ascribed to the isotropic reorientations of the bulky TMA ion, while a deeper one occurring at a lower temperature is attributed to the random reorientations of the methyl groups about the C–N axes. Taking the correlation times of these motions as τ_1 and τ_2 respectively, the proton spin lattice relaxation rate

$$T_1^{-1} = Ag(\tau_{12}) + Bg(\tau_1),\tag{1}$$

where $\tau_{12}^{-1} = \tau_1^{-1} + \tau_2^{-1}$,

and $g(\tau) = [\tau/(1 + \omega^2\tau^2)] + [4\tau/(1 + 4\omega^2\tau^2)],$

ω being the RF angular frequency. The values of A and B are $8\cdot05 \times 10^9$ sec^{-2} and $4\cdot61 \times 10^9$ sec^{-2} respectively. When there are equal number of two inequivalent ions (O'Reilly and Tsang 1967) then

$$2T_{1\,\mathrm{observed}}^{-1} = T_{1,\mathrm{I}}^{-1} + T_{1,\mathrm{II}}^{-1},\tag{2}$$

where $T_{1,\mathrm{I}}$ and $T_{1,\mathrm{II}}$ are the SLR times of type-I and type-II ions. The internal motions being thermally activated and random, the correlation time τ can be expected to follow the Arrhenius type relation

$$\tau = \tau_0 \exp(E_a/kT),\tag{3}$$

where E_a is the activation energy required to overcome the potential barrier hindering the motion, k the Boltzmann constant, T the temperature and τ_0 a constant representing the reciprocal of the jump frequency for the internal motion. It is well known that the
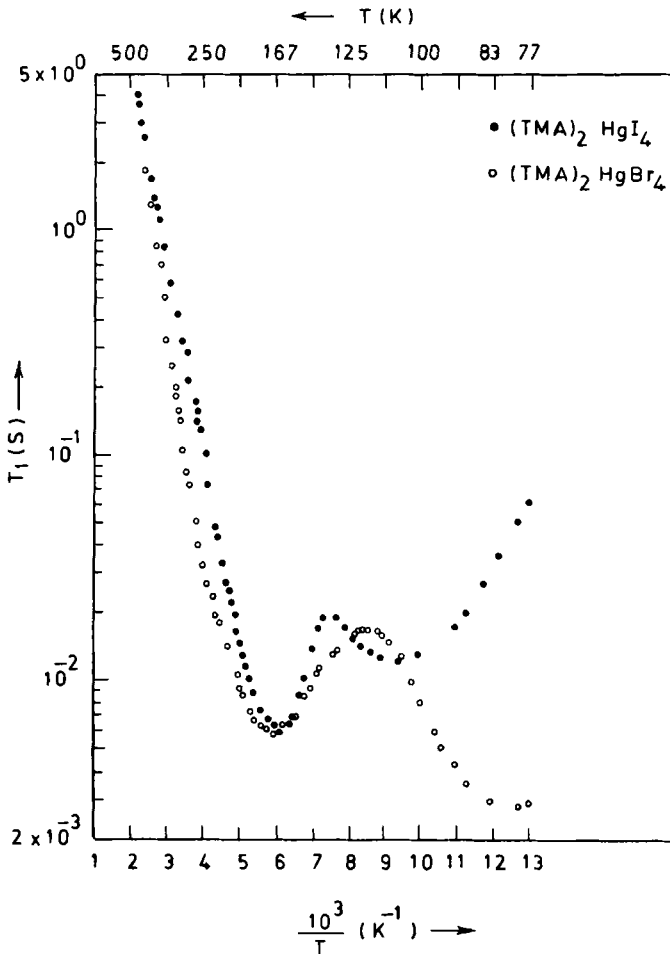
Figure 1. Temperature dependence of T_1 in $(TMA)_2$ $HgBr_4$ and $(TMA)_2$ HgI_4.

maximum value of $g(\tau)$, hence T_{1min} occurs when $\omega\tau = 0.62$. Since we expect that $\tau_{12} < \tau_2 < \tau_1$, a T_{1min} occurs near $\omega\tau_{12} = 0.62$ on the low temperature side and another near $\omega\tau_1 = 0.62$ on the high temperature side. The T_1 vs $10^3/T$ curve for $(TMA)_2HgBr_4$ has two distinct T_1 minima, one at 166·7 K of 5·85 msec, and the other at 80 K of 2·9 msec. The value of T_{1min} at 166·7 K which is close to the value expected at 10 MHz due to the random reorientations of the methyl group from the SLR model due to Albert *et al* (1972) tempts one to attribute this T_{1min} to the random reorientations of the methyl groups. However, a representative value of the activation energy E_a of the mobile group leading to the T_{1min} can be estimated from the linear portion of the T_1 versus $10^3/T$ curve in the high temperature region. A least-squares fit of the experimental data to the expected theoretical shape using (1) and (3) leads to a more accurate value of E_a. Details of the computations carried out on DEC-1090 computer have been described elsewhere (Sarma 1982). The value of 5·2 kcal/mol so obtained for E_a is close to the value of E_a corresponding to the tumbling motion of the TMA ion in TMAHgBr$_3$ (Sarma and Ramakrishna 1984a). Hence it might be inferred that the

isotropic reorientations of the TMA ion slow down as we approach 166·7 K from high temperatures, and the SLR at 166·7 K has contribution from the reorientational motion of the TMA ion and the methyl group as well. The relative contributions to the relaxation rate from the TMA ion and the methyl group motions at $T_{1\,min}$ has been found from the theoretical analysis of the experimental data using (1) and (3) (Sarma 1982). The relative contributions to the relaxation rate so found at $T_{1\,min}$ of 5·85 msec, in $(TMA)_2HgBr_4$ .from TMA ion and methyl group are 104 and 51·4 respectively. The T_1 versus $10^3/T$ curve for $(TMA)_2HgI_4$ also has two distinct T_1 minima, one at 163·9 K of 5·9 msec, and another at 105·3 K of 12 msec. In this compound also the value of $T_{1\,min}$ at 163·9 K, might appear to be due to the random reorientations of the methyl group. But the value of 4·1 kcal/mol for E_a computed as explained earlier is close to that due to the reorientations of the TMA ion in $(TMA)HgI_3$ (Sarma and Ramakrishna 1984a). The relative contributions to the relaxation rate from TMA ion and the methyl group motions at $T_{1\,min}$ of 5·9 msec, in $(TMA)_2HgI_4$ were 104 and 6·4 respectively from the theoretical analysis of the experimental data using (1) and (3) (Sarma 1982). Hence it might be inferred that the $T_{1\,min}$ at 163·9 K in $(TMA)_2HgI_4$ also has contributions from the motion of the TMA ion and the methyl group and the motion of the TMA ion slows down as we approach 163·9 K from higher temperatures.

Although the crystal structure of $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ is reported (Kamenar and Nagl 1976) to be orthorhombic at room temperature as for $(TMA)_2ZnCl_4$ (Wiesner *et al* 1967), the latter compound undergoes five successive phase transitions (Sawada *et al* 1978). The T_1 minima observed in $(TMA)_2ZnCl_4$ were ascribed (Niemela and Heinila 1981) to arise from two inequivalent TMA ions. The T_1 is expected to pass through two minima of equal value (O'Reilly and Tsang 1967) for $(NH_4)_2SO_4$, in case the two T_1 minima observed were due to the presence of two inequivalent TMA ions. Further the values of $T_{1\,min}$ observed in $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ differ too much from the value of $T_{1\,min}$ expected at 10 MHz due to the presence of inequivalent TMA ions as estimated from equations (1) and (2). Hence the T_1 minima observed in $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ are not likely to be due to the presence of inequivalent TMA ions, as observed in $(TMA)_2HgCl_4$ also (Sarma and Ramakrishna 1984b).

The crystal structure of $TMACdCl_3$ permits the possibility of one of the four methyl groups to have a different correlation time compared to that of the other three, on the basis of which occurrence of a $T_{1\,min}$ corresponding to the TMA ion on the low temperature side was accounted for (Tsang and Utton 1976). The crystal structure of $(TMA)_2HgI_4$ does not lend support to a similar possibility. Hence it is unlikely that the $T_{1\,min}$ at 105·3 K in $(TMA)_2HgI_4$ could be due to the TMA ion reorientations.

The value of 2·9 msec of the $T_{1\,min}$ at 80 K in $(TMA)_2HgBr_4$ is too low to be attributed either to the reorientations of the TMA ion or the methyl group. The occurrence of the $T_{1\,min}$ at 80 K and 105·3 K in $(TMA)_2HgBr_4$ and $(TMA)_2HgI_4$ respectively indicates an internal motion having a Fourier component at 10 MHz in these compounds which is not explained by the SLR model of Albert *et al* (1972). The temperature of 80 K is too high to attribute the $T_{1\,min}$ to tunnelling reorientations.

The motion which is likely to be present at 80 K in $(TMA)_2HgBr_4$ and at 105·3 K in $(TMA)_2HgI_4$, contributing to the SLR at low temperatures in these compounds, might be the torsional oscillations of the CH_3 groups about the C–N axes. The reorientational freedom of the TMA ion is frozen as the temperature is decreased, but a small fraction of the motional freedom still remains at lower temperatures. This could be a small angle

Table 1. Results of theoretical analysis of the experimental data

Compound	Activation Energy E_a (for TMA ion) Kcal/mol	Relative contribution to the relaxation rate at $T_{1\,min}$ from	
		TMA ion	CH$_3$ group
(TMA)$_2$HgCl$_4$*	6·6	104	28·2
(TMA)$_2$HgBr$_4$	5·2	104	51·4
(TMA)$_2$HgI$_4$	4·1	104	6·4

* Sarma and Ramakrishna (1984b)

reorientation of the methyl groups in the TMA ion around their staggered conformation. Such a motion was inferred to be present in some TMA compounds (Prabhumirashi *et al* 1981), contributing to the spin-lattice relaxation.

Table 1 shows that the activation energy corresponding to the reorientation motion of the TMA ion decreases as Cl is substituted by Br and I in (TMA)$_2$HgCl$_4$. Such a trend can be seen in TMA halides (Albert *et al* 1972) and TMA trihalomercurates (Sarma and Ramakrishna 1984a).

The $[(CH_3)_4N]^+$ and $[HgX_4]^{2-}$ tetrahedra deviate from the ideal tetrahedral geometry, and all X—H$_3$C distances (X = halide atom) are not the same (Kamenar and Nagl 1976). The interaction between the hydrogen and the halide atoms is dependent on the distance H . . . X which changes not only with the size of the halide ion, but also with the distorsion of the $[HgX_4]^{2-}$ tetrahedra and the (TMA)$^+$ ion from tetrahedral geometry. The combined effect of the distorsion and the size of the ion might be leading to a high value of relative contribution to the relaxation rate at $T_{1\,min}$ from the methyl group in bromide compared to that in the iodide.

Thus the spin-lattice relaxational behaviour of (TMA)$_2$HgBr$_4$ and (TMA)$_2$HgI$_4$ can be seen to be entirely different from that of (TMA)$_2$ZnCl$_4$, and that of (TMA)$_2$HgCl$_4$. The replacement of Zn by Hg in (TMA)$_2$ZnCl$_4$ and the replacement of Cl by the other halogens drastically affects the internal motions of the TMA ion and the methyl group in these A$_2$BX$_4$ type of compounds.

Acknowledgement

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