Ionic Motion of Phenethylammonium Ion in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) as Studied by ^{1}H NMR

Takahiro Ueda, Mariko Omo *, Katsuyuki Shimizu *, Hiroshi Ohki *,
and Tsutomu Okuda *

Department of Physical Chemistry, National Institute of Materials and Chemical Research,
Tsukuba, Ibaraki 305, Japan
* Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama,
Higashi-Hiroshima 739, Japan

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The temperature dependences at 110 to 400 K of the ^{1}H spin-lattice relaxation time (T_1) of the phenethylammonium ion in phenethylammonium lead(II) halides, $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I), revealed that this ion shows reorientation of the NH_3 moiety around the three-fold axis and torsional motion of the alkyl chain (CH_2CH_2). Below room temperature, the chloride and the bromide yielded two minima of ^{1}H T_1 originating from NH_3 reorientation, whereas the iodide yielded only one minimum. These findings indicate that there are two kinds of NH_3 sites in the chloride and bromide but only one in the iodide. The T_1 minimum observed below room temperature gave similar activation energies of the NH_3 reorientation, $E_a = 15.7$, 15.1 and 15.5 kJ mol^{-1} for the chloride, bromide and iodide, respectively, suggesting that the corresponding NH_3 groups are located at similar environments. Above room temperature, the T_1 minimum in the chloride and bromide gave larger E_a values of the NH_3 reorientation: $E_a = 23.6$ and 20.2 kJ mol^{-1} for the chloride and bromide, respectively. These findings suggest that the NH_3 groups form stronger hydrogen bonding with halogen atoms (N–H ... X). Furthermore, the amplitude of the CH_2CH_2 motion is discussed, using the two sites jump model. The activation energies for the CH_2CH_2 motion in these compounds are almost equal ($E_a = 29.1$, 30.0 and 28.2 kJ mol^{-1} for the chloride, bromide and iodide, respectively), but that the torsional angles become larger in the order iodide $\ll$ bromide < chloride.

Key words: NMR, Phenethylammonium lead(II) halides, Molecular motion, Disorder.

1. Introduction

It is known that phenethylammonium lead(II) halides, $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) have a two-dimensional layered perovskite-type structure [1]. At about 200 K the iodide (hereafter abbreviated as Ph-PbI_4) is monoclinic, space group C2/m with the lattice parameters $a = 3.2508$ nm, $b = 0.6131$ nm, $c = 0.6185$ nm and $\beta = 93.80°$. The inorganic layer is built of corner-sharing PbI_6 octahedra and the organic layer of phenethylammonium ions ($C_6H_5CH_2CH_2NH_3^+$), the phenyl groups facing each other. Each layer is stacking alternatively. The bromide and the chloride (hereafter abbreviated as Ph-$PbBr_4$ and Ph-$PbCl_4$, respectively) are isomorphous with the iodide [1]. These three halides are interesting because of their optical and electronic properties originating from the natural multi-quantum well structure [2, 3] and because of phenomena closely related to the dynamical behavior of the phenethylammonium ion, such as phase transitions and glass formation [4, 5].

In our previous work of ^{13}C CP/MAS NMR on $[C_6H_5CH_2CH_2NH_3]_2[CH_3NH_3]_{n-1}Pb_nI_{3n+1}$ ($n = 1, 2$), we found that the phenyl groups undergo a 180° flip motion around the two-fold axis, of which the activation energy and the pre-exponential factor are 25 kJ mol^{-1} and 8×10^{-10} s for the iodide with $n = 1$, and 26 kJ mol^{-1} and 6×10^{-10} s for the iodide with $n = 2$ [6]. However, the thermal motion of the NH_3 and CH_2CH_2 groups have not yet been clarified.

In the present work, the lattice parameters of Ph-PbX_4 were determined using X-ray powder diffraction, the temperature dependence of the ^{1}H spin-lattice relaxation times (T_1) for $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) were measured and the motional modes of phenethylammonium ion in Ph-PbX_4 are discussed.

2. Experimental

Sample Preparation

Ph-$PbCl_4$ was synthesized by the method used for preparing $[C_6H_5NH_3]_2CuCl_4$ [7]. $PbCl_2$ and phenethylamine ($C_6H_5CH_2CH_2NH_3$) were dissolved in

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Reprint requests to Dr. T. Ueda. Fax: +81 298 54 45 24.

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concentrated hydrochloric acid in the molar ratio 1:6. The mixture was heated and completely dissolved. Thin white quadratic plates of Ph-$PbCl_4$ were grown by cooling the solution. The crystals were dried at ca. 60 °C under reduced pressure. Crystals of Ph-$PbBr_4$ were obtained in the same way from concentrated hydrobromic acid. The samples of Ph-PbI_4 were obtained on described in [6]. The samples were sealed into glass ampoules with He heat exchange gas.

X-Ray Powder Diffraction Measurement

X-ray powder diffraction patterns were measured using a Rigaku RAD-B X-ray diffractometer at room temperature. The reflection data were collected over the reflection angle $10° \leq 2\theta \leq 60°$. The mean X-ray wave length was 0.15404 nm (the mean value of Cu $K\alpha_1$ and $K\alpha_2$). The lattice parameters were determined by simulation of the diffraction patterns using the RIETAN 94 program for Rietverd analysis [8].

^{1}H Spin-Lattice Relaxation Time (T_1) Measurement

The ^{1}H NMR measurements were carried out with a Bruker Model CXP-100 pulsed spectrometer. The ^{1}H spin-lattice relaxation times (T_1) were measured using the 90°-τ-90° method at ^{1}H Larmor frequencies of 12 and 22.5 MHz. The ^{1}H magnetization of all materials recovered exponentially. A unique value of T_1 could be determined at each temperature. The experimental error was <5%. The temperature was controlled within 1 K by a flow of nitrogen gas, using a Bruker VT-1000 unit.

3. Results and Analysis

X-Ray Powder Diffraction

All the samples yielded diffraction patterns characteristic of a layered structure, i.e. intense reflections from the (0, 0, 2n) plane and else weak reflections. For Ph-PbI_4, the crystal lattice parameters were obtained by comparison of the experimental patterns with simulated ones on the basis of the monoclinic structure with space group C/2m reported by Calabrese et al. [1]. The lattice parameters thus obtained are in good agreement with the literature values [1]. For the other two compounds, the lattice parameters were determined by assuming the same crystal lattice as that of the iodide. The obtained lattice parameters are listed in Table 1. The lattice parameters of Ph-PbX_4 depend on the halogen atom in the PbX_4^{2-}-layer. As the ionic radius of the halogen atom increases, the crystal lattice of Ph-PbX_4 expands along the *b*- and the *c*-axis, whereas it contracts along the *a*-axis. The interlayer distance evaluated from *a* and *β* is 3.358 nm for Ph-$PbCl_4$, 3.336 nm for Ph-$PbBr_4$, and 3.244 nm for Ph-PbI_4. These values rise with increasing *a*. Nevertheless, the volume of the crystal lattice contracts as the ionic radius of the halogen atoms becomes larger.

Table 1. Lattice parameters for Ph-PbX_4 (X = Cl, Br, I) determined from X-ray powder diffraction patterns.

X	*a*/nm	*b*/nm	*c*/nm	*β*/deg.	$V/(nm)^3$
Cl	3.375	0.5201	0.5537	95.73	0.9672
Br	3.340	0.5952	0.5741	92.95	1.1398
I	3.251	0.6131	0.6185	93.80	1.2300

Table 2. The minima of T_1 (T_1(min.)) and their temperature ($T_{min.}$) observed in the T_1 vs. $1/T$ plots.

Substance	12 MHz		22.5 MHz		Mode
	$T_{min.}$/K	T_1(min.)/ms	$T_{min.}$/K	T_1(min.)/ms	
Ph-$PbCl_4$	164	44	177	74	I
	228	39	235	71	I′
	306	214	313	267	II
Ph-$PbBr_4$	154	42	166	74	I
	208	35	221	71	I′
	320	270	326	520	II
Ph-PbI_4	161	24	172	39	I
	309	1800	313	2100	II

^{1}H Spin-Lattice Relaxation

1. Ph-PbX_4

Figures 1–3 show that the ^{1}H T_1 vs. $1/T$ curves give three minima for Ph-$PbCl_4$ and Ph-$PbBr_4$, and two minima for Ph-PbI_4. The values of the T_1 minima and their temperatures are summarized in Table 2. When the Larmor frequency is changed from 12 MHz to 22.5 MHz, the T_1 minima become longer and their temperature becomes larger. These findings suggest that three kinds of motional modes exist in the phenethylammonium ion of Ph-$PbCl_4$ and Ph-$PbBr_4$, and two kinds in that of Ph-PbI_4. Hereafter, the motional modes corresponding to the T_1 minima are denoted with increasing temperature as mode I, mode I′, and mode II for the chloride and bromide, and mode I and mode II for the iodide. Above 360 K,

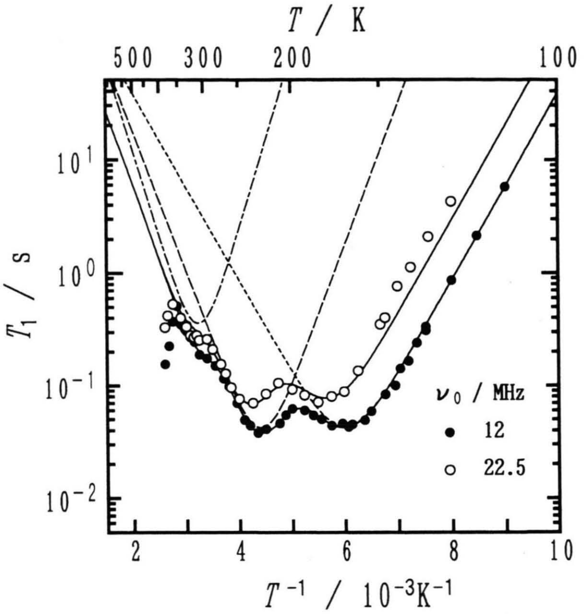

Fig. 1. Temperature dependence of the ^{1}H spin-lattice relaxation times (T_1) in Ph-PbCl$_4$. For T_1 observed at 12 MHz, the short-dashed, long-dashed and short-long-dashed lines represent the results of the least square's fittings for the component of mode I, mode I′, and mode II, respectively. The total T_1 resulting from the three components, is represented by the solid line. For T_1 observed at 22.5 MHz, the solid line represents the results of the simulation.

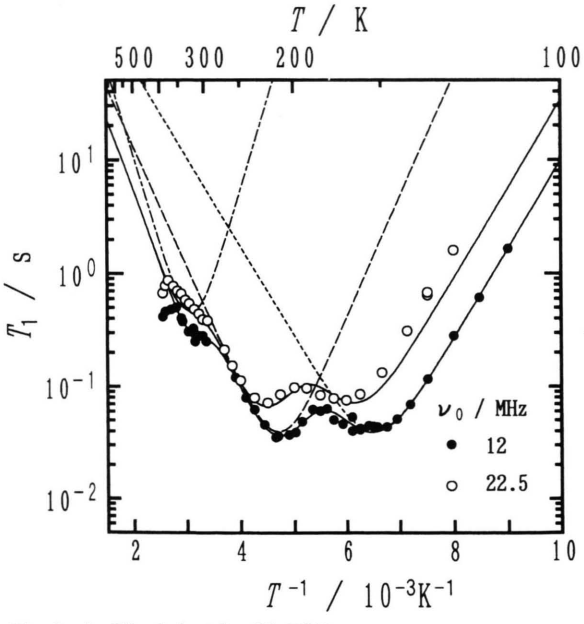

Fig. 2. As Fig. 1, but for Ph-PbBr$_4$.

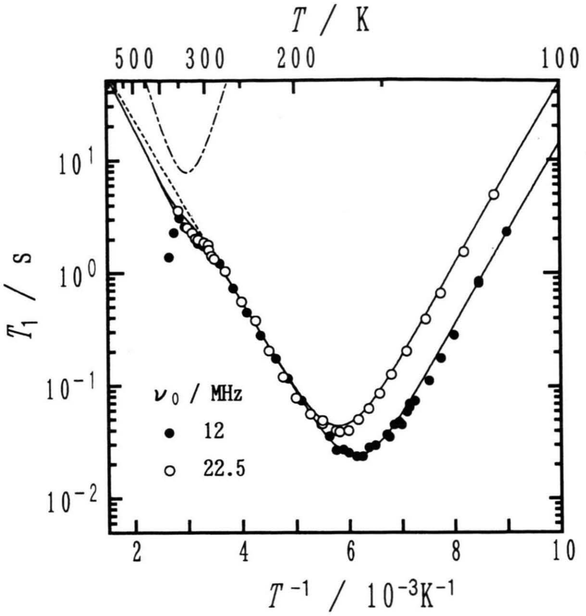

Fig. 3. Temperature dependence of the ^{1}H spin-lattice relaxation times (T_1) in Ph-PbI$_4$. For T_1 observed at 12 MHz, the short-dashed and short-long-dashed lines represent the results of the least square's fittings for the component of mode I, mode II respectively. The total T_1 resulting from the three components, is represented by the solid line. For T_1 observed at 22.5 MHz, the solid line represents the results of the simulation.

^{1}H T_1 in Ph-PbCl$_4$ becomes shorter again, suggesting that a new motion in the phenethylammonium ion is excited above this temperature.

The profiles of the T_1 vs. $1/T$ curves of Ph-PbI$_4$ are different from those of Ph-PbCl$_4$ and Ph-PbBr$_4$. The minimum corresponding to mode I′ disappears in Ph-PbI$_4$. The minimum value of T_1 for mode I in Ph PbI$_4$ is half of those in Ph-PbCl$_4$ and Ph-PbBr$_4$, whereas that for mode II in Ph-PbI$_4$ is 8 times longer than that in Ph-PbCl$_4$ and 4 times longer than that in Ph-PbBr$_4$.

2. ^{1}H T_1 *Analysis*

In order to discuss the dynamical behavior of the phenethylammonium ion, we evaluate the activation energies and pre-exponential factors by data fitting using the BPP relaxation theory [9].

In systems with coexisting motional modes, the total $1/T_1$ is the sum of the ^{1}H spin-lattice relaxation rates corresponding to these motional modes, if correlation effects between these modes can be neglected and the modes take independently part in the different

Table 3. Activation parameters determined from ^{1}H T_1 for Ph-PbX_4 (X = Cl, Br, I).

X	Mode	C_i/rad^2 s^{-2}	τ_{0i}/s	E_a^i/kJ mol^{-1}
Cl	I	1.24×10^9	9.5×10^{-14}	15.7
	I′	1.28×10^9	3.0×10^{-14}	23.6
	II	0.15×10^9	10.0×10^{-14}	29.1
Br	I	1.34×10^9	6.1×10^{-14}	15.1
	I′	1.36×10^9	8.6×10^{-14}	20.2
	II	0.12×10^9	12.0×10^{-14}	30.0
I	I	2.24×10^9	9.2×10^{-14}	15.5
	II	0.7×10^7	25.0×10^{-14}	28.2

relaxation processes. As a motional mode *i* is characterized by a correlation time τ_{ci}, the total $1/T_1$ is represented by

$$1/T_1 = \sum_i C_i \left[\frac{\tau_{ci}}{1+\omega_0^2 \tau_{ci}^2} + \frac{4\tau_{ci}}{1+4\omega_0^2 \tau_{ci}^2} \right]. \qquad (1)$$

where C_i is the average dipolar interaction for the mode *i*, and ω_0 is the ^{1}H Larmor frequency. Assuming thermal activations, the temperature dependence of τ_{ci} represented by Arrhenius law

$$\tau_{ci} = \tau_{0i} \exp(E_a^i/RT). \qquad (2)$$

The least square's curve fitting was performed by applying (1) and (2) on the T_1 data observed at 12 MHz. The results of the data fitting are shown in Figs. 1–3, and the activation parameters are listed in Table 3. The temperature dependences of ^{1}H T_1 at 22.5 MHz, shown in the figures, are calculated by using the activation parameters thus determined. The results are in good agreement with the experimental data and show that the relaxation behavior obeys the BPP relaxation theory very well.

4. Discussion

Motional Mode of Phenethylammonium Ion

The phenethylammonium ion consists of three functional groups, NH_3, CH_2CH_2, and C_6H_5. If the spin temperature is the same in the whole spin system, the experimental $1/T_1$ is given by [10, 11]

$$1/T_1 = \frac{1}{N}\left[\frac{n_{(NH_3)}}{T_1^{(NH_3)}} + \frac{n_{(CH_2CH_2)}}{T_1^{(CH_2CH_2)}} + \frac{n_{(C_6H_5)}}{T_1^{(C_6H_5)}} \right], \qquad (4)$$

where $n_{(NH_3)}$, $n_{(CH_2CH_2)}$ and $n_{(C_6H_5)}$ are the numbers of protons in NH_3, CH_2CH_2, and C_6H_5, respectively, and N is their total number.

Reorientation of the NH_3 group around the three-fold axis is undergone most easily. So, the total T_1 will be dominated by the relaxation time $T_1^{(NH_3)}$ at relatively low temperature. Therefore, the T_1 minima corresponding to the modes I and I′ are considered to originate from the modulation of dipolar interaction owing to the NH_3 reorientation in the phenethylammonium ion. This is also supported by the comparison of the experimental C_i values with the theoretical ones. For the NH_3 reorientation around the three-fold axis, the theoretical value of C_{NH_3} in the phenethylammonium ion is represented by [10]

$$C_{NH_3} = \frac{9}{20} \frac{n_{(NH_3)}}{N} \frac{\gamma^4 \hbar^2}{r^6}, \qquad (6)$$

where γ is the gyromagnetic ratio of the proton and *r* the interproton distance in the NH_3 group, whose typical value is 0.1706 nm [10]. The theoretical value of C_{NH_3} is calculated to be 2.6×10^9 rad^2 s^{-2}. The experimental C_i value for mode I in Ph-PbI_4 (2.24×10^9 rad^2 s^{-2}) is in good agreement with the theoretical one. On the other hand, for Ph-$PbCl_4$ and Ph-$PbBr_4$ the experimental C_i values for the mode I and I′ are about one half of the theoretical one ($\sim 1.3 \times 10^9$ rad^2 s^{-2}) in both compounds. This suggests that in Ph-$PbCl_4$ and Ph-$PbBr_4$ there are two kinds of distinguishable NH_3 sites which are occupied by the NH_3 groups with equivalent population 0.5:0.5.

The CH_2CH_2 and C_6H_5 groups less mobile than the NH_3 group. In fact, we found previously that above room temperature the C_6H_5 group of the phenethylammonium ion in Ph-PbI_4 undergoes a 180° flip motion with a time scale of $10^{-6} \sim 10^{-5}$ s [6]. The time scale for this motion is too slow to contribute to the ^{1}H T_1 efficiently. Therefore, $T_1^{(CH_2CH_2)}$ will contribute more efficiently than $T_1^{(C_6H_5)}$ to the total T_1 and brings about the minimum corresponding to the mode II. $T_1^{(C_6H_5)}$ will be responsible for the decrease of T_1 above 360 K. In order to discuss the motional mode of the CH_2CH_2 group in more detail, we propose the model shown in Figure 4. Although the CH_2CH_2 group can rotate independently around the $C_1 - C_\alpha$ and $C_\alpha - C_\beta$ bonds, torsional motion around each bond with small flip angles is considered to be the most probable motion of the CH_2CH_2 group because the NH_3 and C_6H_5 groups restrict the motion of CH_2CH_2 group. The torsional angles about the $C_\alpha - C_\beta$ and $C_1 - C_\alpha$ bonds shall be named ϕ_a

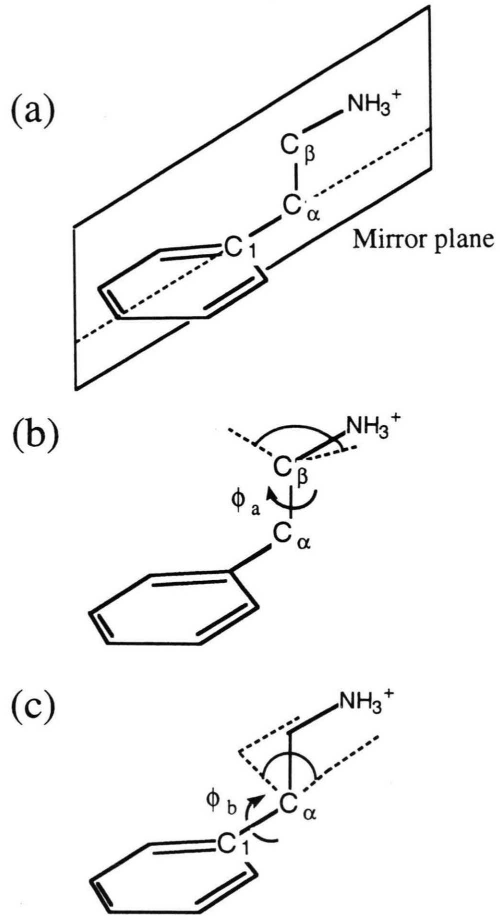

Fig. 4. Model for the motion of the CH_2CH_2 group in the phenethylammonium ion. (a) The most stable conformation. The alkyl chain holds the *trans*-conformation and is lying in a mirror plane. (b) Rotation of the alkyl chain around the $C_\alpha - C_\beta$ bond. For clockwise rotation the angle ϕ_a is positive, and for counterclockwise negative. (c) Rotation of the alkyl chain around the $C_1 - C_\alpha$ bond. For clockwise rotation the angle ϕ_b is positive, and for counterclockwise negative. The CH_2CH_2 group undergoes torsional motion rotating the $C_\alpha - C_\beta$ and $C_1 - C_\alpha$ bond simultaneously with small flip angles of ϕ_a and ϕ_b.

and ϕ_b, respectively. The phenethylammonium ion has the most stable conformation when the C_β takes an axial position to the phenyl group and the $C_1 - C_\alpha - C_\beta - N$ takes a *trans* conformation ($\phi_a = 0°$ and $\phi_b = 0°$). The most stable conformation possesses a mirror plane standing perpendicular to the plane of the phenyl group, on which the CH_2CH_2 and NH_3 group are lying. The conformation of the phenethylammonium ion, characterized by ϕ_a and ϕ_b, is symmetrical with respect to the mirror plane. When the CH_2CH_2 group jumps between these conformations, the motion of the CH_2CH_2 group can be treated by a two sites jump model between one conformation (A site) and its symmetrical one (B site). Assuming equivalent population at the A and B sites, the corresponding relaxation constant $C_{CH_2CH_2}$ is expressed by [12–14]

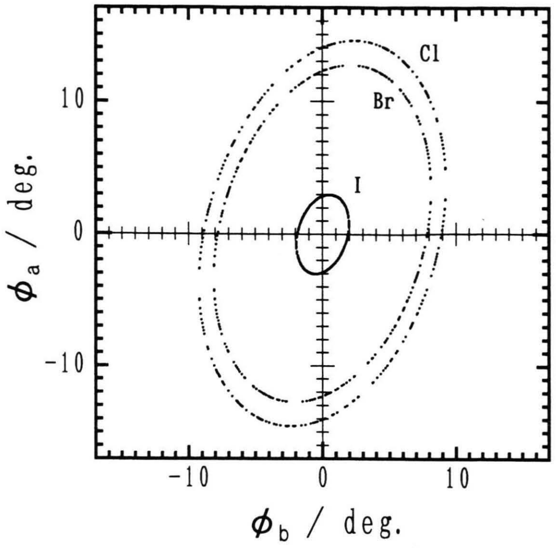

Fig. 5. The flip angles ϕ_a and ϕ_b of the CH_2CH_2 group in phenethylammonium ion, satisfying the experimental values of C_i.

$$C_{CH_2CH_2} = \frac{3}{20}\,\frac{n_{(CH_2CH_2)}}{N}\,\gamma^4\hbar^2\sum_{i<j} \cdot\left[R_{ijA}^{-6} + R_{ijB}^{-6} - R_{ijA}^{-3}R_{ijB}^{-3}(3\cos^2\theta_{ij} - 1)\right], \tag{7}$$

where R_{ijA} and R_{ijB} are the interatomic distances in the conformation A and B, respectively, and θ_{ij} is the angle between the R_{ijA} and R_{ijB} vectors. R_{ijA}, R_{ijB} and θ_{ij} can be expressed by using the flip angles ϕ_a and ϕ_b. Assuming the molecular structure of the phenethylammonium ion determined in the $C_6H_5CH_2CH_2NH_3Cl$ crystal [15], (7) makes it possible to seek a pair of the flip angles ϕ_a and ϕ_b which satisfies the experimental value of C_i. Figure 5 shows the pairs of the flip angles ϕ_a and ϕ_b determined for each compound. The size of the ellipses represents the amplitude of the fluctuation of the CH_2CH_2 group. The remarkable aspect in Fig. 5 is the relative magnitude of the flip angles among the three compounds. The flip angles are within ± 15° for ϕ_a and ± 10° for ϕ_b in Ph-$PbCl_4$, whereas they are within ± 3° for

ϕ_a and ± 2° for ϕ_b in Ph-PbI_4. This finding reveals that the amplitude of the CH_2CH_2 motion is larger in the order $I \ll Br < Cl$ for the series of Ph-PbX_4, although the corresponding activation energy E_a changes little among three compounds.

Local Structure of Phenethylammonium Ion

The local structure around the NH_3 group, especially about the NH_3 site, was examined through the activation energy (E_a) of the NH_3 reorientation. In systems possessing the hydrogen bonding N–H...X, the strength of the hydrogen bonding is the dominant factor for the E_a values of the NH_3 reorientation. For example, in hydrogen bonding systems such as CH_3NH_3X [10, 16, 17] and $(CH_3NH_3)_2TeX_6$ [18] (X = Cl, Br, I) the strength of the hydrogen bonding has been studied through the E_a values of the NH_3 reorientation in $CH_3NH_3^+$, which becomes stronger in the order $I < Br < Cl$. If the NH_3 group forms hydrogen bonding in Ph-PbX_4, the E_a value of NH_3 reorientation should increase in the order $I < Br < Cl$. The experimental values of E_a for mode I in the three compounds are of the order 15.5 ± 0.5 kJ mol^{-1}. On the other hand, the E_a values for mode I′, i.e., 20.2 kJ mol^{-1} for Ph-$PbBr_4$ and 23.6 kJ mol^{-1} for Ph-$PbCl_4$, are larger than for mode I. Furthermore, E_a of model I′ of Ph-$PbCl_4$ is larger than that of Ph-$PbBr_4$. These findings reveal that the NH_3 group corresponding to mode I has a similar environment in the three compounds and is scarce affected by hydrogen bonding, whereas the NH_3 group corresponding to mode I′ is affected by the hydrogen bond N–H...X.

Next, we discuss the anomalies observed in the *a*-distance and the interlayer distance of Ph-PbX_4, both of which become larger in the order $I < Br < Cl$ in spite of a decrease in the ionic radius of the halogen atoms. This may be interpreted by the dynamical behavior of the phenethylammonium ion located between the inorganic layers. Both the large amplitude motion of the CH_2CH_2 group and the disorder of the NH_3 group bring about a larger free volume around the alkyl chain in the phenethylammonium ions and at the interface between the organic and inorganic layers. The increase in free volume of the organic layers extends the crystal lattice. The free volume of the phenethylammonium ion, expected from our results, is larger in the following order; Ph-PbI_4 < Ph-$PbBr_4$ < Ph-$PbCl_4$. On the other hand, the average volume of a phenethylammonium ion, as derived from the lattice parameters and the ionic radii of Pb^{2+} and X^- [19, 20], is estimated to be 0.94×10^{-4} m^3 mol^{-1} for Ph-$PbCl_4$, 1.07×10^{-4} m^3 mol^{-1} for Ph-$PbBr_4$ and 1.08×10^{-4} m^3 mol^{-1} for Ph-PbI_4. The average volume is larger in the reverse order of the free volume expected from the dynamical behavior of the phenethylammonium ion. The difference these the trends seems to come from the evaluation of the average volume without taking account of the shape and the local structure of the phenethylammonium ion. Actually, the free volume of the phenethylammonium ion reflects the local motion and the structure of the organic ion rather than the average volume. The phenyl groups as well as the NH_3 and CH_2CH_2 groups may play an important role in extending the organic layers. The distances between the phenyl groups facing each other in those systems, and the free volume around them, will relate more directly to the lattice extension along the *a*-axis than the distances between the NH_3 and CH_2CH_2 groups. Thus, information about the motion of the phenyl groups will advance the discussion.

5. Conclusion

The molecular motion of the phenethylammonium ion located between the inorganic PbX_4^{2-} layers in $[C_6H_5CH_2CH_2NH_3]_2PbX_4$ (X = Cl, Br, I) has been investigated by means of the temperature dependence of the ^1H spin-lattice relaxation time (T_1). The motional modes of the phenethylammonium ion were assigned on the basis of the analysis of the relaxation constant determining the minimum values of T_1. The activation energy (E_a) and the pre-exponential factor (τ_0) for each motional mode were determined from data fitting using the BPP theory. On the basis of the E_a values, the local structure of the phenethylammonium ion was discussed. The following aspects were elucidated:

(1) The two NH_3 groups in Ph-$PbCl_4$ and Ph-$PbBr_4$ occupy two different sites; one is little affected by hydrogen bonding and the other is strongly affected by the bond N–H...X.

(2) The CH_2CH_2 group undergoes a two-sites jump motion between the sites causing torsion of the C_1–C_a and C_a–C_b bonds, and the magnitude of the flip angles becomes larger in the order Ph-PbI_4 ≪ Ph-$PbBr_4$ < Ph-$PbCl_4$.

(3) The *a*-values of the Ph-PbX_4 crystals increase in the order Ph-PbI_4 < Ph-$PbBr_4$ < Ph-$PbCl_4$, which is the reverse order of the ionic radii of the halogen atoms. The motion of the phenethylammonium ion is considered to be one of the reasons for the anomalous lattice expansion along the *a*-axis.

[1] J. Calabrese, N. L. Jones, R. L. Harlow, N. Herron, D. L. Thorn, and Y. Wang, J. Amer. Chem. Soc. **113,** 2328 (1991).

[2] X. Hong, T. Ishihara, and A. V. Nurmikko, Phys. Rev. **B45,** 6961 (1992).

[3] X. Hong, T. Ishihara, and A. V. Nurmikko, Solid State Commun. **84,** 657 (1992).

[4] C. Q. Xu, S. Fukuta, H. Sakakura, T. Kondo, R. Ito, Y. Takahashi, and K. Kumata, Solid State Commun. **77,** 923 (1991).

[5] T. Maris, G. Bravic, N. B. Chanh, J. M. Leger, J. C. Bissey, A. Villesuzanne, R. Zouari, and A. Daoud, J. Phys. Chem. Solids **57,** 1963 (1996).

[6] T. Ueda, K. Shimizu, H. Ohki, and T. Okuda, Z. Naturforsch. **51a,** 910 (1996).

[7] K. P. Larsen, Acta Chem. Scand. **A28,** 194 (1974).

[8] F. Izumi, The Rietveld Method, R. A. Young ed., University Press, Oxford 1993, Chap. 13.

[9] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73,** 679 (1948).

[10] S. Albert and J. A. Ripmeester, J. Chem. Phys. **58,** 541 (1973).

[11] T. Ueda, S. Takeda, N. Nakamura, and H. Chihara, Bull. Chem. Soc. Japan **64,** 1299 (1991).

[12] E. R. Andrew and L. Latanowicz, J. Magn. Reson. **68,** 232 (1986).

[13] Z. Pajak, L. Latanowicz, and A. Katrusiak, Phys. State. Sol. **(a) 130,** 421 (1992).

[14] T. Ueda, S. Hayashi, and K. Hayamizu, Phys. Rev. **B48,** 5837 (1993).

[15] P. G. Tsoucaris, Acta Cryst. **14,** 909 (1961).

[16] H. Ishida, R. Ikeda, and D. Nakamura, J. Phys. Chem. **86,** 1003 (1982).

[17] H. Ishida, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **59,** 915 (1986).

[18] Y. Furukawa, H. Kiriyama, and R. Ikeda, Bull. Chem. Soc. Japan **54,** 103 (1981).

[19] R. D. Shannon and C. T. Prewitt, Acta Cryst. **B25,** 925 (1969).

[20] R. D. Shannon, Acta Cryst. **A32,** 751 (1976).