13C CP/MAS NMR Study of the Layered Compounds
[C6H5CH2CH2NH3]2[CH3NH3]fI_1Pbnl3n+1 (n = 1, 2)

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13C CP/MAS NMR spectra were measured on the layered compounds [C6H5CH2CH2NH3]2
[CH3NH3]fI_1Pbnl3n+1 (n = 1, 2). The linewidth of the resonance peak corresponding to the phenyl
carbons changed with temperature. The maximum broadening took place at 363 K for both com-
pounds. The activation energy E_a for the reorientation of the phenyl group was determined to be
25 kJ mol⁻¹ for n = 1 and 26 kJ mol⁻¹ for n = 2. The frequency factor τ_0 was evaluated from the
linewidth at 363 K. The value of the second moment, estimated from the maximum linewidth, was
interpreted by assuming a 180° flip of the phenyl group around its two-fold axis. The similarity of
the activation energies for the reorientation of the phenyl group suggested that the local structure
and the molecular motion of the organic cations is little affected by the difference in the sub-structure
of the inorganic layer in those compounds.

Key words: 13C CP/MAS NMR, Molecular motion, Layered compounds, Activation parameters,
Local structure.

1. Introduction

Recently, layered compounds,
[C6H5CH2CH2NH3]2[CH3NH3]fI_1Pbnl3n+1 (n = 1, 2)

have been synthesized to establish their behavior as two-dimensional semiconductors and to construct a
natural multi-quantum well system [1]. These compounds have a two-dimensional layered perovskite-
type structure in which, if n = 1, the inorganic semiconductor layers, consisting of PbI^2⁻, are sandwiched
between organic insulating spacers consisting of phenethylammonium ion, C6H5CH2CH2NH3⁺. In
the natural multi-quantum well system, the former act as “wells” and the latter as “barriers”.

The structure of both compounds has been determined by X-ray diffraction using single crystals
[1]. The space group of [C6H5CH2CH2NH3]2
[CH3NH3]fI_1Pbnl3n+1 (hereafter abbreviated as Ph-Me-PbI3) is triclinic P1 with the lattice parameters
a = 0.8794 nm, b = 0.8792 nm, c = 2.2766 nm, α = 94.02°, β = 97.02°, and γ = 90.18° at room tempera-
ture. The inorganic perovskite-like [CH3NH3]PbI^2⁻ layer (bilayer) is built up of methylammonium ions
and corner-sharing PbI6 octahedra twisted by ca. 12.1° from the tetragonal positions. The space groups of
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and corner-sharing PbI6 octahedra twisted by ca. 12.1° from the tetragonal positions. The phenethylam-
nonium ions are lying between the inorganic layers, the phenyl groups facing each other. Disorder of the
organic cations has also been reported [1]. In Ph-

PbI4, the organic cations are disordered across mirror planes, whereas in Ph-Me-PbI3, they are very poorly
located by disorder and/or large thermal motion.

In these compounds the optical and the electronic properties, originating from the natural multi-quantum
well structure, have been examined in detail by means of optical absorption, reflectance, photo-current,
and photoluminescence spectra [2, 3]. However, the structural disorder and the molecular motion of the
organic cations have not been studied yet, although considerable disorder of the organic cations
has been observed. It is expected that the anisotropy of the intermolecular interaction in the two-dimen-
sional systems may bring about some interesting phe-
nomina such as phase transition and glass formation of the organic cations.

The $^{13}$C CP(cross polarization)/MAS NMR spectrum can give dynamic and structural information independently of the carbon in the organic molecules. Especially, measurement of the line-broadening in $^{13}$C CP/MAS NMR spectra can yield an activation energy $E_a$ and a frequency factor $\tau_0$ for the molecular motion. This procedure has been applied by Rothwell and Waugh to determine the activation parameters of hexamethylenes, hexamethylethane and adamantane, undergoing rapid molecular reorientation [4].

In the present study, we have measured the temperature dependence of $^{13}$C CP/MAS NMR spectra of phenethylammonium ions in Ph-PbI$_4$ and Ph-Me-Pb$_2$I$_7$, have derived $E_a$ and $\tau_0$ from the temperature dependence of the linewidths and have discussed the mode of the molecular motion and the local structure of the organic cations.

2. Experimental

Ph-PbI$_4$ and Ph-Me-Pb$_2$I$_7$ were synthesized according to [5, 6]. The precursors phenethylammonium iodide ($C_6H_5CH_2CH_2NH_3$I) and methylammonium iodide ($CH_3NH_3$I) were prepared by neutralization of phenethylamine ($C_6H_5CH_2CH_2NH_2$) and methylamine ($CH_3NH_2$), respectively, with hydroiodic acid (HI) in aqueous solution. The excess HI and H$_2$O, as well as the impurity of iodine, were removed by drying the compounds in vacuo at ca. 60 °C for several days. Acetonitrile solutions containing $C_6H_5CH_2CH_2NH_3$I, $CH_3NH_3$I and PbI$_3$ with stoichiometric ratios were heated at 60 °C under N$_2$ atmosphere. The solvent was removed by flowing N$_2$ gas until the crystallization of the desired substances (Ph-PbI$_4$ or Ph-Me-Pb$_2$I$_7$) started. The precipitate was filtered and dried at ca. 40 °C under reduced pressure. Analysis for Ph-PbI$_4$ found: H, 2.54; C, 20.78; N, 2.91; I, 51.96%, Calcd.: H, 2.52; C, 20.03; N, 2.92; I, 52.59% and for Ph-Me-Pb$_2$I$_7$, found: H, 1.94; C, 13.54; N, 2.64; I, 56.01%, Calcd.: H, 1.92; C, 12.93; N, 2.66; I, 55.94%.

$^{13}$C CP/MAS NMR spectra were measured with a Bruker MSL-400 spectrometer operating at a Larmor frequency of 100.613 MHz for carbon-13. A sample spinning rate of ca. 6 kHz was employed by use of a ZrO$_2$ sample rotor, the dimension of which is $\phi$ 4 mm × 18 mm. The spectra were recorded at temperatures from 295 to 368 K under $^1$H irradiation with a de-coupling field $v_1$ = 57 kHz. The temperature was controlled by heating the bearing gas within ± 2 K using a Bruker VT-1000 unit. As external standard of the chemical shift hexamethylenbenzene was used, in which the chemical shift for the methyl carbon is known to be 17.17 ppm downfield from tetramethylsilane (TMS) [7].

3. Results and Discussion

Peak Assignment of the $^{13}$C CP/MAS NMR Spectra of Ph-PbI$_4$ and Ph-Me-Pb$_2$I$_7$

Figure 1 shows the $^{13}$C CP/MAS NMR spectra of Ph-PbI$_4$ and Ph-Me-Pb$_2$I$_7$ at room temperature. In Ph-PbI$_4$ it consists of five peaks, three in the region of 120 to 140 ppm with relative intensity ratios 1:4:1 and two in the region of 30 to 50 ppm with the ratio 1:1. In Ph-Me-Pb$_2$I$_7$, the spectrum has an additional peak at 30.5 ppm. The experimental chemical shifts, measured from TMS, and their assignment to the carbon atoms of the phenethylammonium ion, together with the literature values for phenethylamine (PEA) in CDCl$_3$ and phenethylammonium chloride (PEA·HCl) in D$_2$O [8], are listed in Table 1. The additional peak observed in Ph-Me-Pb$_2$I$_7$ is considered to originate from the methyl group in CH$_3$NH$_3^+$ located in the inorganic layers.

![Fig. 1. $^{13}$C CP/MAS NMR spectra of Ph-PbI$_4$ (a) and Ph-Me-Pb$_2$I$_7$ (b) at room temperature. The peaks with asterisks are spinning sidebands.](image-url)
Table 1. $^{13}$C chemical shifts determined from $^{13}$C CP/MAS NMR spectra and literature.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Chemical shift values in ppm from TMS</th>
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<tbody>
<tr>
<td>Ph-Pbl$_4$</td>
<td>C$_1$: 137.6, C$_2$: 130.7, C$_3$: 127.7, C$_4$: 34.1, C$_5$: 44.5, CH$_3$: 30.5</td>
</tr>
<tr>
<td>Ph-Me-Pb$_2$I$_7$</td>
<td>C$_1$: 137.7, C$_2$: 130.8, C$_3$: 127.8, C$_4$: 34.1, C$_5$: 45.0, CH$_3$: 30.5</td>
</tr>
<tr>
<td>PEA$^a$</td>
<td>C$_1$: 139.99, C$_2$: 129.05, C$_3$: 128.75, C$_4$: 126.44, C$_5$: 39.84, C$_6$: 43.24</td>
</tr>
<tr>
<td>PEA·HCl$^b$</td>
<td>C$_1$: 139.50, C$_2$: 131.67, C$_3$: 131.85, C$_4$: 130.15, C$_5$: 35.35, C$_6$: 43.24</td>
</tr>
</tbody>
</table>

$^a$ Solvent: CDCl$_3$ [8]; $^b$ Solvent: D$_2$O [8].

**Temperature Dependence of the Linewidths of the Phenyl Carbons in $^{13}$C CP/MAS NMR Spectra**

Figure 2 shows the temperature dependence of the $^{13}$C CP/MAS NMR signals from the carbon atoms of the phenyl group in Ph-Pbl$_4$ and Ph-Me-Pb$_2$I$_7$. The linewidths of the peaks from C$_2$(C$_6$) and C$_3$(C$_5$) broaden drastically on heating. In both substances, the linewidth broadens from 1 ~ 2 ppm at 295 K to about 10 ppm at 368 K. However, the linewidths of the peaks from C$_1$ and C$_4$ appear to dependent little on temperature, maintaining 1 ~ 2 ppm over the whole temperature range. This suggests that the phenyl group reorientates around a two-fold axis passing through the C$_1$ and the C$_4$ carbons, with the order of $^1$H decoupling frequency.

Generally, molecular motion in solids can cause linebroadening by providing relaxation pathways for the transverse $^{13}$C magnetization. When $^{13}$C is coupled by a **stochastically and isotropically** modulated dipole-dipole interaction to $^1$H under rf irradiation, the $^{13}$C spin-spin relaxation rate $1/T_2$ is given by [4, 9]

$$\frac{1}{T_2} = \frac{g_H^2 g_C^2 h^2}{5 r_{CH}^6} \left[ \frac{\tau_c}{1 + \omega_1^2 \tau_c^2} \right],$$

(1)

where $g_C$ and $g_H$ are the gyromagnetic ratios of $^{13}$C and $^1$H, respectively, $r_{CH}$ is the internuclear distance between $^{13}$C and $^1$H, $\omega_1$ ($= 2 \pi v_1$) is the strength of the rf irradiation ($^1$H decoupling) field, and $\tau_c$ is the correlation time for the stochastic modulation of the $^{13}$C-$^1$H dipolar interaction. The prefactor on the right hand side of (1) is equal to the $^{13}$C-$^1$H Van Vleck second moment $M_2$ expressed in rad$^2$/sec$^2$. The NMR linewidth $\Delta\nu$, which is expressed in Hz, is proportional to $1/T_2$. When the line shape of the $^{13}$C CP/MAS NMR spectra is approximated by a Lorentzian curve, the relation $\Delta\nu = 1/\pi T_2$ is satisfied [9].

Assuming an Arrhenius activation process for the correlation time $\tau_c$,

$$\tau_c = \tau_0 \exp\left(\frac{E_u}{RT}\right),$$

(2)

a plot of $\log(1/T_2)$ vs. the $1/T$, gives a $\Lambda$-shaped curve; its slope on the both sides of the maximum of $1/T_2$ gives the activation energies, and the value of $1/T_2$ maximum is used to determine the $M_2$ value. The analysis of the $M_2$ values obtained by the model calculation on the basis of the details of molecular structure leads to the mode of molecular motion contributing to the linebroadening. Furthermore, $\tau_0$ can be determined from the knowledge of $\omega_1$ and the temperature $T'$ at which the maximum broadening takes place,

$$\tau_0 = \omega_1^{-1} \exp\left(-\frac{E_u}{RT'}\right),$$

(3)

which follows from (2) under the condition $\omega_1 \tau_c = 1$.

In order to discuss the molecular reorientation quantitatively, the temperature dependence of the linewidth $\Delta\nu$ is inferred by a least squares curve fitting procedure assuming Lorentzian shape. Figure 3 shows $\Delta\nu$ vs. $1/T$ for the two substances, yielding according to (1) and (2) the activation energy of the molecular motion modulating the $^{13}$C-$^1$H dipolar interaction. In Ph PbI$_4$ and Ph-Me-Pb$_2$I$_7$, the activation energies for the reorientation of the phenyl group are evaluated to be 25 kJ mol$^{-1}$ and 26 kJ mol$^{-1}$, respectively. Furthermore, the peak appears to be most...
The thickness of the organic layer and the molecular volume occupied by the organic cation are estimated to be about 1000 Hz by the least squares curve fitting. This temperature may be considered to be the maximum value, in a similar manner as $r_{CH} = 0.108 \text{ nm}$. This is twice the experimental value. The discrepancy in the second moment between the experimental and the theoretical values suggests that the phenyl group undergoes the reorientation anisotropically. When the molecule undergoes anisotropic motion, $M_2$ reduces by a factor $F$ depending on the mode of the molecular motion [10]. The second moment, reduced by the anisotropic motion, is represented by $\Delta M_2 = \frac{1}{2} M_2 (\text{rigid})$. $\Delta M_2$ contributes to the linebroadening in $^{13}$C CP/MAS NMR spectra. Thus, the prefactor on the right hand side of (1) must be replaced by $\Delta M_2$, as anisotropic motion is taking place. Assuming that the phenyl group reorientates around the two-fold axis with $180^\circ$ flip angle, as described in Fig. 4, the reduction factor $F$ is represented by

$$F = 1 - \frac{3}{4} \sin^2 2\theta,$$

where $\theta$ is the angle between the rotation axis and the $^{13}$C $-$ $^1$H vector [10]. In the phenyl group, a typical value of $\theta$ is $60^\circ$ as shown in Figure 4. Considering the reduction factor $\Delta M_2$ is $2.5 \times 10^9 \text{ rad}^2/\text{s}^2$, which is in good agreement with the experimental value $M_2 (\text{exp.}) = 2.3 \times 10^9 \text{ rad}^2/\text{s}^2$. This consideration leads to the conclusion that the phenyl group flips by $180^\circ$.

**Local Structure of the Phenethylammonium Ion in Ph-Pbi$_4$ and Ph-Me-Pb$_2$I$_7$**

On the basis of the activation energies evaluated above, we discuss the local structure of the phenethylammonium ion in Ph-Pbi$_4$ and Ph-Me-Pb$_2$I$_7$. The values of $E_a$ are 25 kJ mol$^{-1}$ and 26 kJ mol$^{-1}$ for Ph-Pbi$_4$ and Ph-Me-Pb$_2$I$_7$, respectively. Approximately, the activation energy will reflect the intermolecular interaction. That is, the similar values in $E_a$ mean that the phenethylammonium ions interact with each other in both substances in a similar manner. Furthermore, this aspect will bring about the similar environments surrounding an organic cation. For instance, the thickness of the organic layer and the molecular volume occupied by the organic cation are estimated to be

$$2.3 \times 10^9 \text{ rad}^2/\text{s}^2.$$
mated by using the lattice constants to be 0.944 nm and \(1.08 \times 10^{-4} \text{ m}^3\text{ mol}^{-1}\) for \(\text{Ph-PbI}_4\), and 0.898 nm and \(1.05 \times 10^{-4} \text{ m}^3\text{ mol}^{-1}\) for \(\text{Ph-Me-Pb}_2\text{I}_7\), respectively. These values also suggest the above aspect. One can conclude that the structure in the organic layer is little affected by the difference of the structure of the inorganic layer in those compounds.

The \(E_a\) values observed in our substances are lower than in other compounds, in which the phenyl group undergoes reorientation around the two-fold axis. For example, an activation energy of 40 kJ mol\(^{-1}\) has been reported for azo- and azoxybenzene solved in poly-(methylmethacrylate) (PMMA), as determined by means of \(^2\text{H} \text{NMR}\) [11]. In the tyrosine side chain of crystalline enkephalin, an activation energy of 42 kJ mol\(^{-1}\) has been reported [12]. In these materials it is assumed that the phenyl group reorients relatively easily around its twofold-axis because the phenyl group is located in a synthetic polymer with low crystallinity and/or a natural pentapeptide with structural disorder and has a large free volume around it. Our activation energies are about one half of these. This indicates that the disorder in the organic cations is considerably larger than in the two materials. That is, the disorder will cause stacking faults of the phenyl rings and loose packing of the organic cations, and therefore the free volume around the organic cation becomes large.

Detailed information on the thermal expansion and compressibility for these compounds as well as the pressure dependence of \(E_a\) and lattice parameters is necessary for a further discussion of the relation between the free volume and \(E_a\).