Structural analysis of alkyl chain conformation in the layered organic–inorganic hybrids \((C_nH_{2n+1}NH_3)_2PbI_4\) 
\((n = 12, 16, 18)\) by IR spectroscopy

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Abstract

The conformational order and planarity of alkyl chains in the organic–inorganic hybrid materials \((C_nH_{2n+1}NH_3)_2PbI_4\), have been examined using infrared spectroscopy. The structure of the inorganic PbI\(_4\) slabs in these compounds are invariant with respect to the value of \(n\). These inorganic slabs are sandwiched by bilayers of long alkylammonium chains. The coupling of vibrational modes of all-trans segments of the alkyl chains produce band progressions that are diagnostic of the all-trans conformation. From an analysis of the rocking, twisting, and wagging vibrational mode progressions we establish that irrespective of the value of \(n\) all methylene units of the alkyl chain in \((C_nH_{2n+1}NH_3)_2PbI_4\) are in trans registry at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Layered organic–inorganic hybrid compounds have been widely studied [1], since they can, in principle, combine properties of the inorganic and organic parts within a single system. In the molecular hybrids of interest to us, organic groups are interleaved between inorganic sheets and held in place either by covalent or ionic bonding [2]. The majority of the organic–inorganic molecular composites that have been studied so far derive from the layered perovskite structure and comprise inorganic perovskite sheets alternating with either a double-layer of organic primary ammonium cations or a single layer of organic diammonium cations [3]. Applications of such materials include the development of functional magnetic [2], electronic [4] and optoelectronic [5] materials. In this Letter, we focus on molecular hybrids derived from Pb(II) iodides: \((C_nH_{2n+1}NH_3)_2PbI_4\) \((n = 12, 16, 18)\). These systems are natural semiconductor/insulator quantum-well structures, with the semiconducting inorganic portion being confined to two dimensions, and separated from one another by the insulating organic layers.

Details of the ordering of the Pb–I inorganic backbone structure of the \((C_nH_{2n+1}NH_3)_2PbI_4\) compounds are reasonably well understood from
X-ray diffraction measurements [6]. Local structural information on the molecular conformation of
the alkyl chains, and especially for larger $n$, are however not available. Preliminary studies have
established that in these compounds the alkyl chains adopt an essentially all trans conformation and are
tilted away from the interlayer normal by an angle of $55^\circ$ [7]. This has been arrived at from the variation
of the interlayer spacing as a function of interlayer spacing and also from the orientation dependence of
the infrared spectra. We are attracted to infrared spectroscopy to characterize alkyl chain confor-
mation in these hybrids because of its effectiveness in determining low concentrations of disorder
gauze conformers) in an otherwise ordered system. On the other hand, diffraction studies of a
system that comprised, for example, 95% trans chains and 5% chains with gauche defects, would
reveal the presence of such disorder only through poor thermal parameters. Any sort of quantifica-
tion of disorder would be difficult to achieve through an average probe such as X-ray diffraction.
This problem is overcome through the use of a local probe such as vibrational spectroscopy.

The method used here depends on the variation of frequencies of the methylene wagging and
rocking–twisting modes with chain conformation. It is well known that these vibrational modes in the
IR spectra of ordered alkyl chains may be described as coupled oscillators, which produce band pro-
gressions diagnostic of the all-trans conformation [8,9]. Modes of all methylene units in trans registry
are equally involved in giving rise to a progression of regularly spaced modes corresponding to
standing waves extending over all contributing methylene units. The observed frequency pattern is
characteristic of the number of CH$_2$ groups in trans registry. Structural applications of these modes
have been reported for the characterization of lipid bilayers [10], gels [11], triglycerols [13], and inter-
calated surfactant bilayers [12].

2. Background on progression bands of the alkyl chain

The delocalized vibrational modes of long chain molecules have been interpreted on the basis of
vibrational modes of an infinite polymethylene chain [14]. Conformational order within the alkyl
chains causes a coupling of the methylene vibrational modes and the resulting vibrational spectra
can be analyzed based on dispersion curves by plotting the frequencies $v$ as a function of the phase angle $\phi$
between neighboring methylene units [8,9]. These dispersions have been compared with the theoretical dispersion curves for methyl-
ene vibrational modes obtained by a normal coordinate analysis of an infinite polymethylene
chain. For an infinite polymethylene chain, only vibrational modes at $\phi = 0$ or $\pi$ are infrared and/or
Raman active. In the case of a finite chain, in addition to the $\phi = 0$ or $\pi$ mode, a series of bands,
only progression bands, appear in the IR and/or Raman spectrum. These bands have been studied
for $n$-alkanes [8,9], $n$-alcohols [15] and fatty acids [16]. Progression bands are usually weak in inten-
sity. However, it has been pointed out that end group substitution usually enhances the intensity of
these progression bands as compared to the crystalline $n$-alkanes [11].

Vibrational modes in an all-trans methylene chain are described through a coupled oscillator
model for which the eigenvalues of the vibrational secular equation are given by [8]:

$$4\pi^2 v^2 = H_0 + 2 \sum H_m (\cos m \phi_k),$$

where $H_0$ and $H_m$ are the matrix elements of the secular determinant. $\phi$ are the phase differences
between adjacent oscillators as given by:

$$\phi_k = k \pi / (N + 1) \quad (k = 1, 2, 3, \ldots, N),$$

where $N$ is the number of oscillators in the chain, which in this instance is the number of methylene
units of the alkyl chain which are in trans registry. The progression bands appearing in the spectrum
are analyzed by assigning a $k$ value after identifying the particular mode to which it belongs.
When correctly assigned a smooth curve results from a plot of $v_k$ vs. $\phi_k$. The $v_3$ and $v_4$ modes arise
from CH$_2$ wagging and C–C stretching modes, respectively, of the methylene chain. In the $v_7$ and
$v_8$ modes coupling between the rocking and twisting modes occur. At $\phi = 0$, the $v_7$ modes is
pure rocking and $v_8$ twisting. These modes for a single methylene group are shown in Fig. 1. As
the phase angle increases the mixing of rocking and twisting occurs and finally at $\phi = \pi$ the assignment is reversed; $v_7$ is pure twisting and $v_8$ pure rocking. For the simplest possible chain imaginable, identical harmonic oscillators with nearest neighbor coupling, the integer $k$ has a well-defined meaning; it indicates the number of antinodes in the standing wave associated with each vibration. For terminally substituted alkyl chains all integral values of $k$ allowed by Eq. (2) are observable [15].

3. Experimental

$(C_nH_{2n+1}NH_3)_2PbI_4$ compounds were prepared by mixing stoichiometric quantities of PbI$_2$ and $C_nH_{2n+1}NH_2$ in hydroiodic acid and refluxing to obtain a clear yellow solution. The solution was then cooled slowly to precipitate the $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds. The compounds were washed with distilled water till the filtrate showed complete absence of acid. The chemical composition of the organic part was established by C, H, N analysis. ($n = 12$: C – 26.63%; N – 2.56%; H – 5.73%; $n = 16$: C – 33.56%; N – 2.39%; H – 6.51%). Powder X-ray diffraction patterns were recorded in the $\theta/2\theta$ Bragg–Brentano geometry on a Siemens D5005 diffractometer employing CuK$\alpha$ radiation. FT–IR spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ compounds were recorded as a KBr pellet on a Bruker IFS55 or a Perkin–Elmer spectrum 2000 spectrometer at 2 cm$^{-1}$ resolution.

4. Results and discussion

Fig. 2 shows the low angle region of the X-ray diffraction patterns of the $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12, 16, 18$) compounds. Only 00$l$ lines are observed due to the extremely high degree of preferred orientation arising from the manner in which the sample was mounted. The 00$l$ reflections can be counted as corresponding to $l = 1, 2, 3, \ldots$, or $l = 2, 4, 6, \ldots$ We have chosen the latter based on the established structure of some $(C_nH_{2n+1}NH_3)_2MX_4$ species [17]. We consider each unit cell as stacking two PbI$_4^{2-}$ slabs and four alkyl ammonium chains along the $c$ direction. The interlayer spacing ($c/2$) for the $n = 12, 16$ and 18 compounds are 25.2, 30.5 and 33.4 Å, respectively.

Fig. 3 shows the infrared spectra in the 1400–1150 cm$^{-1}$ region for the $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12, 16, 18$) compounds. The intense band at 1375 cm$^{-1}$ is due to the umbrella inversion mode of the terminal methyl groups. The remaining bands in this region arise from the wagging ($m_3$) and twisting–rocking ($v_7$) progression bands from all-trans segments of the $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12, 16, 18$) compounds. It may be seen from Fig. 3 that the number of progression bands...
observed increases with a corresponding decrease in inter band separation as the alkyl chain length increases. The twisting–rocking progression bands \( \nu_7 \) are seen as weak shoulders to the \( \nu_3 \) progression bands. These are more clearly seen for the \( n = 12 \) compound.

Infrared spectrum in the 1100–700 cm\(^{-1}\) region is shown in Fig. 4. The bands at 914 and 965 cm\(^{-1}\) are due to the C–N stretching. The rocking–twisting \( \nu_8 \) progression series as well as the C–C stretching \( \nu_4 \) bands appear in this spectral region. The \( \nu_8 \) bands appearing below 900 cm\(^{-1}\) are easily identified since this region is relatively free of

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Fig. 3. Infrared spectra in the 1400–1100 cm\(^{-1}\) region of \( (C_nH_{2n+1}NH_3)_2PbI_4 \) (\( n = 12, 16, 18 \)).

Fig. 4. Infrared spectra in the 1100–700 cm\(^{-1}\) region of \( (C_nH_{2n+1}NH_3)_2PbI_4 \) (\( n = 12, 16, 18 \)).
interfering bands. In the region above 900 cm\(^{-1}\) the presence of bands due to C–N stretching as well the C–C stretching, the \(v_4\) progression, makes identification of the individual \(v_8\) progression bands difficult. The C–N stretching bands are also known to shift the positions of the \(v_8\) progression bands above 900 cm\(^{-1}\). A tentative assignment of the \(v_4\) bands is shown in Fig. 4.

The \(v_3\) wagging progression, \(v_5\) rocking–twisting progression and \(v_7\) twisting–rocking progression series were analyzed by assigning appropriate \(k\) values (Table 1) from a comparison with the reported values for crystalline \(n\)-alkanes. The frequencies of the progression bands were then plotted as a function of \(\phi (= \pi k/(N + 1))\). The assignment of the progression bands is indicated in Figs. 3 and 4. The bands are labeled by their \(k\) value. For the \(v_3\), \(v_7\) and \(v_8\) progression series, a smooth dispersion curve was obtained only when \(N\), the number of oscillators in Eq. (2), was taken to be equal to the number of methylene units in the alkyl chains of \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4\) \((n = 12, 16, 18)\). The resulting dispersion for the \(n = 12, 16\) and 18 compounds is shown in Fig. 5. It may be seen that for a particular mode all points lie on an identical curve irrespective of the alkyl chain length. The experimental dispersion curve for the \(v_3\), \(v_7\), and \(v_8\) progressions in fact lie on the calculated dispersion curve (solid line in Fig. 5) for an infinite polymethylene chain \([8,14]\). The dispersion for \(v_4\) band is not indicated since there is ambiguity in assignment of \(k\) values because of the degeneracy associated with this mode. The fact that the experimental points lie on identical dispersion curve is evidence for the validity of the assignments of \(k\) values and consequently of the choice of \(N\) the number of coupled oscillators, in Eq. (2). These results unequivocally establish that at room temperature all methylene units, irrespective of the alkyl chain length, are in \textit{trans} registry and that the alkyl chains in \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4\) \((n = 12, 16, 18)\) adopt an all-\textit{trans} planar conformation.

References