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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Received 2 March 2002

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

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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° [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 conformation in these hybrids because of its effectiveness in determining low concentrations of disorder (*gauche* 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 quantification 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 progressions 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 intercalated 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 ν as a function of the phase angle ϕ between neighboring methylene units [8,9]. These dispersions have been compared with the theoretical dispersion curves for methylene 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 π are infrared and/or Raman active. In the case of a finite chain, in addition to the $\phi = 0$ or π mode, a series of bands, namely 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 intensity. 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]:

$$4\pi^2\nu^2 = H_0 + 2 \sum H_m(\cos m\phi_k), \quad (1)$$

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

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

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 ν_k vs. ϕ_k . The ν_3 and ν_4 modes arise from CH_2 wagging and C–C stretching modes, respectively, of the methylene chain. In the ν_7 and ν_8 modes coupling between the rocking and twisting modes occur. At $\phi = 0$, the ν_7 modes is pure rocking and ν_8 twisting. These modes for a single methylene group are shown in Fig. 1. As

Fig. 1. Wagging, twisting and rocking vibrational modes of an isolated methylene unit.

the phase angle increases the mixing of rocking and twisting occurs and finally at $\phi = \pi$ the assignment is reversed; ν_7 is pure twisting and ν_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 $00l$ lines are observed due to the extremely high degree of preferred orientation arising from the manner in which the sample was mounted. The $00l$ reflections can be counted as corresponding to $l = 1, 2, 3, \dots$, or $l = 2, 4, 6, \dots$. 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 $1400\text{--}1150\text{ cm}^{-1}$ 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 (ν_3) and twisting–rocking (ν_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

Fig. 2. X-ray diffraction patterns showing the $00l$ reflections of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12, 16, 18$).

Fig. 3. Infrared spectra in the 1400–1100 cm^{-1} region of $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ ($n = 12, 16, 18$).

observed increases with a corresponding decrease in inter band separation as the alkyl chain length increases. The twisting–rocking progression bands (ν_7) are seen as weak shoulders to the ν_3 progression bands. These are more clearly seen for the $n = 12$ compound.

Fig. 4. Infrared spectra in the 1100–700 cm^{-1} region of $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ ($n = 12, 16, 18$).

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 (ν_8) progression series as well as the C–C stretching (ν_4) bands appear in this spectral region. The ν_8 bands appearing below 900 cm^{-1} are easily identified since this region is relatively free of

Table 1

$n = 12$		$n = 18$		$n = 18$	
ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment
1327	W_6	1327	W_8	1328	W_9
1312	W_5	1313	W_7	1312	W_8
1292	W_4	1303	W_6	1304	W_7
1275	T_4	1285	W_5	1291	W_6
1265	W_3	1264	W_4	1284	T_7
1248	T_3	1249	T_4	1271	W_5
1237	W_2	1242	W_3	1254	W_4
1217	T_2	1226	T_3	1234	W_3
1205	W_1	1219	W_2	1213	W_2
1185	T_1	1204	T_2	1200	T_2
922	R_3	1196	W_1	1193	W_1
876	R_4	1183	T_1	946	R_4
834	R_5	927	R_4	881	R_6
792	R_6	886	R_5	852	R_7
763	R_7	859	R_6	822	R_8
741	R_8	825	R_7	792	R_9
720	R_{10}, R_{11}	793	R_8	768	R_{10}
		766	R_9	757	R_{11}
		755	R_{10}	742	R_{12}
		737	R_{11}	720	$R_{13}-R_{17}$
		720	$R_{12}-R_{15}$		

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 ν_4 progression, makes identification of the individual ν_8 progression bands difficult. The C–N stretching bands are also known to shift the positions of the ν_8 progression bands above 900 cm^{-1} . A tentative assignment of the ν_4 bands is shown in Fig. 4.

The ν_3 wagging progression, ν_8 rocking–twisting progression and ν_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 $\phi (= k\pi/(N+1))$. The assignment of the progression bands is indicated in Figs. 3 and 4. The bands are labeled by their k value. For the ν_3 , ν_7 and ν_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 ν_3 , ν_7 , and ν_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 ν_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 *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-*trans* planar conformation.

Fig. 5. Dispersion of the methylene wagging (ν_3), twisting–rocking (ν_7) and rocking–twisting (ν_8) modes of $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{PbI}_4$ ($n = 12, 16, 18$). Solid lines are the calculated dispersion curves for an infinite polymethylene chain [8,14]. Dotted line corresponds to the C–C stretching band progression (ν_4) which is not analyzed here.

References

- [1] D.B. Mitzi, Prog. Inorg. Chem. 48 (1999) 1.
- [2] P. Day, Philos. Trans. R. Soc. London A 314 (1985) 145.
- [3] G.C. Papavassiliou, Prog. Solid State Chem. 25 (1997) 125.
- [4] C.R. Kagan, D.B. Mitzi, C.D. Dimitrakopoulos, Science 286 (1999) 945.
- [5] T. Kataoka, T. Kondo, R. Ito, S. Sasaki, K. Uchida, N. Miura, Phys. B 201 (1994) 423.
- [6] D.B. Mitzi, Chem. Mater. 8 (1996) 761.
- [7] N.V. Venkataraman, S. Bhagyalakshmi, S. Vasudevan, R. Seshadri (communicated).
- [8] R.G. Snyder, J.H. Schachtschneider, Spectrochim. Acta. 19 (1963) 85.
- [9] R.G. Snyder, J. Mol. Spectrosc. 4 (1960) 411.
- [10] L. Senak, D. Moore, R. Mendelsohn, J. Phys. Chem. 96 (1992) 2749.
- [11] W.H. Yan, H.L. Strauss, R.G. Snyder, J. Phys. Chem. 104 (2000) 4229.
- [12] N.V. Venkataraman, S. Vasudevan, J. Phys. Chem. B 105 (2001) 7639.
- [13] J. Yano, F. Kaneko, M. Kobayashi, K. Sato, J. Phys. Chem. 101 (1997) 8112.
- [14] M. Tasumi, T. Shimonouchi, T. Miyazawa, J. Mol. Spectrosc. 9 (1962) 261.
- [15] M. Tasumi, T. Shimonouchi, A. Watanabe, R. Goto, Spectrochim. Acta 20 (1964) 629.
- [16] M. Kobayashi, F. Kaneko, K. Sato, M. Suzuki, J. Phys. Chem. 93 (1993) 485.
- [17] T. Ishihara, J. Takahashi, Phys. Rev. B 42 (1990) 11099.