From eq 12 we have $\gamma[\alpha] = \gamma[\chi_m^p] + 1/T$, and thus $\gamma[(T_1^{-1})_e]$ $\simeq \gamma[\alpha]$ at -55 °C. This indicates that the temperature variation of $(1/T_1)_e$ for ¹H is mainly due to that of α in eq 13 or, in other words, the relaxation rate increases with an increase in the number of paramagnetic electrons due to the dissociation of the spin-paired diamagnetic species with increasing temperature.

Conclusion

From the observed linear relation between the Knight shifts of ¹⁴N and ¹H, the origin of the negative shifts of ¹H of ammonia molecules in metal-ammonia solutions can be attributed to the indirect hyperfine interaction between the excess electrons on ¹⁴N

nuclei and ¹H through the N-H bond. The observed maximum in the curves for the relaxation rates of ¹⁴N and ¹H is explained by the contribution from the hyperfine interaction with the excess electrons. The average solvation numbers of the solvated electrons and monomers is determined to be $\bar{n} = 5-7$ from the present NMR data. The temperature dependence of the Knight shifts of ¹⁴N is mainly due to the temperature variation of the paramagnetic electron susceptibility over the whole concentration range studied.

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Vibrational Study of the Dynamics of *n*-Decylammonium Chains in the Perovskite-Type Layer Compound (C₁₀H₂₁NH₃)₂CdCl₄

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The perovskite-type compound $(C_{10}H_{21}NH_{3})_2CdCl_4$ ($C_{10}Cd$) exhibits two phase transitions, at 35 and 39 °C, connected with reorientations of the whole decylammonium chains and melting of the hydrocarbon parts. A temperature-dependence study of the infrared and Raman spectra of $C_{10}Cd$ and three selectively deuterated derivatives, $C_{10}Cd$ -1,1-d₂, $C_{10}Cd$ -2,2-d₂, and $C_{10}Cd-4,4-d_2$, provides evidence for coupling between the two types of chain dynamics and allows for a more precise description of the conformational disorder of decylammonium cations in the high-temperature phases.

Introduction

The perovskite-type layer compounds of general formula $(C_nH_{2n+1}NH_3)_2MCl_4$ (short notation, C_nM) have drawn the attention of numerous scientists during the past 10 years.¹⁻⁹ They crystallize in nearly isolated inorganic sheets constituted of corner-sharing MCl₆ octahedra with a divalent metal ion in their center (M = Cd²⁺, Mn²⁺, Cu²⁺, ...) which form a two-dimensional solid matrix.

The cavities between octahedra are occupied by the NH₃ polar heads of the n-alkylammonium groups which are involved in NH---Cl hydrogen bonds. Thus, the metallic sheets are sandwiched between hydrocarbon layers. Both van der Waals interactions between the alkyl ends and Coulomb forces between the positively charged organic ions and the negatively charged octahedra account for the interlayer bonding.¹⁰

These compounds show a large variety of structural phase transitions¹⁻¹⁰ governed by the dynamics of the alkylammonium

groups and by the "rotations" of the MCl₆ octahedra about the three crystallographic axes. Up to now, these structural phase transitions have been divided into two classes: (a) order-disorder transitions of the rigid alkylammonium chains and (b) conformational transitions leading to a partial "melting" of the hydro-carbon part of the chains. This second type exists only if the number of carbon atoms is large enough $(n \ge 4)$.

Of the compounds which undergo these two kinds of phase transitions, $(C_{10}H_{21}NH_3)_2CdCl_4$ ($C_{10}Cd$) has been the most extensively studied.⁹ The results of different techniques (X-ray diffraction, calorimetric, and dielectric measurements, ¹H NMR spin-lattice relaxation and second-moment investigations, ³⁵Cl and ¹⁴N quadrupole resonance spectroscopy,⁹ and ¹³C NMR measurements¹¹) have shown that $C_{10}Cd$ undergoes two first-order phase transitions at $T_{c1} = 35$ °C and $T_{c2} = 39$ °C. The structure of the low-temperature phase (LT) is ordered.

Its projections on the (\bar{b},\bar{c}) and (\bar{a},\bar{b}) planes are reproduced in Figure 1. Alkylammonium chain axes are tilted by $\pm 40^{\circ}$ with respect to the normal to the layers (\bar{c} axis) and form a zigzag arrangement along it. There are two types of inequivalent chains (A and B) which are packed together. They correspond to almost extended conformations with only a single gauche configuration about the bond between the first and the second carbon atoms for A chains and between the second and the third ones for B chains. ¹H NMR spin-lattice relaxation investigations show the existence of a slow process in the intermediate-temperature phase

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Figure 1. Low-temperature phase structure of $C_{10}Cd$ after ref 9: (a) projection along the \bar{a} axis, (b) projection along the \bar{c} axis. The two types of independent chains, A and B, and only the equatorial Cl atoms are shown.

(IMT). The NMR second-moment variations are compatible with a flipping of neighboring chains around their long axis by 90° in opposite directions. In this movement, the polar NH₃ groups also flip between two possible orientations in the cavities. Thus, the first transition at T_{c1} has been interpreted as a dynamical order-disorder transition of rigid alkyl chains.

The techniques mentioned above⁹ have also shown that the second transition is connected with a "melting" of the hydrocarbon parts of the chains which become, on the average, perpendicular to the layer. This melting corresponds to fast kink diffusion and has been confirmed by X-ray diffraction.⁹ Figure 2 shows a superposition of two sections of the electron density map parallel to the (\bar{a},\bar{c}) plane, containing the alkylammonium chains and the Cd and Cl atoms.

The hydrocarbon part of C₁₀Cd represents the first example of a smectic lipid bilayer embedded in a crystalline matrix.¹¹ Thus, the two transitions of C10Cd are similar to those observed in lipid bilayer membranes.

The aim of the present work is to obtain a more precise description of the dynamics of alkylammonium chains in the two disordered phases of $C_{10}Cd$. With this purpose, we have applied two complementary techniques, Raman scattering and infrared absorption spectroscopies, to C₁₀Cd and to three selectively bideuterated derivatives, When the dynamics are slow enough, vibrational spectroscopies provide information on the structure of the different conformers. Furthermore, with suitable deuteration of the alkyl chains, it is possible to map out their molecular conformation site by site, since the CD₂ rocking mode infrared frequencies¹²⁻¹⁵ depend on the conformation of the two C-C bonds on either side of the CD_2 group.

The electron density map of the high-temperature phase (HT)⁹ (Figure 2) shows that the average positions of the first atoms of the alkylammonium chains, C(1) to C(4), are poorly defined whereas the terminal part forms a continuous distribution parallel



Figure 2. Superposition of two sections of the electron density map of $C_{10}Cd$ perpendicular to the \bar{b} axis in the high-temperature phase (published in ref 9). One section contains the Cd, axial Cl, N, and C atoms whereas the other section contains the equatorial Cl atoms. The two symmetry equivalent and statistically distributed chains are on both sides of the mirror plane transforming the left- to the right-hand side of the figures.

to the \bar{c} axis and is split into two symmetry equivalent and statistically distributed chains on both sides of the (\bar{b},\bar{c}) mirror plane; these correspond to the two positions of the NH_3 heads. Because of the above characteristics of the electron density map, we have selected the compounds deuterated on the first, second, or fourth carbon atom.

In the first part of our discussion, vibrational spectra of the four compounds in the ordered low-temperature phase are analyzed. Then, the spectroscopic evidence leading to a better understanding of the dynamics of the cation in the two disordered phases is presented; this allows for a more precise description of the disorder in the alkylammonium layers.

Experimental Section

A. Chemical Synthesis. Compounds $C_{10}Cd$ were prepared following the method described by Kind and Roos:¹⁶ mixing of decylammonium chloride with cadmium chloride in ethanol led to the formation of the complex which precipitated; after separation, it was recrystallized several times from methanol before use. Decyl and decyl- d_2 -ammonium chlorides were obtained by bubbling gaseous HCl through decylamine (Fluka; purity ≥99%) or decyl- d_2 -amines.

The preparation of $C_{10}Cd-1$, $1-d_2$, $C_{10}Cd-2$, $2-d_2$, and $C_{10}Cd-2$ 4,4- d_2 complexes thus required the synthesis of the corresponding deuterated decylamines.

(a) Synthesis of $C_9H_{19}CD_2NH_2$. This amine was obtained by (1) reduction of the commercial decanenitrile (Aldrich, stated purity >99%) by LiAlD₄ (from CEA, isotopic purity >98%), (2) hydrolysis of the reaction mixture by sulfuric aqueous solution, and then (3) neutralization with sodium hydroxide solution (10 **M**).

$$C_{9}H_{19}CN \xrightarrow{(1) \text{ AlLiD}_{4}}_{(2) \text{ H}_{5}SO_{4}} C_{9}H_{19}D_{2}NH_{2}$$
(3) NaOH

The isotopic yield was superior to 97%.

(b) Synthesis of $C_8H_{17}CD_2CH_2NH_2$. Treatment of decanoic acid with 1% NaOD at 200 °C for 72 h following Tulloch¹⁷ led to the formation of α -deuterated decanoic acid. Reaction with chlorosulfonyl isocyanate followed by N,N-dimethylformamide¹⁸

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TABLE I: Force Constants^a of the NH₃ Polar Head of C₁₀Cd^c



^{*a*} Force constant notations are taken from ref 21b. ^{*b*} Force constant units: stretch, mdyn/Å; stretch-bend, mdyn/rad; bend and torsion, mdyn·Å/rad². ^{*c*} Only the interactions different from the corresponding ones in the Snyder's force field of the *n*-paraffins are reported.

transformed this acid into the corresponding nitrile which was reduced by lithium aluminum hydride to yield decyl-2,2- d_2 -amine (isotopic yield >95%).

(c) Synthesis of $C_6H_{13}CD_2(CH_2)_3NH_2$. The corresponding acid, $C_6H_{13}CD_2(CH_2)_3COOH$, was prepared from octanoic acid according to the method described by Tulloch¹⁷ for selective deuteration of fatty acids. Then it was converted into the nitrile following the method described by Spener and Mangold¹⁹ (cf. also ref 18); the nitrile was finally reduced into amine by LiAlH₄.

Mass spectrometric investigations gave an isotopic yield of 90% of dideuteration $(C_6H_{13}CD_2(CH_2)_3NH_2)$ and 10% of monodeuteration $(C_6H_{13} CHD(CH_2)_3NH_2)$.

B. Experimental Procedures. Raman spectra of the powdered specimen were recorded from 5 to 3100 cm^{-1} with a Coderg T800 spectrometer and a Spectra-Physics Model 171 argon ion laser. The 514.5-nm line was used with a power less than 700 mW. The sample temperature was regulated within ± 0.5 °C with a Coderg CRN2 continuous nitrogen flow cryostat.

Infrared spectra were measured with a Perkin-Elmer 180 spectrometer. Operating parameters were chosen to provide a resolution of $1-2 \text{ cm}^{-1}$. The temperature of the cell, cooled by a continuous nitrogen flow, was controlled to ± 0.5 °C. Infrared spectra were recorded with both powdered and monocrystalline samples. The powdered samples consisted of a dispersion of the compound in Nujol or fluorolube mull sandwiched between CsI windows. The monocrystalline ones were small platelets of $5 \times 5 \times l \text{ mm}^3$ (with *l* varying from 0.1 to 0.5 mm). They were studied with the source polarization parallel to either the \bar{a} or \bar{b} crystallographic axis.

Spectroscopic Study of the Structure of $C_{10}Cd$ in the Ordered Phase

A detailed analysis of the spectra observed in the low-temperature phase is needed to obtain a good understanding of the decylammonium ion dynamics in the two disordered phases.

According to X-ray diffraction the structure of the low-temperature phase is described by the space group $P2_1/n$; the factor group is isomorphic to the C_{2h} point group, and the number of molecular entities in the unit cell is four. The two types of chains (A or B) possess C_1 symmetry, and thus each of the 99 vibrational fundamental frequencies of the individual decylammonium cations gives rise to a component in each of the symmetry species of the C_{2h} factor group. Consequently, each mode is infrared and Raman allowed.

In order to facilitate the interpretation of the spectra, we have performed a normal-coordinate calculation based on the traditional solution of the secular equation for the two conformations A and B of the decylammonium chain. The standard tetrahedral geometry is assumed, with C-C, C-H, N-C, and N-H bond lengths equal to 1.54, 1.093, 1.51, and 0.97 Å, respectively. For the hydrocarbon part, the force field used is that derived by Snyder²⁰

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Figure 3. Infrared survey spectra of $C_{10}Cd$ between 300 and 1300 cm⁻¹ in the three phases. Progression bands corresponding only to A or B chain vibrations are labeled in the low-temperature phase spectrum.

TABLE II: Characteristic Frequencies (ν_{obsd} , cm⁻¹) of A and B Chains and Corresponding Assignments

<u> </u>	A		<u>B</u>			
1316	W	(IR, R)				
863	P ₆	(IR, R)	844	P ₅	(IR, R)	
832	P ₅	(IR, R)		-	,	
810	P_4	(IR)	784	P₄	(IR)	
			537	LAM	(IR)	
515	LAM,	(IR)		C C	. ,	
481	LAM ₄	(IR)	474	LAM₄	(IR)	
374	LAM ₃	(IR)	362	LAM ₃	(IR)	
344	LAM ₂	(IR)		5		

for liquid *n*-paraffins. For the NH₃ group vibrations, we have adjusted the force constants proposed by Destrade et al.^{21a} for glycylglycine hydrochloride. Table I contains those NH₃ force constants and interactions that were chosen to be different from the corresponding ones in Snyder's force field.

X-ray diffraction shows that, in the low-temperature phase, the chain configurations are nearly extended. Thus, it is useful to compare the spectra of the hydrocarbon chains with those for solid *n*-alkanes. These vibrations may be divided into two types: nonlocalized modes which involve the entire chain and vibrations which correspond to motions localized in definite points of the cation.

(a) Nonlocalized modes give rise to progression bands which are mainly observed in the infrared spectrum. From previous experiments, ^{14,15} it is known that the most characteristic progressions of bands in the *n*-paraffins are those associated with the CH₂ rocking motions (denoted P_k) and CH₂ wagging motions (W_k). The integer subscript k which is used to label each mode in a progression is related to the relative phase difference between the motions of adjacent methylene groups along the chain.²² Due to the nonlocalized nature of this type of vibration, the number, the frequency, and the intensity of the bands are dependent on both chain length and chain conformation.^{14,15,22}

Figure 3 displays an infrared survey spectrum of hydrogenated $C_{10}Cd$ between 1350 and 300 cm⁻¹. By comparing this spectrum with the results of normal-coordinate calculations and with the infrared spectrum of the $C_{10}Mn$ compound whose chains are all in the B configuration,²³ it is possible to discriminate between progression bands of A and B chains. A summary of these assignments is reported in Table II. The modes whose frequencies are most sensitive to chain conformation are those associated with the CH₂ rocking and wagging motions as in *n*-paraffins^{14,15} and

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Figure 4. Raman spectra of $C_{10}Cd$ in the three phases between 1000 and 1180 cm⁻¹.



Figure 5. Low-frequency Raman spectra of $C_{10}Cd$ in the three phases. In particular, the temperature dependence of the LAM (near 230 cm⁻¹) is evidenced.

with the skeletal deformations (labeled LAM_k).

The most intense bands in the Raman spectrum of long *n*-alkyl chains correspond to the limiting k = 0 modes of an infinite chain. This is also true in the Raman spectrum of C₁₀Cd in its low-temperature phase: characteristic bands of trans planar chains are observed, for instance, at 1063, 1143, and 1173 cm⁻¹ (Figure 4). However, the frequency of the longitudinal acoustic mode (LAM-1), 230 cm⁻¹ (Figure 5), is higher than expected for an all-trans chain (209 cm⁻¹) or for chains of the same length engaged in hydrogen bonds, such as *n*-decylamine (213 cm⁻¹) or decylammonium chloride (217 cm⁻¹); thus, this high value is mainly due to a conformational effect and is consistent with the existence of a gauche conformation in the vicinity of the NH₃ polar head.²⁴

(b) The second type of vibration involves motions which are localized in part of the chain. Some examples can be found in the NH_3 deformation vibrations at 1589 and 1488 cm⁻¹ (Figure 6) and in methyl vibrations such as the rocking mode at 890 cm⁻¹ and the symmetric deformation at 1376 cm⁻¹. The frequencies of these modes are only dependent on local conformation and are practically independent of chain length. Strong polarization effects observed for some of these bands (at 890 cm⁻¹ for instance) confirm the immobility of the corresponding part of the chain.

The CD₂ rocking vibrations of selectively deuterated compounds are also localized modes. The infrared spectrum of $C_{10}Cd-1,1-d_2$ shows two absorptions at 654 and 712 cm⁻¹ (Figure 7). This



Figure 6. Temperature dependence of the infrared spectrum (1400-1600 cm^{-1}) of monocrystalline C₁₀Cd.



Figure 7. Temperature dependence of the infrared spectra (in transmittance) in the range of the CD₂ rocking vibrations for (a) $C_{10}Cd-1,1-d_2$, (b) $C_{10}Cd-2,2-d_2$, and (c) $C_{10}Cd-4,4-d_2$ samples.

confirms the existence of two types of chains in which the N-C and the first two C-C bonds can define a trans or gauche configuration. The gauche conformation is evidenced by the absorption at 712 cm^{-1} and the trans one by that at 654 cm^{-1} . The infrared spectrum of $C_{10}Cd-2, 2-d_2$ at room temperature is more complex. Instead of the two absorptions at about 650 and 660 cm⁻¹ predicted by normal-mode calculations for B and A chains, one observes three bands, one rather intense at 665 cm^{-1} and two very weak at 655 and 630 cm⁻¹. The weak absorption at 630 cm⁻¹ vanishes at -50 °C and could be due to a small number of TT sequences; however, as the X-ray structure of this ordered phase at room temperature indicates the presence of A and B chains only, it seems more sensible to attribute it to a difference band.²⁵ Because of the great difference in the intensities of the two other absorptions, it is hazardous to assign them to respectively A and B chain vibrations.¹⁵ It seems more reasonable to attribute the peak at 665 cm⁻¹ to the CD₂ rocking vibration of both chains. The weak feature at 655 cm⁻¹ and the one near 660 cm⁻¹ in the LT spectrum of $C_{10}Cd-4,4-d_2$ (Figure 7b,c) come probably from a CHD impurity vibration.¹³ The $C_{10}Cd-4,4-d_2$ infrared spectrum shows a clear, sharp, and isolated band at 622 cm⁻¹ as expected when the conformations of the two C-C bonds on either side of the CD_2 group are trans.¹²

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Figure 8. Raman spectra of $C_{10}Cd$ in the three phases (a) in the methylene deformation region and (b) in the C-H bond stretching region.

In conclusion, the study of both localized and nonlocalized modes in the spectra of $C_{10}Cd$ and its three selectively deuterated derivatives in the low-temperature phase confirms the structure of the alkylammonium chains determined by X-ray diffraction.

The spectra of this phase are typical of an ordered solid; indeed, the low-frequency Raman spectrum displays well-defined lines. Moreover, some bands are split into two components, owing to intermolecular coupling;²⁶ examples in the infrared spectrum are the absorptions at 720, 1460, and 1480 cm⁻¹ corresponding to the CH₂ rocking, CH₂ deformation, and NH₃ symmetric deformation modes, respectively. Such splittings show the existence of more than two molecules in the unit cell, a result also in agreement with X-ray data.

The spectral domains corresponding to the CH stretching (2830-3000 cm⁻¹) and bending (1420-1480 cm⁻¹) vibrations look like those of solid *n*-paraffins. The Raman spectrum is more informative (Figure 8). The scattering wing on the high-frequency side of the 2846-cm⁻¹ line ($\nu_s(CH_2)$) is due to intermolecular forces.27-29 Among the poorly defined maxima observed at frequencies higher than 2882 cm⁻¹ ($\nu_a(CH_2)$, two have been assigned to methyl stretching vibrations (2930 and 2961 cm⁻¹); the other ones are due to an intramolecular Fermi resonance between $\nu_{\rm s}({\rm CH}_2)$ and the quasi-continuum of the bending, $\delta(\phi_k)$, progression bands overtones.³⁰ The line at 1424 cm⁻¹ is a component of the factor group split $\delta(0)$ vibration; the other component is split into two lines at 1440 and 1463 cm⁻¹ by a Fermi resonance with the combination of the two $r(CH_2)$ vibrations at 719 and 726 cm⁻¹.27

Thus, the study of these spectral regions gives further evidence for the existence of inter- and intramolecular coupling in an almost extended chain.27,28,30

Changes in the Vibrational Spectra of the Two Disordered Phases

A. Intermediate Temperature Phase. At first glance, vibrational spectra of the intermediate temperature phase are not strongly different from those observed in the low-temperature phase. The Raman spectrum of $C_{10}Cd$ is always typical of a solid containing chains in an extended configuration. Furthermore, no new bands are observed which would indicate the appearance of a conformer different from A and B chains.

The changes in the spectra on going from the LT to IMT phases are of two types: (1) The factor group splitting decreases, and there is a loss of polarization for most of the localized modes, compatible with the occurrence of rigid chain reorientational motions. (2) The intensities of all the bands specifically assigned to A chain vibrations are reduced.

(a) Factor group splittings of the nonlocalized modes such as the 720-cm⁻¹ rocking fundamental or the CH₂ deformation modes near 1460 cm⁻¹ are greatly reduced in the IMT phase infrared spectra. As the distance between two neighboring chains is approximately the same as in the low-temperature phase (a and blattice parameters are nearly constant⁹), the reduction of the factor group splittings of nonlocalized modes indicates a relative disorder in chain orientations; this is compatible with the onset of $\pm 90^{\circ}$ cation rotations about their longitudinal axis as evidenced by ¹H NMR spin-lattice relaxation and second-moment investigations.9 However, the wing on the high-frequency side of the 2846-cm⁻¹ line does not weaken significantly, which shows that crystal effects on $\delta(0)$ remain important. The frequencies of the NH₃ deformations decrease; NH---Cl bonds become weaker.

The persistence of the splitting into two components of the NH₃ symmetric deformation mode (near 1480 cm⁻¹) indicates that the motions of the two polar heads in the same cavity on each side of a layer are correlated.

The bands characteristic of $r_{\parallel}(NH_3)$ (near 1250 cm⁻¹) and of $r(CD_2)$ of B chains in $C_{10}Cd-1$, $1-d_2$ are no longer polarized, which confirms the vanishing of the octahedra distorsion around the \bar{c} axis (Figure 1b); the same behavior is observed for the bands corresponding to $r_{\parallel}(CH_3)$ of the A chains and to some $\nu(C-C)$ vibrations. This is in agreement with the existence of a statistical symmetry plane, containing the long axis of the chains, since the $\pm 90^{\circ}$ rotation shifts the dipolar moments directed along \bar{a} in the (b,\bar{c}) plane.

(b) The second characteristic feature of IMT phase vibrational spectra is the weakening in the intensity of all the bands specifically assigned to A chain vibrations. This phenomenon is observed both in Raman and infrared spectra of $C_{10}Cd$ and is particularly well illustrated by the CH₂ wagging-twisting modes at 1316 and 1286 cm⁻¹, the CH₂ rocking progression bands at 863, 832, and 810 cm⁻¹, and the skeletal deformation modes at 515, 481, 440, 374, and 344 cm⁻¹.

The spectra of the selectively deuterated derivatives also exhibit similar features. The most direct evidence of the decrease in A chain concentration is given by the CD₂ rocking mode of $C_{10}Cd-1, 1-d_2$. The weakening of the 712-cm⁻¹ band intensity is reproduced in Figure 7a. In order to evaluate the relative concentrations in A and B chains, we have determined the integrated intensity of the isolated 654-cm⁻¹ band which corresponds to the trans bond between the first two carbon atoms in B chains. To follow the temperature dependence of this intensity, we have chosen the NH₃ symmetric deformation peak intensity as an internal reference. Under these conditions, one measures a relative increase of 50% in the 654-cm⁻¹ band intensity in the intermediate-temperature phase; there are about 75% B chains and 25% A chains in this phase.

The other techniques applied to the study of the intermediate phase of $C_{10}Cd^9$ have shown that the two types of octahedral cavities which contain A and B chains in the LT phase remain symmetrically inequivalent in the IMT phase for which the space group Pmnn has been proposed. The average concentrations of A and B chains determined above are not compatible with this structure, unless one assumes the existence of an internal motion which allows the interconversion of A and B conformers, at least in the cavities which contained A chains in the low-temperature phase.

In summary, this vibrational study of the IMT phase gives evidence of a beginning of melting in the first part of decylammonium cations in addition to the $\pm 90^{\circ}$ rotations of the whole chains as previously revealed by NMR investigations.

B. High-Temperature Phase. In the high-temperature (HT) phase, melting of the hydrocarbon part of cations is clearly shown by the analysis of the Raman and infrared spectra.

(a) The Raman spectrum of $C_{10}Cd$ no longer shows the features characteristic of almost extended chains:

(1) The longitudinal acoustic mode disappears and only a broad and weak band is observed near 240 cm⁻¹ (Figure 5). Never-

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TABLE III: Different Possible Conformers of the Decylammonium Chain under the Assumption of One Kink in a Cation

Ν	C ₁	C ₂	С3	C ₄	C ₅	C ₆	C ₇	C ₈	C, (C ₁₀
	G T G	T G T	T T T	T T T	Т Т G'	T T T	G' T T	Т G' Т		p_1 p_2 p_3
	T T T	G T T	T G T	T T G	T T T	G' T T	T G' T	Т Т С'		P4 P5 P6
	G T T	T G T	G' T G	Т G' Т	T T G'	T T T	T T T	T T T		р ₇ р ₈ р9
	T T T	T T T	T T T	G T T	T G T	G' T G	T G' T	T T G'		$p_{10} \\ p_{11} \\ p_{12}$

theless, its frequency and its half-width are still smaller than those of liquid undecane;²⁴ the number of chain conformers is probably lower in C_{10} Cd, and the decylammonium ions possess a more extended "averaged" conformation.

(2) Limiting k = 0 mode bands, which are the only ones observed in long trans planar chains, broaden because of the overlapping of bands from different conformers (Figure 4). Their intensity decreases with respect to that of some other peaks which originate from gauche (G) structures¹⁴ (for instance, the 1076-cm⁻¹ band).

(3) Further evidence of numerous G bond structures can be found in the decrease in the intensity of the 1463-cm⁻¹ shoulder, which is due to intramolecular coupling of trans (T) structures.²⁶ In addition, the antisymmetric CH₂ stretching mode band at 2885 cm⁻¹ merges into a broad scattering near 3000 cm⁻¹; intermolecular forces are greatly modified.²⁹

(b) The infrared spectra of $C_{10}Cd$ and its three selectively deuterated derivatives allow us to obtain more precise information on the positions of G structures. Progression bands due to nonlocalized rocking, wagging, or skeletal deformations tend to overlap and form a continuous background. Thus, most peaks observed originate from localized modes. Moreover, it has been shown²⁰ that, in liquid *n*-alkanes, some bands in the methylene wagging region result from localized vibrations associated with short sequences of bonds having a specific conformation. For example, the band at 1342 cm⁻¹ is assigned to an end (near the methyl) gauche structure vibration, the shoulder at 1367 cm^{-1} and the broad band at 1306 cm⁻¹ have been shown to result from GTG' sequences, and the infrared peak at 1353 cm⁻¹ is due to unstrained GG structures. However, both the frequency and the intensity of CH₂ wagging progression bands are perturbed by inductive effects of highly polar end groups;³¹ we have thus performed a normal-mode calculation on chain conformations belonging to these types of structures, in order to evaluate to what extent the presence of the NH₃ disturbs the frequency of localized vibrations. We find that they are very slightly shifted. Moreover, we have observed that all these modes (except that at 1367 cm⁻¹) contain NH₃ contributions which can enhance their intensity.³¹ In fact, no absorption at 1367 cm⁻¹ is observed in the $C_{10}Cd$ high-temperature phase infrared spectrum whereas the strong and broad band at 1306 cm⁻¹ supports the existence of kinks $(GT_{2n+1}G')$ structures) in the hydrocarbon part of the decylammonium chains (Figure 9).

In contrast with what is encountered in *n*-paraffins, no absorption associated with specific sequences of bond structures has been observed near 1353 or 1342 cm⁻¹ (the one at 1339 cm⁻¹ also exists in the LT and IMT phases spectra and does not seem conformation dependent). So, the probability of GG or end gauche structures in *n*-decylammonium chains is very small. Thus, this vibrational spectroscopic analysis provides evidence for the presence of "kinks" in the conformationally disordered high-temperature phase of C_{10} Cd, in agreement with the X-ray diffraction pattern which shows that the longitudinal axis of decylammonium ions is perpendicular to the layer planes in the HT phase.



Figure 9. Temperature dependence of the infrared spectrum (1200-1400 cm⁻¹) of monocrystalline C_{10} Cd. Two polarizations are shown: along the *b* axis (solid line) or along the *a* axis (dashes). Characteristic regions of defect structures (in *n*-paraffins) are indicated in the high-temperature phase spectrum.

A more accurate localization of these defects is obtained through a study of the CD₂ rocking modes in the selectively deuterated compounds. In the high-temperature phase infrared spectrum of $C_{10}Cd-1$, $1-d_2$, the 712-cm⁻¹ band due to the first gauche structure (near the NH₃ polar head) has completely vanished (Figure 7a). By measuring the integrated intensity of the 654-cm⁻¹ absorption and using the 1480-cm⁻¹ peak as internal standard, one finds that the probability of a gauche conformation between the first and the second carbon atoms is lower than 5%. The analysis of the $C_{10}Cd-2,2-d_2$ spectrum (Figure 7b) is more complex, owing to the occurrence of the difference band in the vicinity of the absorption due to a TT structure at the beginning of the chain (whose frequency is expected between 622 and 630 cm⁻¹). The existence of TT sequences is clearly demonstrated by the strong intensity increase of the 630-cm⁻¹ absorption. However, as the intrinsic intensity of this band is unknown, the TT or TG concentrations must be evaluated by intensity measurements at 660 cm^{-1} . Under the assumption that the intensity of the weak 655-cm⁻¹ absorption is constant, one can estimate a relative decrease of the 660-cm⁻¹ band intensity by about 25% (the NH₃ symmetric deformation mode at 1480 cm⁻¹ is always taken as an internal standard). The small shift of the TG band frequency is surely due to geometrical changes around the G or T structures,¹² owing to a modification of the cavities. The CD_2 rocking mode spectrum of $C_{10}Cd-4, 4-d_2$ (figure 7c) is very similar to that of liquid *n*-alkanes.^{14,15} Here, the NH₃ polar head is too far from the deuterated methylene group to modify the frequency and the intensity of the rocking mode. Thus, if one assumes that the intrinsic intensities of the TT and TG vibrations are almost equal as in *n*-alkanes,¹⁵ the observed intensities of 622- and 650-cm⁻¹ bands afford a direct measure of the relative concentrations of TT and TG structures. The evaluation of the TT band weakening

⁽³¹⁾ Zbinden, R. "Infrared Spectroscopy of High Polymers"; Academic Press: New York, 1964.

relative to the NH₃ absorption leads to the same values of relative concentrations: $C_{\rm TT} \sim 70\%$ and $C_{\rm TG} \sim 30\%$.

At this stage, we have demonstrated by vibrational spectroscopy that the defects of alkylammonium chains are "kink structures". As deduced from X-ray diffraction measurements of the c lattice parameter,⁵ one can assume that only one kink exists in a chain, so that only the 12 configurations of the alkylammonium cations summarized in Table III are possible.

As no end gauche structure has been observed, the possibilities of the 2nd, 6th, and 12th configurations are related by the following equation:

$$p_2 + p_6 + p_{12} \sim 0$$

There are less than 5% of G structures near NH₃ polar groups:

$$p_1 + p_3 + p_7 \le 5\%$$

About 25% of chains possess a TT sequence around the second carbon:

$$p_5 + p_6 + p_9 + p_{10} + p_{11} + p_{12} \sim 25\%$$

About 30% of chains possess a TG or GT sequence around the 4th carbon atom:

$$p_5 + p_6 + p_7 + p_8 + p_9 + p_{10} \sim 30\%$$

These four equations lead to the following ones:

$$p_4 + p_8 \sim 70\%$$

 $p_4 + p_{11} \sim 65\%$

with $p_8 \le 30\%$ and $p_{11} \le 25\%$.

It turns out that the cation configuration (TGTTTG'TT) is greatly favored in the HT phase of $C_{10}Cd$ since it occurs at least two times out of five. The first part of the alkylammonium chain is relatively rigid since the first structure is T most of the time and the second one is G about three times out of four. The middle of the chain seems more flexible, and despite of what is observed in lipid bilayered membranes or *n*-alkanes, no end gauche structure is found at the decylammonium tail.

Conclusions

From this vibrational study, new information about the cation structure in the two disordered phases of $C_{10}Cd$ has been obtained. Indeed, as the correlation times governing the dynamics of the decylammonium chain are relatively long ($\tau_c \ge 10^{-9}$ s), each cation

position and conformer have been observed, and using selective deuterations, we have determined the average local molecular structure of the hydrocarbon part of the chains.

For the low-temperature phase, we have been able to confirm the molecular structure of the decylammonium ion as proposed from X-ray results.⁹ Infrared and Raman spectra of this phase are characteristic of an ordered solid in which alkylammonium chains exhibit two almost extended configurations with only one gauche structure either between the first two carbon atoms or between the second and the third ones.

Vibrational spectra of the IMT phase give evidence of a rotation around the first C-C bond transforming A into B chains. An interconversion of A and B conformers, at least in the cavities which contain A chains in the LT phase, is suggested in order to account for the structure proposed from previous studies.⁹ Since melting also occurs at the same time as reorientational motions in other long-chain compounds of the series,³² it seems sensible to expect a coupling of the two types of dynamics.

In the high-temperature phases, the chain flexibility is transferred to its middle part. The three C-C or C-N bonds of each chain end are rigid and form a trans structure. Between them, kink motions take place. One of these configurations (TGTTTG'TT) seems to be favored since it occurs between two and three times out of five.

We thus conclude that the nature of the melting of hydrocarbon parts in these bidimensional compounds is strongly dependent on the interactions of the alkylammonium chains with the semirigid inorganic cavities. As a matter of fact, a different conformational disorder takes place in *n*-alkanes or in lipid biomembranes where the tails are more flexible. Further results on compounds of this series with variable chain length have been obtained. They will be published in due course.

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Infrared Spectroscopy of Cu/ZnO Catalysts for the Water-Gas Shift Reaction and Methanol Synthesis

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A bidentate formate species adsorbed on a zinc site was a common intermediate in the water-gas shift and methanol synthesis reactions on Cu/ZnO catalysts. Adsorbed formaldehyde and methoxy species were identified as additional intermediates in the reaction pathway for methanol synthesis. An adsorbed carbonyl species on a reduced copper site was an activating agent for the reduction of formate groups to formaldehyde and methoxy species at 200 °C.

Introduction

The water-gas shift reaction

 $CO + H_2O = CO_2 + H_2$

and the methanol synthesis reactions $CO + 2H_2 = CH_3OH$

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

are catalyzed by copper-zinc mixed metal oxides having similar compositions. During methanol synthesis conditions, all three reactions can occur simultaneously on the catalyst surface. In spite of extensive studies of these catalytic systems, very little is known about the elementary reaction steps, the adsorbed inter-

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