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Langmuir-Blodgett deposition selects carboxylate headgroup coordination

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Infrared reflection-absorption spectroscopy results on stearic acid Langmuir monolayers containing Mn, Co, and Cd ions show that on the water surface, the ions induce unidentate and bidentate (both chelate and bridged) coordination in the carboxylate headgroup with some trace of undissociated acid. Moreover, with Cd and Mn ions in subphase, the preferred coordination is found to be unidentate, whereas for Co, bidentate chelate is most preferred. After transfer onto amorphous substrate, not all coordinations are found to exist in the same ratio for the deposited metal stearate monolayers. More specifically, after transfer, Mn is found to coordinate with the carboxylate group as bidentate chelate, Cd as unidentate and bidentate bridged (with unidentate as the preferred coordination), and Co as preferably bidentate bridged (although all coordinations are present). Results suggest a specific interaction in each case, as the metal-carboxylate pair at the water surface is transferred to the substrate surface during Langmuir-Blodgett deposition.

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I. INTRODUCTION

The Langmuir-Blodgett (LB) technique of deposition of amphiphilic monomolecular layers on a water surface (Langmuir monolayers) has been expected to cause modification to the structure of these monolayers due to the reorganization of the molecules on the vertically moving substrate through the horizontally arranged monolayer [1]. For fatty-acid monolayers it has been observed to change the in-plane two-dimensional lattice structure quite significantly [2]. Studies of major in-plane structural rearrangements [3–6] for free fatty acids include works by Brzezinski and Peterson [3], Shih *et al.* [4], and Steitz *et al.* [5], all of whom found differences between the known structures of the monolayers on water and the structures observed on solid substrates. Works on structural rearrangements of fatty acid monolayers [7–9] and metal-bearing fatty acid monolayers [10,11] have also been extensively carried out by various groups. These structural rearrangements indicate a change in molecular conformation [12] which may be due to either supramolecular interactions or chemical bonding or both. Our aim is to investigate which out of these occur during the transfer process in LB deposition. A simple way to understand this is to study the metal-carboxylate coordination at the water surface in Langmuir monolayers and at the substrate surface in LB films. If the preference only changes from one to the other, the change is due to supramolecular forces, while emergence of new coordinations would suggest a change in bonding. Various methods have been employed to clarify the microscopic structure of Langmuir monolayers. Among those, infrared spectroscopy [13] has the advantage of being a fast and nondestructive technique, which is sensitive to changes in the molecular conformation.

In this paper we present infrared reflection-absorption spectroscopy (IRAS) results on stearic acid Langmuir monolayers on water containing manganese, cobalt, and cadmium ions and on monolayers transferred from these subphases onto amorphous substrate via LB deposition. The focus of our investigation was the carboxylate headgroup coordination on the water surface for different metals and the change in this coordination on LB deposition. We have previously shown from x-ray reflectivity analysis [14,15] that in LB monolayers and multilayers of Mn- and Co-bearing stearic acid this coordination is predominantly bidentate while it is unidentate in Cd-bearing acid. In this work, through direct IRAS measurement, we investigate the coordinations of the metal ions with the carboxylate moiety and relate them to the structures of these amphiphilic monolayers both on water and on the substrate. Moreover, we have tried learn what effect the transfer process has on these metal carboxylate complex formations.

II. EXPERIMENTAL DETAILS

Fourier transform infrared (FTIR) spectroscopy of Langmuir monolayers (LMs) of stearic acid (StA) at the water surface in the presence of three different subphase metal ions (i.e., Cd^{2+}, Mn^{2+}, and Co^{2+}) was carried out in reflection mode. For this, a mini Langmuir trough (Specac) attached to the reflection mode accessary of the FTIR spectrometer (Spectrum GX, Perkin-Elmer) was used. At first, 0.5 mM chloride solutions of the respective metal ions were prepared in beakers using Milli-Q water (with a resistivity of 18.2 MΩ cm). The pH was adjusted to 6–6.5 by addition of sodium bicarbonate ($NaHCO_3$, Merck, 99%). The solutions were then poured in the trough to form the subphase. The dissociation of the carboxylate group is dependent on the type of subphase ions present, specifically on their association constants with the carboxylate ion [16,17]. In order to study the metal-headgroup interactions at the air-water interface and during transfer to the substrate, we have maintained the same pH used as for multilayer deposition of these metal stearates [14,15], as a change in the latter would also affect the metal-carboxylate bonding [18] and hence our results.

Next, stearic acid ($C_{17}H_{35}COOH$, Sigma-Aldrich, 99%) [spreading volume (SV) $= 8\ \mu$l] was added from a 0.5 mg/ml chloroform solution, to form the monolayer. SV was calculated such that when compressed to a particular barrier position (i.e., for a known trough area), the stearic acid monolayer

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is in its most condensed phase (area per molecule ~21 Å^2). This is because the mini trough did not have a surface pressure measuring setup, and the pressure could only be obtained from the surface pressure versus molecular area (π-A) isotherms of stearic acid with the respective metal ions in subphase (taken separately in a KSV-5000 Langmuir trough). However, in order to check that the aforementioned barrier positions corresponded to the condensed phase of the isotherms (surface pressure ~30 mN/m), the surface pressures of the monolayers were separately measured at identical conditions using the pressure balance of a different LB trough (NIMA). The measured values were 28.5, 30.4, and 31.3 mN/m for StA with Cd, Mn, and Co ions in subphase, respectively, which were consistent with the values of surface pressure inferred from area/molecule measurements. For clarity, the StA monolayers in the presence of Cd, Mn, and Co ions are called Cd-StA, Mn-StA, and Co-StA, respectively. FTIR spectra of the three M-StA (M = Cd, Mn, and Co) were taken under specular conditions with an incident angle of 70° from normal, at a resolution of 4 cm^{-1}, in order to obtain the maximum count. A mercury cadmium telluride (MCT) detector was used to maintain a high signal-to-noise (SNR) ratio. Using the KSV 5000 LB trough, single monolayer (ML) films of cadmium stearate (CdSt), manganese stearate (MnSt), and cobalt stearate (CoSt) were deposited on hydrophilic silicon (100) substrate by the LB technique [19] from their respective Langmuir monolayers, the latter being formed under the same conditions as mentioned above. Details of the film deposition process are given elsewhere [14]. The three 1-ML films were deposited at a surface pressure of 30 mN/m (i.e., area/mol ~21 Å^2) at 20 °C at a dipping speed of 3 mm/min by an upstroke of the substrate from water to air through the interface. FTIR spectra of the three films were taken in transmission mode at a resolution of 4.0 cm^{-1} using the MCT detector.

III. RESULTS AND DISCUSSION

A. Metal-carboxylate coordinations

Metal cations can bind to the carboxylate group in several ways. The first is ionic binding, where the cation does not share electrons with the carboxylate group. The second is the unidentate type, where a metal atom covalently binds to one of the carboxylate oxygen. The third is the bidentate chelate type, where a metal atom binds covalently to both oxygen atoms of the carboxylate group. The fourth is the bidentate bridging type, where two different metal atoms bind covalently to each of the oxygen atoms of the carboxylate group. Deacon and Phillips [20] have pointed out that the bonding type of metal acetates in the solid state can be classified by the difference (Δ) between the antisymmetric and symmetric COO stretching frequencies, i.e., Δ(unidentate) > Δ(ionic) (164 cm^{-1}) [21] > Δ(bidentate bridging) > Δ(bidentate chelate). Typically, the value of delta for bidentate bridging coordination is somewhat close to that for a dissociated carboxylate ion Δ (COO$^-$) [21,22], such that the delta values of bidentate chelate (unidentate) coordination are less (greater) than Δ (COO$^-$).

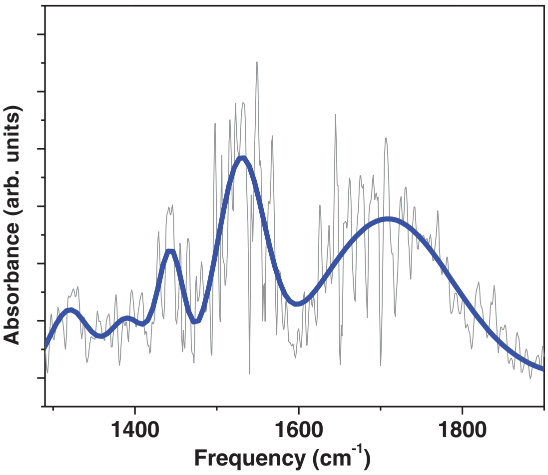

FIG. 1. (Color online) Portion of FTIR spectra (thin gray line) of stearic acid monolayer on water showing the carboxylate stretch modes. The bold blue line is the composite of Gaussian fits to individual peaks in the data.

B. Headgroup coordinations at the water surface

FTIR spectra of StA, Cd-StA, Mn-StA, and Co-StA were analyzed (after performing a Kramers-Kronig correction) to obtain information about the different metal-carboxylate coordinations occurring at the water surface. For that, the typical carboxylate (COO) stretching frequency region (~1300 to 1900 cm^{-1}) of the individual spectra have been fitted with a Gaussian function. Although in this region of the spectra a series of equally intense sharp peaks due to methylene deformation modes (scissor, rock, wag, and twist) show up, they do not mask the broader carboxylate stretch modes. Thus, in fitting the spectra, contributions from these deformation modes have been neglected, and only the COO modes have been assigned. The aforementioned portion of the spectra for StA is shown in Fig. 1, and those for Cd-StA, Mn-StA, and Co-StA are shown in Fig. 2. It must be mentioned here that the observed noise in the IRAS data of the Langmuir monolayers is inherent in the system itself, as the signal from a monomolecular layer is very weak. Nevertheless, these peak positions, along with the relevant shifts, are consistent with data obtained from the LB multilayers having much better signal-to-noise ratio [14,15]. The assigned COO modes are given in Table I. The spectra of all the MSt's are more or less the same, with seven prominent peaks in each. These are compared with the five fitted peaks of StA on water without any metal ion in the subphase. The results are discussed in detail below.

1. IR spectra of the StA monolayer on water

The StA spectra (Fig. 1) shows five prominent peaks, two strong ones at 1529 cm^{-1} and 1709 cm^{-1} corresponding to the carboxylate asymmetric stretch modes and two peaks of comparatively lesser intensity at 1320 and 1391 cm^{-1} corresponding to the carboxylate symmetric stretch modes, with a fifth peak of medium intensity, observed at 1444 cm^{-1}, attributed to the methylene scissor mode [24]. The peak pairs 1709 and 1320 cm^{-1} correspond to the asymmetric

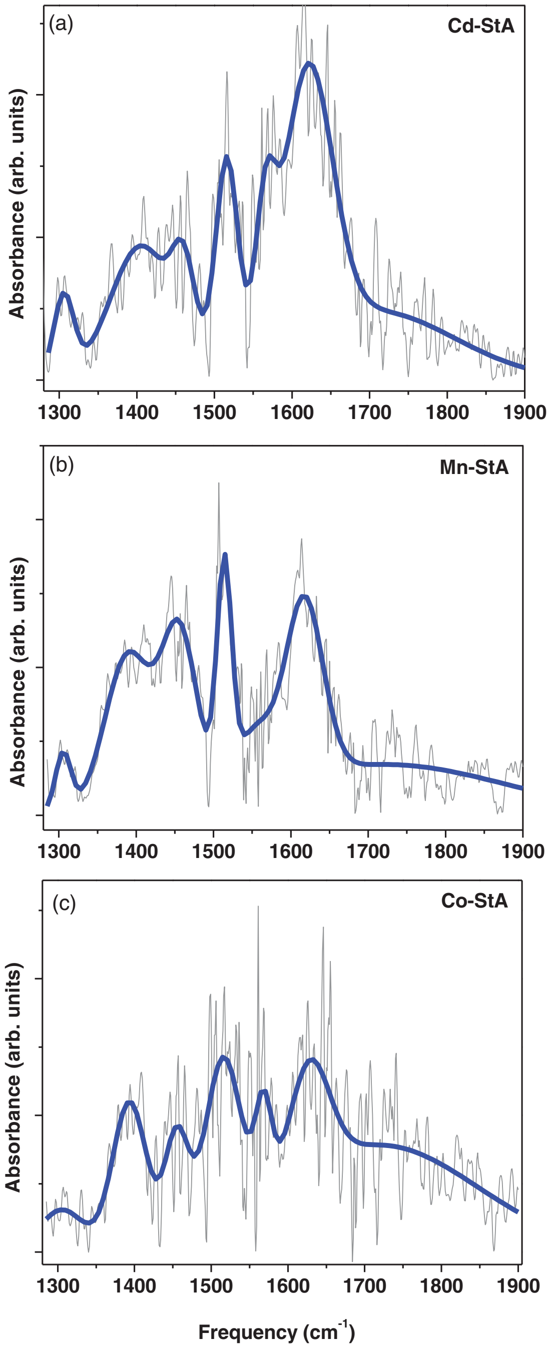

FIG. 2. (Color online) Portion of FTIR spectra (thin gray line) showing carboxylate stretch modes of the stearic acid monolayer on water containing (a) Cd, (b) Mn, and (c) Co ions in subphase. The bold blue line is the composite of Gaussian fits to individual peaks in the data.

and symmetric stretch modes of undissociated acid [21,23], whereas the peak pairs 1529 and 1391 cm^{-1} correspond to those for dissociated acid, i.e., for the carboxylate ion at the water surface [21,23]. The difference in symmetric (ν_s) and asymmetric (ν_a) COO stretching frequencies (Δ) for both undissociated and dissociated acid was estimated. For the former, (Δ) = 389 cm^{-1} whereas for the latter (Δ) = 138 cm^{-1}.

TABLE I. IRAS data of stearic acid monolayers on water.

Carboxylate stretch modes (ν cm^{-1})				Peak
StA	Cd-StA	Mn-StA	Co-StA	assignment[a]
1320	1306	1306	1305	ν(C–O)
1391	1405	1389	1393	ν_s(COO)
1444	1461	1456	1455	$\delta(CH_2)$ scissor
–	1516	1513	1515	ν_{a1}(COO)
1528	1566	1554	1568	ν_{a2}(COO)
–	1621	1617	1628	ν_{a3}(COO)
1709	1705	1720	1718	ν(C=O)

[a] Subscripts a and s refer to asymmetric and symmetric, respectively, and δ is deformation.

2. IR spectra of the MSt monolayer on water

As seen from Table I, Cd-StA [Fig. 2(a)], Mn-StA [Fig. 2(b)], and Co-StA [Fig. 2(c)] spectra have been fit with seven prominent peaks. The peak pairs corresponding to undissociated acid is present in both cases, although in considerably lesser amount compared to that of StA, with the symmetric stretch mode (1320 cm^{-1}) downshifted by about 15 cm^{-1}. The methylene scissor mode (1444 cm^{-1} in StA), also present in CdSt, MnSt, and CoSt spectra at 1461, 1456, and 1455 cm^{-1}, respectively, show a slight frequency upshift (17 cm^{-1} for CdSt, 12 cm^{-1} for MnSt, and 11 cm^{-1} for CoSt), suggesting a slightly better ordering among the tails with respect to free acid. They have more or less the same intensity as that of StA, suggesting no strong interaction of tails due to this change in headgroup structure coming from the presence of metal ions in subphase. However, the symmetric and asymmetric stretch modes of dissociated acid, i.e., the carboxylate ion, are different for the different metals.

In order to better understand the dissociated acid peaks, the composite fits are plotted in one graph for the three metal ions and for StA (Fig. 3). Both symmetric and asymmetric stretch modes in metal stearates are shifted and considerably enhanced in intensity. To elaborate, in stearic acid, the COO

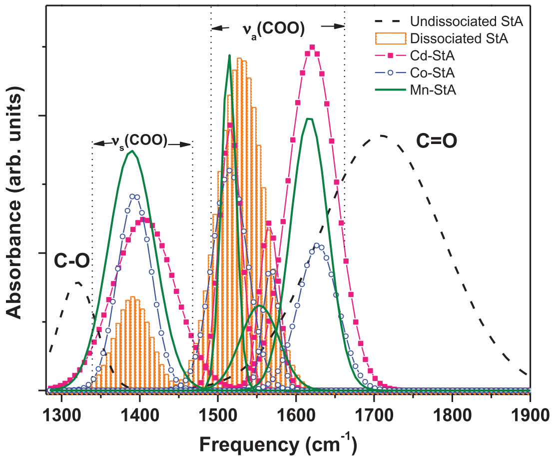

FIG. 3. (Color online) The COO stretch modes (peak fits) of Cd-StA (connected solid squares in pink), Mn-StA (bold green line), and Co-StA (connected open circles in blue) along with that of dissociated (dotted orange bar graph) and undissociated (dashed black line) stearic acid on water.

TABLE II. Δ values for M-StA.

Δ_{ai}	Cd-StA	Mn-StA	Co-StA
Δ_{a1}	111	124	122
Δ_{a2}	161	165	175
Δ_{a3}	216	228	325

symmetric stretch is observed at 1391 cm^{-1}. The same stretch is observed at 1405, 1389, and 1393 cm^{-1} for Cd-StA, Mn-StA, and Co-StA, respectively. Similarly, the COO asymmetric stretch, observed at 1529 cm^{-1} in StA, is not found in the other MSt spectra. Instead, three peaks, all assigned to COO asymmetric stretch modes (i.e., ν_{a1}, ν_{a2}, and ν_{a3}) are observed in the MSt spectra. For example, in Cd-StA, $\nu_{a1} = 1516$ cm^{-1}, $\nu_{a2} = 1566$ cm^{-1}, and $\nu_{a3} = 1621$ cm^{-1}. Similarly, $\nu_{a1} = 1513$ (1515) cm^{-1}, $\nu_{a2} = 1554$ (1568) cm^{-1}, and $\nu_{a3} = 1617$ (1628) cm^{-1} for Mn-StA (Co-StA). The differences in asymmetric and symmetric stretching frequencies (Δ) were calculated for StA and the three M-StA, giving one value ($\Delta = 138$) for the former and three sets of values (Δ_1, Δ_2, and Δ_3) for the latter. All values of Δ are given in Table II.

As seen from the table, $\Delta_1 < \Delta$, which corresponds to bidentate chelate coordination, whereas both Δ_2 and Δ_3 being greater than Δ correspond to two of the other three coordinations (i.e., bridge, ionic, or unidentate). Now since unidentate coordination has the highest Δ value, and since, for ionic bonding, $\Delta \sim 160$–170 cm^{-1}, we assign Δ_3 to unidentate coordination. However, the assignment of Δ_2 is a little ambiguous, since it can indicate both a bidentate bridged coordination or an ionic bonding. In case of a bidentate bridged coordination, the Δ value is usually close to that of the dissociated carboxylate ion, as observed in bulk samples. In our case, $\Delta = 138$ whereas $\Delta_2 \sim 170$, the latter typically corresponding to ionic bonding [25]. On the other hand, x-ray reflectivity and near edge x-ray absorption fine structure (NEXAFS) studies of the monolayers and multilayers of these MSt films deposited on Si substrates [14,26] confirm the existence of bidentate bridged coordination in the headgroups. Moreover, as shown in Fig. 3, it appears that the intense peak at 1529 cm^{-1} observed in StA is rather split into two lesser intense peaks on either side of it (for example, at 1516 and 1566 cm^{-1} in Cd-StA). Finally, as the individual Δ values vary from sample to sample they are very unlikely to come from ionic binding and, hence, Δ_2 is assigned to bidentate bridged coordination rather than ionic bonding. Thus, we see that at the water surface all types of coordination are allowed for stearic acid with Cd, Mn, and Co ions in subphase.

C. Headgroup coordinations at the substrate surface

The spectra of 1-ML CdSt [Fig. 4(a)], MnSt [Fig. 4(b)], and CoSt [Fig. 4(c)] films have been fit with Gaussian functions. Here again, only the COO peaks (both dissociated and undissociated) have been assigned (Table III), by comparing the spectra with that of bulk stearic acid [26]. We have compared the metal-stearate films with bulk stearic acid for the following reasons: (1) stearic acid LB layers on amorphous substrates are in general less stable than their metal salts, and hence they are difficult to transfer; (2) due to very little coverage, a stearic acid LB monolayer would give extremely weak IR spectra, and hence it will be difficult to compare with those of other metal stearate films; and (3) in our work, we have only compared the positions of the C–O and C=O stretches of metal-stearate monolayers with those of bulk StA. The C=O stretch value, observed at 1700 cm^{-1} in bulk stearic acid,

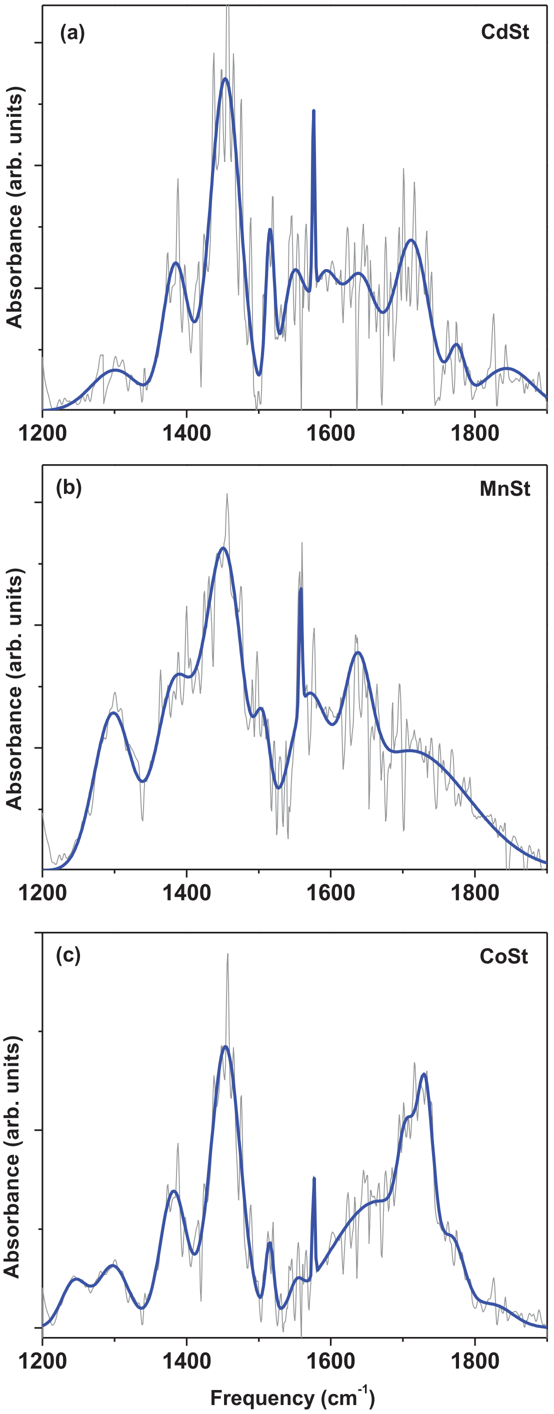

FIG. 4. (Color online) Portion of FTIR spectra (thin gray line) showing carboxylate stretch modes of (a) CdSt, (b) MnSt, and (c) CoSt monolayers on hydrophilic silicon substrate. The bold blue line is the composite of Gaussian fits to individual peaks in the data.

TABLE III. FTIR data for MSt monolayers on Si.

COO stretch modes (ν cm^{-1})			
CdSt	MnSt	CoSt	Assignment[a]
–	–	1244	ν(C–O)
1301	1298	1298	ν(C–O)
1385	1383	1382	ν_s(COO)
1454	1452	1453	$\delta(CH_2)$ scissor
–	1506	–	ν_{a1}(COO)
1516	–	1515	ν_{a2}(COO)
1548	–	1552	ν_{a3}(COO)
1576	1558	1576	
1591	1568	1666	
1640	1637	1704	ν(C=O)
1712	1710	1731	
1775	–	1770	
1844	–	1830	

[a] Subscripts a and s refer to asymmetric and symmetric, respectively, and δ is deformation.

TABLE IV. Δ values for MSt.

Δ_{ai}	CdSt	MnSt	CoSt
Δ_{a1}	–	123	–
Δ_{a2}	131	–	133
Δ_{a3}	163	–	170

remains the same for stearic acid LB multilayers deposited on Ge substrates at an experimental condition different from ours [27]. Thus comparison with a stearic acid LB monolayer does not affect our results. For clarity, the fitted spectra of CdSt, MnSt, CoSt and bulk StA have been plotted separately (Fig. 5). As seen from the figure, the MSt spectra show the presence of undissociated acid in negligible amounts compared to bulk StA. The C–O stretch modes are at 1301, 1298, and 1298 cm^{-1} for CdSt, MnSt, and CoSt, respectively. Similarly, all peaks beyond 1576 cm^{-1} in both CdSt and CoSt (1568 cm^{-1} for MnSt) are assigned to C=O stretch modes since they fall within the region of the C=O mode in bulk StA and hence are not individually assigned. Again the peak at 1558 cm^{-1} in MnSt, although falling in the region of dissociated COO stretch, is sharp and hence is not a signature of carboxylate coordination, as the latter are usually broad [25]. Similar sharp peaks are present in the CdSt and CoSt spectra at 1576 cm^{-1}, which lies within the region of C=O stretch modes, and it appears that the same peak is rather downshifted to 1558 cm^{-1} in MnSt and so it is also not assigned. The methylene scissor mode, present at 1454, 1452, and 1453 cm^{-1} in CdSt, MnSt, and CoSt, shows a slight downshift compared to Cd-StA but remains unchanged compared to MnSt-A and Co-StA. The COO symmetric stretch is observed at 1385, 1383, and 1382 cm^{-1} in CdSt, MnSt, and CoSt. Now, the COO asymmetric stretch modes are observed at 1516 and 1548 cm^{-1} in CdSt and 1515 cm^{-1} and 1552 cm^{-1} in CoSt. However, for MnSt, there is only one peak at 1506 cm^{-1}, corresponding to the COO asymmetric stretch mode. Thus it is found that, in both CdSt and CoSt, there are two sets of values for Δ (i.e., Δ_2 and Δ_3, corresponding to bidentate bridged and unidentate coordinations), in contrast to the three sets of Δ values obtained for the M-StA system, indicating that one of the bidentate coordinations (chelate) is not transferred onto the substrate. However, in MnSt, $\Delta = \Delta_1$ corresponds to bidentate chelate coordination, in contrast to the presence of all three coordinations in Mn-StA, showing the specific selectivity of the chelate configuration during transfer of the StA monolayer in the presence of Mn ions. The assigned values are given in Table IV. It must be mentioned here that the assignments of Δ values for the transferred films have been made by comparing the values for like systems from both the literature [18,28] and our other results [14,15,26]. However, these assignments do not strictly match those of Cd-StA, Mn-StA, and Co-StA. This is because, although the coordination type is the same, the strength of the metal-carboxylate coordination is likely to vary at the water surface and at the substrate surface. Thus, our results show that, at the substrate surface, not all coordinations exist. Rather, specific coordinations are selected depending upon the metal ion type. We have tried to calculate the ratio of unidentate and bidentate coordinations in order to quantitatively estimate the coordination selection during transfer. This is discussed in the next section.

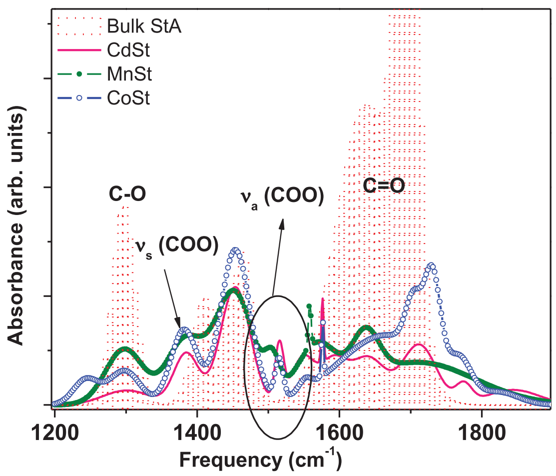

FIG. 5. (Color online) The COO stretch modes (peak fits) of CdSt (solid pink line), MnSt (connected solid circles in green), and CoSt (connected open circles in blue) monolayers along with that of bulk stearic acid (dotted red bar graph) on silicon substrate.

D. Coordination preference

A preliminary calculation involving the area under the peaks for symmetric and asymmetric COO stretch modes was carried out to estimate the relative ratios of the different types of coordination present. For this, the ratio C_i ($i = 1, 2, 3$) given by

$$C_i = a_i/a_0 \tag{1}$$

was computed, where a_i (a_0) is the area under the peaks of the asymmetric (symmetric) stretch mode of the dissociated carboxylate ion. The C values (Table V) show that, in Cd-StA and Mn-StA, unidentate coordinated carboxylate groups form the majority, whereas, in Co-StA, most COO groups coordinate with the Co ions via bidentate chelate coordination.

TABLE V. C values for MSt.

C_i	Cd-StA	Mn-StA	Co-StA	CdSt	MnSt	CoSt
C_1	0.55	0.45	1.16	–	–	0.22
C_2	0.31	0.30	0.30	0.39	0.31	–
C_3	1.56	0.92	0.86	0.81	0.12	–

Again, the ratio C was calculated for the MSt monolayers. Results show that, in CdSt, unidentate coordination is still preferred whereas, in MnSt and CoSt, bidentate coordination is the majority. Comparing with the ratios for M-StA monolayers, we find that, during transfer, CdSt coordination preference remains practically unaltered, whereas those for MnSt and CoSt change significantly. For Mn ions, majority coordination was unidentate and it completely changed to chelate on transfer, whereas for CoSt the majority coordination changed from chelate to bidentate bridged. Our results thus confirm that carboxylate coordination is altered during the transfer process and is strongly related to the metal ion type.

Some metal ions, such as Pb, are known to spontaneously form a two-dimensional lattice of hydrated trimers below the Langmuir monolayer of amphiphilic acids [29], though no direct evidence of such hydrated ionic lattices has been obtained, to our knowledge, for the metals considered in this work. Hence a change or a preference for a particular metal-carboxylate coordination on transfer from the water surface to a solid surface involves specific changes in the molecule-surface interactions. We have found that, while all coordinations are allowed on the water surface, the solid surface allows only particular coordinations, depending on the metal involved. This may be interpreted as a process of selecting certain coordinations by the solid surface through preferential bonding, rather than the solid surface actively changing the metal-carboxylate coordination during the transfer. Admittedly, our investigations at this stage cannot give a definite answer to this question. Dynamical studies during film transfer may clarify this further and these are planned for the future. Our preliminary results thus suggest strong and metal-specific supramolecular bondings mediated by the hydrophillic substrate surface as a selection mechanism for the metal-headgroup coordination that is transferred. A recent simulation has highlighted the role of short-range interactions at hydrophilic substrate surfaces in stabilizing polyelectrolytes through polarization of water molecules hydrogen bonded to the polymer [30]. A similar mechanism may be at work here, selecting the headgroup coordination through the selection of specifically oriented water molecules attached to the headgroup during transfer.

IV. CONCLUSION AND OUTLOOK

Infrared reflection-absorption spectroscopy results on Cd-StA, Mn-StA, and Co-StA Langmuir monolayers on a water surface show that, in the presence of subphase metal ions, dissociated stearic acid forms unidentate, bidentate bridged, and bidentate chelate coordinations, with the former two preferring unidentate and the latter preferring bidentate coordination. These Langmuir monolayers, when transferred onto amorphous substrate, do not show all types of coordination. Specific coordinations are selected depending upon metal ion type. Our results show that the transferred CdSt and CoSt monolayers contain both unidentate and bidentate bridged coordination in the carboxylate headgroup whereas the MnSt monolayer has only bidentate chelate coordination. We cannot offer an exact mechanism for this selection process for specific metal-carboxylate coordination by the substrate surface. We can only propose that the selection may be mediated through preferences for supramolecular bonding of the dangling bonds of the silicon surface [SiO_x-$Si(OH)_x$] with particular metal-carboxylate coordination (unidentate, bidentate-bridged, or bidentate chelate).

ACKNOWLEDGMENT

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