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Structural Comparison of Self-Assembled Monolayers of *n*-Alkanoic Acids on the Surfaces of Silver, Copper, and Aluminum

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Abstract: Self-assembled monolayers of *n*-alkanoic acid, $(CH_3(CH_2)_mCOOH$, $m = 2$–18, 22), were formed on the native oxide surfaces of Ag, Cu, and Al. The structure of the monolayers was probed with optical ellipsometry, contact angle measurement, and reflection absorption IR spectroscopy. The results suggest that the structure of the adsorbed film strongly depends on the metal substrate, as well as the chain length of the acid involved. The metal substrate dominates the binding geometry of the head group and probably the packing density. The chain length also affects the packing density and the conformation of the molecular chain. The ultimate structure is a compromise of all interactions. Acids dissociate completely on all three of the metals and form carboxylate overlayers. On the surface of silver, the two oxygen atoms of the carboxylate bind to the surface nearly symmetrically, and the molecular chain extends trans zigzag for *all* the acids examined. The same tilt angle (estimated between 15 and 25° from surface normal) was suggested for all the acids. While on the surface of aluminum and copper, the carboxylate binds to the surface asymmetrically, and for shorter chain acids, the molecular chains are disordered and liquid-like. As the chain length increases, the cohesive interaction increases and the packing becomes denser. Eventually, the molecular chains pack straight up for the long chain acid. In doing so, some strained or gauche conformations near the carboxylate head group develop as the binding geometry, which is preset by the metal surface, can not accommodate such an orientation. Such strain is more serious on an aluminum surface and less so on a copper surface.

Introduction

Self-assembled monolayers (SAMs) have been the topic of extensive research lately for both their fundamental importance in understanding interfacial properties as well as their potential application in technologies.[1,2] Systems that were found to form highly organized films include alkylsiloxanes on natively oxidized SiO_2,[3-6] *n*-alkanoic acids on natively oxidized Al[7] and Ag,[8] dialkyl disulfides,[9] dialkyl sulfides[10] on Au, and alkanethiol on Au,[11-14] Ag,[15-17] Cu,[17] and GaAs.[18] The structures of these systems are similar in that densely packed, oriented monolayer assemblies can be formed. Yet fine differences in structural details and properties exist depending on the binding amphiphiles as well as the substrates. For example, a polysiloxane network is believed to be responsible for the highly stable, robust alkylsiloxane monolayer on a SiO_2 surface. Alkanethiol forms polar metal–thiolate bonds, giving very stable monolayer assemblies on Au and Ag. Ionic bonding is involved in the acid/metal oxide system. In the latter two systems, the constituents of the film can undergo exchange, to a certain extent, with external constituents in the contacting solution after the monolayer formation is completed.[7,19,20]

The structural details for alkanethiol on Au and Ag are also different. Various techniques including IR,[17] electron diffraction,[21] and Raman[22] afford a rather consistent picture about the film structure: on gold, the molecular chain is tilted at about 27° from the surface normal with sulfur atoms forming an epitaxial $(\sqrt{3} \times \sqrt{3})R30°$ overlayer on a predominantly Au(111) lattice. On silver, the hydrocarbon chain is tilted much less, at about 13° from the surface normal.[23] A restructured binding overlayer[17] or multidomain system[16] has been proposed for interpretation the different results observed on Au and Ag. Alkanethiol on GaAs constitutes yet another class of structure, tilted at 57° due to larger lattice spacing on the GaAs(100) surface. These results also suggest that the surface chemical bond between substrates (binding geometry, site density, and symmetry...) very much dictates the structure of the adsorbed monolayer. Superimposed on this are the intermolecular forces. The ultimate

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structure is a compromise between surface binding interaction and intermolecular forces. While a lot of application can be envisioned from the various SAM systems, an understanding of the molecular details in various systems is crucial in further design of molecular systems based on them.

Adsorption of carboxylic acid on a metal surface has been the subject of many studies,[24-29] mainly due to interest in areas of lubrication, corrosion, and catalysis. Conflicting results regarding the structure of the adsorbed film (multilayer, submonolayer, ordered, disordered ...) have been reported, particularly on "reactive" metals such as aluminum and copper. Different observations presumably may have much to do with the varied preparation procedures involved. The formation of SAMs of *n*-alkanoic acid on aluminum has been examined by Allara and Nuzzo.[7] SAMs of arachidic acid and *n*-perfluorocarboxylic acid on Ag have also been reported.[8] There has been no account of a corresponding monolayer on Cu. This paper reports a systematic study of the structure of self-assembled monolayer films of *n*-alkanoic acids on the surfaces of Ag, in comparison with corresponding films formed on the surface of Cu and Al. Important differences were found between these three surfaces. The results were rationalized by head group geometry and probably lattice effect. These systems provide an interesting contrast to thiol on gold and thiol on silver systems and may shed light on the mechanism of SAM formation in general.

Experimental Section

Materials. The even-numbered carbon *n*-alkanoic acids and pentadecanoic acid were obtained from E. Merck, and the odd-numbered carbon acids were purchased from Tokyo Chemical Industry, Co. The acids were either distilled or recrystallized before use. *n*-Hexadecane obtained from Aldrich was percolated through neutral alumina (activity 1 from Merck) twice. Aluminum, copper, and silver used for substrates were obtained from Johnson Matthey Electronics and were of 99.99% purity or higher. Single crystal silicon wafers (2-in. diameter) polished on one side were obtained from Semiconductor Processing Co.

Substrate Preparation. The substrates were prepared by thermally evaporating (at 3×10^{-7} Torr using a Ulvac cryo-pumped evaporator) around 2000 Å of aluminum, copper, or silver onto the surface of a 2-in. silicon wafer. An adhesion layer of chromium (~150 Å) was needed in the case of silver. After the substrates returned to room temperature, the chamber was back-filled with high purity nitrogen. The substrates were transferred to a tightly capped wafer container, and substrate constants were measured immediately. The substrates were placed in the acid solution right after measurement. The metal surfaces were exposed to ambient temperature for no more than 10 min. To minimize the effect of different ambient exposure, the substrates were prepared batchwise and used without storing.

Monolayer Preparation. The acids were dissolved in *n*-hexadecane at a concentration of 1 mM and kept at 25 °C. Depending on the substrate and chain length of the acid, the surface might or might not be "oleophobic". It is noticed that if a surface is ever to become oleophobic, it tends to become so within the first half of a minute or so. Nevertheless, all substrates were kept in the solution for at least 3 h before being taken out for characterization. Surfaces that emerged dry and clean from the hexadecane solution were characterized as "as is" (with the back side and edge wiped dry with a hexane-soaked tissue). Both IR and ellipsometry showed that a quick rinsing with hexane on a spinner did not change the structure of the film adsorbed on the Ag and Cu, but the solvent rinsing appeared to remove some film materials from the aluminum surface.[30] Substrates that emerged wet from the adsorbing solution were rinsed with hexane to remove excessive hexadecane solution before characterization. This is the case mainly for shorter chain acids on Al and Cu.

Infrared Measurement. Reflection absorption IR spectra were taken with a Bomem MB-100 spectrometer equipped with a MCT detector. A custom-designed optics similar to that described in the literature[3] with an 86° incidence angle using p-polarization was used. A gold-coated wafer cleaned with ozone[31] was used as a reference for all spectra. A monolayer of perdeuterated docosanethiol on gold was used to check the cleanliness of the reference. One thousand scans were collected at 2-cm^{-1} resolution for signal averaging.

Contact Angle Measurement. Static contact angles were measured with a Rame-Hart NRL Model 100 goniometer. At least three drops were used for the reported contact angle readings, and the readings were reproducible to within 1° on a given sample.

Ellipsometry Measurement. A Rudolph AutoEL ellipsometer was used for thickness measurement. The He–Ne laser (632.8 nm) light incidented at 70° on the sample and reflected into the analyzer. Data were averaged over three–five spots for a given sample. A real index of refraction of 1.47 was assumed for all the films in thickness calculation.

Results

The *n*-alkanoic acids studied encompass a broad range of chain lengths: C4–C20 and C24. While the main interest was in longer acids, which are known to form ordered SAMs in other related systems, the shorter chain acids nevertheless were included to provide important information regarding the head group binding chemistry "in the absence of" strong cohesive chain–chain interactions. It was also of interest to see if there were any gradual changes of properties (microscopical or macroscopical) with chain length. The results are described according to the supporting metal as follows.

Monolayer on Ag. An oleophobic film surface can be formed instantly for all the acids with a chain length above five carbon atoms ($m > 3$). Assuming the same refractive index for all the films (1.47), the calculated ellipsometric thickness versus m was plotted in Figure 1. The dashed line represents the thickness expected for a trans zigzag linear chain oriented perpendicular to the surface. As can be seen from the figure, a roughly linear correlation was found between thickness and chain length. Nevertheless, the thickness was 4–5 Å thinner than the expected line for a normal chain orientation, and the thickness decreased to zero at a chain length of five carbon atoms, which, from IR data, still formed a well-oriented monolayer. The line best fitting the data gave a slope of 1.38 Å/CH_2 (or 1.3 Å/CH_2 if shorter acids ($m < 8$) were excluded). For a normal orientation, a slope of 1.27 Å/CH_2 was expected. The use of the same refractive index for both higher and lower acids may hardly be justified, but the deviation is not enough to explain the vanishing thickness (use of a lower index of refraction, say 1.4, for shorter chain acids results in about a 1-Å increase). The discrepancies in thickness might be attributed to chain tilt (vide infra) as well as a change of substrate constants upon adsorption of the acid (for example, the removal of adsorbates from the ambient environment and/or erosion away of the oxide layer by interaction with the acid). Discrepancies between expected and observed thicknesses have also been reported in other SAM systems such as thiol on Au and thiol on Ag, and factors suggested to contribute to the discrepancy include roughness factor and contamination ..., besides those mentioned above. The ellipsometry data here probably at best provide a qualitative indication that a true monolayer with *similar orientation* was formed for all the acids studied under the conditions used. Multilayer formation was not observed under current conditions.

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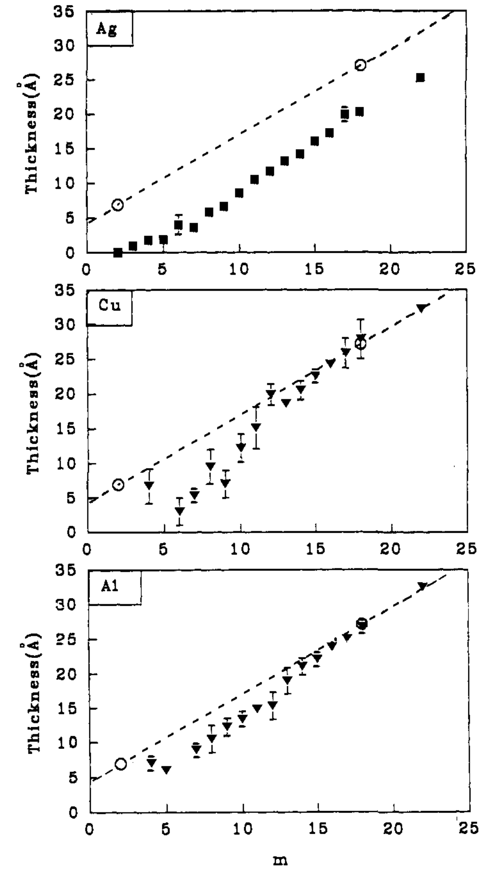

Figure 1. Ellipsometric thickness of the *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, monolayer as a function of chain length. Dashed line represents the calculated thickness for normal orientation.

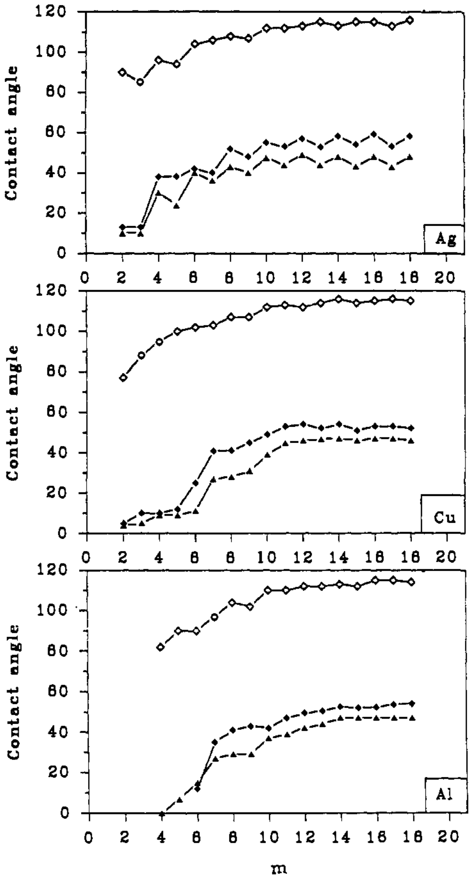

Figure 2. Contact angle on a monolayer surface as a function of chain length of the acids $CH_3(CH_2)_mCOOH$: (△) hexadecane, (♦) bicyclohexyl, (◇) water.

Table I. Vibration Modes Assignment for *n*-Octadecanoic Acid Adsorbed on Different Metals

mode description[a,b]	peak frequency (cm^{-1}) Ag	Cu	Al
$\nu_a(CH_3$, ip), asym stretch	2965	2964	2964
$\nu_s(CH_3$, FRC), sym stretch	2935	2936	2936
$\nu_s(CH_3)$, sym stretch	2877	2877	2877
$\nu_a(CH_2)$, asym stretch	2914	2917	2916–2927
$\nu_s(CH_2)$, sym stretch	2848	2850	2850
$\nu_a(CO_2^-)$, asym stretch	nd	1552	1611
$\nu_s(CO_2^-)$, sym stretch	1404	1441	1478
$\delta(CH_2)$, deformation	1470	*	*
$\delta(CH_3)$, deformation	1382	1381	1381
$\omega(CH_2)$, wagging $\gamma(CH_2)$, twisting	nd	nd	1350–1150

[a] Assignment taken from refs 7 and 8. [b] Abbreviations: asym = asymmetric, sym = symmetric, ip = in plane, op = out of plane, FRC = Fermi resonance component, nd = not detected, * = overlap with $\nu_s(CO_2^-)$.

The contact angle for hexadecane (HD), bicyclohexyl (BCH), and water was measured on the SAM films, and the results are plotted as a function of chain length (Figure 2). For the organic wetting liquids, hexadecane and bicyclohexyl, in addition to a steady increase in contact angle with chain length, there is also a striking alternation pattern in contact angle with chain length all along the series: lower on odd-numbered chains and higher on even-numbered chains. The difference is far beyond the experimental error (±1°). For chain lengths above C12, the values become steady and alternate between 44° and 49° for θ_{HD} and between 54° and 59° for θ_{BCH}. Contact angle values decreased with lower acids. But an alternation trend with chain length is still clearly observed. When water was used as the wetting liquid, the contact angle showed some alternation for shorter chain acids but reached a plateau of 113–115° for chain lengths longer than C12. In view of the sensitivity of the contact angle[32] (~2–5 Å), the data suggest that the odd chain acids and even chain acids are exposing slightly different structures *at the top surface*. Contact angle alternation with chain length for hexadecane was also observed, to a lesser extent, for SAM of alkanethiol on Ag[14,16] *but only for chains shorter than C10! The effect diminished for a longer chain thiol, which presumably formed a more ordered structure*. This could suggest a change of the monolayer structure (e.g., orientation) as the chain length increases.

The reflection–absorption infrared spectra for the acid monolayer on silver are shown in Figure 3. The peak frequencies and mode assignments for a representative case, *n*-octadecanoic acid, are listed in Table I. (Data for all other acids are included in Table II, supplementary material). Some distinct features were noted. In the high frequency region, the intensities for the vibrational modes associated with the terminal CH_3 show fluctuation with chain length: the intensity of the asymmetric stretch mode $\nu_a(CH_3)$, occurring around 2965 cm^{-1}, alternates between odd and even carbon chains and is higher for an odd-numbered carbon chain and lower for an even-numbered carbon chain. The intensity of the symmetric stretch mode $\nu_s(CH_3)$, occurring around 2877 cm^{-1}, alternates in the opposite direction, i.e., higher for an even-numbered carbon chain and lower for an odd-numbered carbon chain. This odd–even effect was present for all the acids examined and is summarized in Figure 4. The peak frequencies for asymmetric and symmetric methylene vibrations, $\nu_a(CH_2)$ and $\nu_s(CH_2)$, show a trend to shift to a lower frequency as the chain length increases: from 2924 and 2854 cm^{-1}, respectively, for a C9 acid to 2914 and 2848 cm^{-1}, respectively, for a C14 and longer acids. These lower frequencies for higher acids (virtually the same as those for the isotropic crystalline bulk sample), have been suggested to be indicative of

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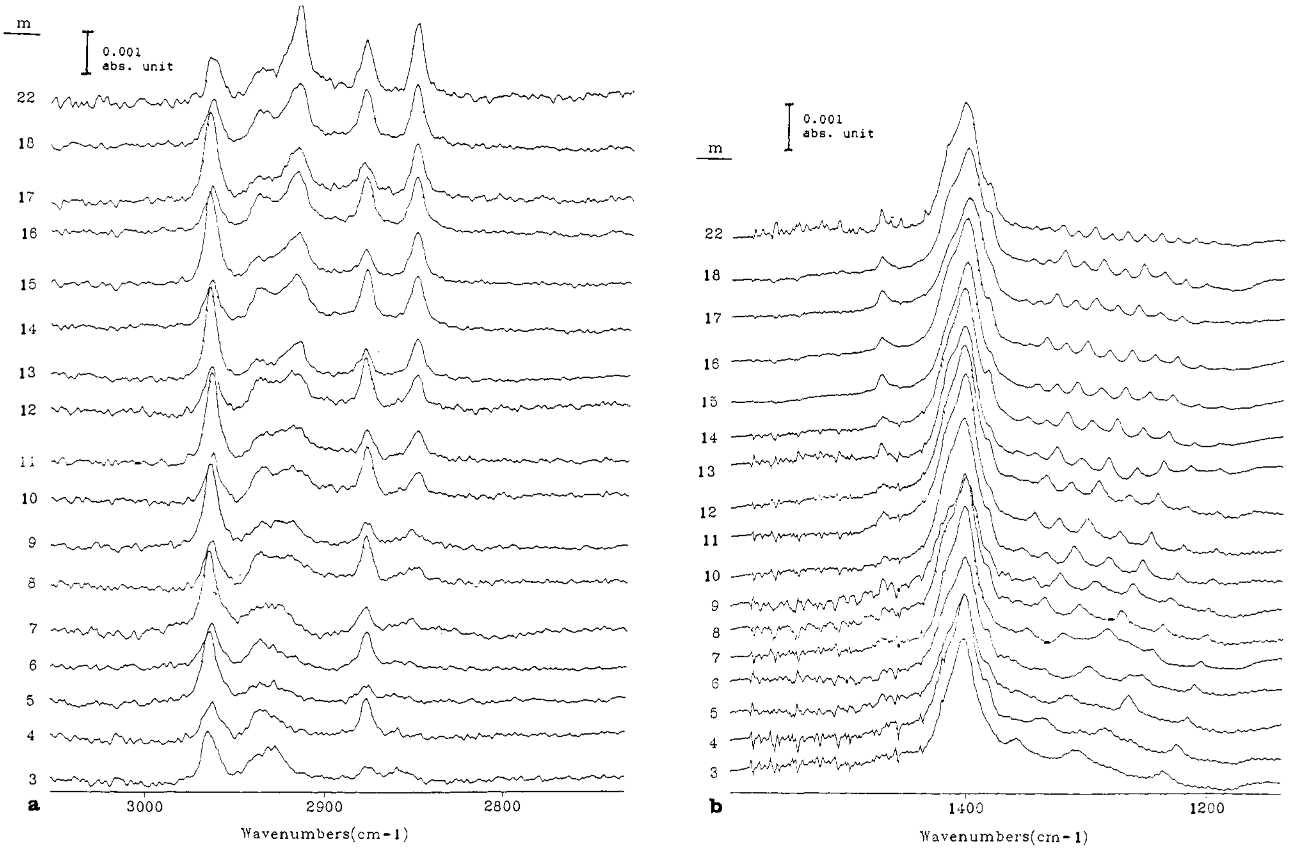

Figure 3. Reflection–absorption IR spectra for a monolayer of *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, on Ag. (a) High-frequency region. (b) Low-frequency region.

a highly ordered or crystalline state.[33,34] The intensities for these modes increase with chain length (Figure 5). In the low-frequency region, the strongest peaks around 1404 cm^{-1} are assigned to the symmetric stretch for a carboxylate group $\nu_s(CO_2^-)$. The asymmetric vibration mode was too weak, if any, to be observed. This observation is valid for both long and short acids, which implies that the binding geometry is similar, independent of the chain length. The CH_2 deformation mode $\delta(CH_2)$ around 1470 cm^{-1} is clearly seen, and it is "not" split. Implications of these observations will be discussed later.

The other distinctive feature is the rather regularly spaced progressional bands, the result of coupling between CH_2 wagging and twisting,[35,36] between 1350 and 1150 cm^{-1}. It is well-established that the number of peaks (and thus the spacing between peaks) strictly depends on the number of CH_2 units that are involved in a trans zigzag linear polymethylene chain. While it may be ambiguous to count the exact number of peaks belonging to this band, the spacing between the peaks decreases progressively with increasing chain length. These spacings almost exactly match the corresponding bands for the bulk crystalline acid sample, although at slightly shifted positions (the shift presumably is due to different head groups, carboxyl and carboxylate, respectively) (supplementary material). For acids shorter than C10, the bulk samples were liquids and thus no progressional band could be observed as a comparison. Yet the monolayer film on Ag clearly showed the progressional bands with spacing increasing with decreasing chain length. The presence of progressional bands compelled the conclusion that the molecular chains are mostly trans zigzag even for chains as short as C5!

Monolayer on Cu. An oleophobic monolayer can be formed for acids with chain lengths of C10 and longer. The ellipsometric thickness versus chain length is included in Figure 1. The error in thickness measurement is substantially larger. The substrate constants change with time faster for copper than for other metals, probably due to the different growth rate of oxide. After the monolayer was covered with acid, the ellipsometric measurements became more reproducible,[37] presumably because of the screening effect of the monolayer toward oxidation. Difficulty in reproducibility was also reported for a thiol on Cu system.[17] For lower acids, the apparent thickness is thin and scattered. This might be due to a lower packing density as well as the removal of adsorbed species by hexane rinsing that was necessary in the cases of nonoleophobic surfaces. For higher acids (chain length longer than 12 carbon atoms), the thickness correlates linearly with chain length and approaches the expected value for a trans zigzag and normally-oriented chain. The best line describing the data for $m > 12$ has a slope of 1.47 Å/CH_2 and a negative intercept at −2.4 Å. The steep slope (compared to the theoretical 1.27 Å/CH_2 for normal orientation) and negative intercept were also observed in an alkanethiol on Au system.[14] Figure 2 (center) shows the static contact angle of the SAMs on Cu surfaces. The θ_{HD} increases with chain length but levels off to a value of 47 ± 1° for acids longer than C14. No fluctuation in contact angle was found. The same behavior was observed with bicyclohexyl as the wetting liquid. The contact angle levels off at around 54°. The water contact angle is also the same within experimental error (116 ± 1°) for higher acids. The contact angle values on higher acids are similar to those reported on other SAM systems of similar chain length, and these values had been thought of as typical for a well-ordered monolayer surface exposing methyl terminal groups.

Figure 6 shows the reflection–absorption infrared spectra for the acid monolayer assemblies. (Peak frequencies for *n*-octadecanoic acid are in Table I, and all other acids are in the supplementary material.) For acids with $m \geq 12$, the spectra are strikingly similar, irrespective of the increase in chain length. In

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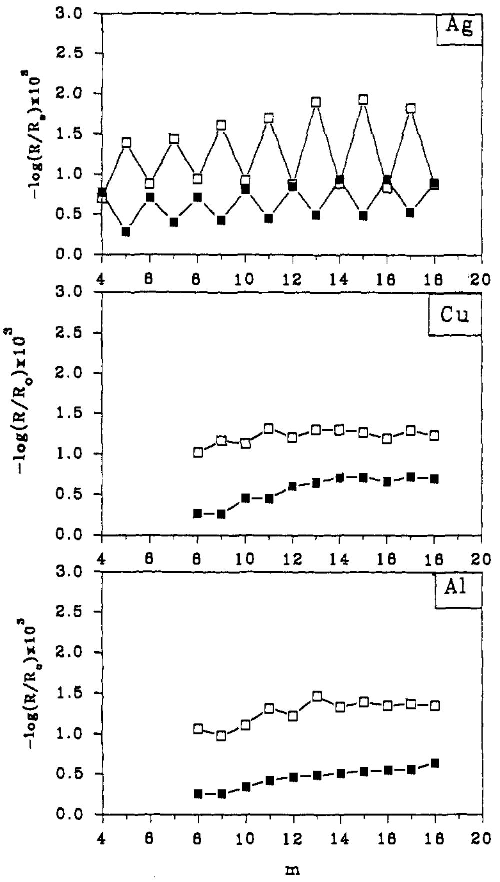

Figure 4. IR intensities for methyl stretching modes as a function of chain length of the *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, monolayer on different metals: (□) $\nu_{as}(CH_3)$, (■) $\nu_s(CH_3)$.

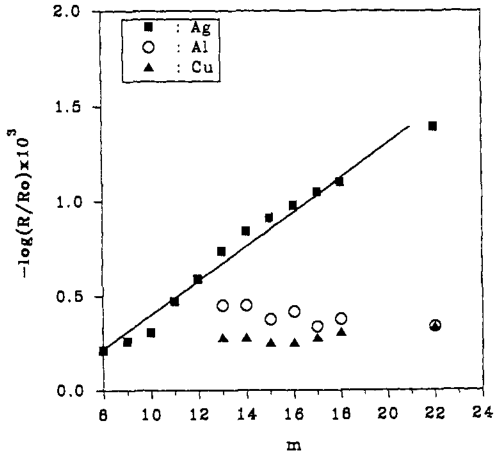

Figure 5. IR intensities for symmetric methylene stretching modes $\nu_s(CH_2)$ as a function of chain length of the *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, monolayer on different metals.

the high frequency range, the ratio of intensities of $\nu_a(CH_3)$ around 2964 cm^{-1} and $\nu_s(CH_2)$ around 2877 cm^{-1} remained nearly the same in going from an even- to an odd-numbered carbon chain, which means the projection of transition dipoles along the surface normal were the same whether it was an odd carbon or even carbon chain. The peak positions for $\nu_a(CH_2)$, barely resolved from the Fermi splitting of the symmetric CH_3 mode, at 2917 cm^{-1}, and the $\nu_s(CH_2)$ mode, at 2850 cm^{-1}, are also indicative of a solid-state for the molecules. Yet their intensities remained nearly constant (Figure 5) irrespective of the fact that the chain length increased from C14 to C24! For lower acids, the peak frequencies gradually shift to higher values, suggesting less ordered systems. In the low-frequency region, the most distinct peak is that around 1441 cm^{-1} for the $\nu_s(CO_2^-)$. This somewhat distorted peak presumably contains the $\delta(CH_2)$ mode, typically occurring around 1470 cm^{-1} in these monolayer systems. The broad band that peaked around 1557 cm^{-1} was assigned as asymmetric stretch mode $\nu_a(CO_2^-)$ for carboxylate.[29] The presence of both peaks in substantial intensity suggests that the carboxylate head group should bind to the surface at an angle so that both transition dipoles have a significant component along the surface normal. The small but distinct peak at 1381 cm^{-1} was associated with symmetric methyl deformation mode $\delta(CH_3)$. Progressional bands, if any, were hardly detected. Again, the important feature to be noted in this region is that the peak shape and relative intensities for the head group carboxylate are very much the same for all the acids. This would imply that the binding geometry for the head group is determined by the interaction between the substrate and head group. The cohesive interaction between chains "does not" appreciably change the binding configuration.

Monolayer on Al. The results for thickness, wetting, and infrared measurements for monolayers of *n*-alkanoic acid assemblies on Al are also collected in Figures 1, 2, and 7. Similar to the case on Cu, for higher acids, the thickness approached that expected for normally aligned chains and a linear correlation between thickness and chain length was found. The straight line describing the relation between thickness and chain length has a slope of 1.39 Å/CH_2 and an intercept at −1.1 Å. Lower acids deviate from this significantly and have apparently thinner films. The trend in contact angle values is also similar to that on Cu in that the contact angle value increases with chain length and levels off to about 46 ± 1° for θ_{HD} and 113 ± 1° for θ_{H_2O}. No odd–even alternation was observed. For IR data, again the spectra for higher acid ($m > 13$) monolayers are quite similar. The intensities for $\nu_a(CH_3)$ and $\nu_s(CH_3)$ modes remain the same for all the films, i.e., they do not alternate with chain length. But the absorption peak for $\nu_a(CH_2)$ is more complicated, with multiple peaks clustering around 2926 cm^{-1} and overlapping with the Fermi splitting of $\nu_s(CH_3)$. This had been noticed before.[7] The $\nu_s(CH_2)$ mode, which peaked at 2850 cm^{-1}, remains nearly the same as the chain length increases from C15 to C20 and appears to even slightly decrease for a C24 acid. These results are summarized in Figure 5. The $\nu_s(CO_2^-)$ mode occurs as a broad band centered around 1478 cm^{-1} and the $\nu_a(CO_2^-)$ band around 1611 cm^{-1}. Both shifted to higher frequencies compared to corresponding bands for the acid/copper system. It is well known that frequencies for carboxylate are variable and depend on counter cations.[38] The implication on structure will be discussed later. The progressional band, again, was hardly detectable. In an earlier study of *n*-alkanoic acid monolayers on aluminum,[7] it was suggested that multiple carboxylate species were present at the surface and theoretical calculations on the orientation of the carboxylate groups required a skewed conformation for the carboxylate group to be present. For shorter chain acids, similar to that on copper, disordered and liquid-like film were obtained. The IR band shape and relative intensity for carboxylate was again the same as that for higher acids, impling the same binding geometry for both long and short chain acids.

Discussion

The structural picture that emerges from the results above is clearly better defined for SAMs on a silver surface. This is depicted in Figure 8. It is suggested that the *n*-alkanoic acid dissociatively adsorbs in a very ordered array and fully occupies the available sites for all the acids examined. The two oxygen atoms of the carboxylate sit nearly symmetrical on the surface. This binding geometry was not significantly affected by the secondary interaction in the self-assembled monolayer system: chain–chain interaction. This binding geometry appeared very favorable for the trans extension of molecular chain. The appearance of a progressional band and thus a trans zigzag conformation even for the shortest C5 chain compelled the

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(38) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1975.

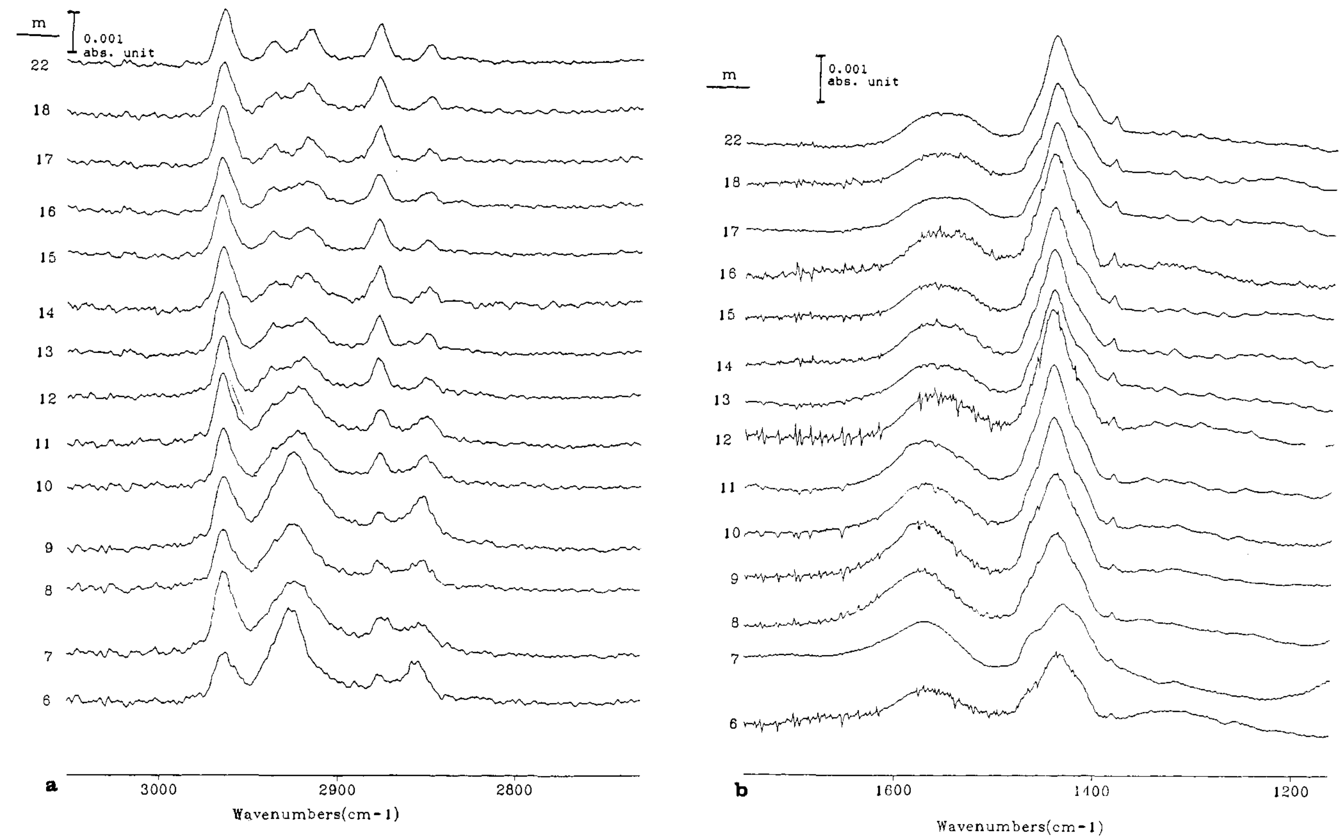

Figure 6. Reflection–absorption IR spectra for a monolayer of *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, on Cu. (a) High-frequency region. (b) Low-frequency region.

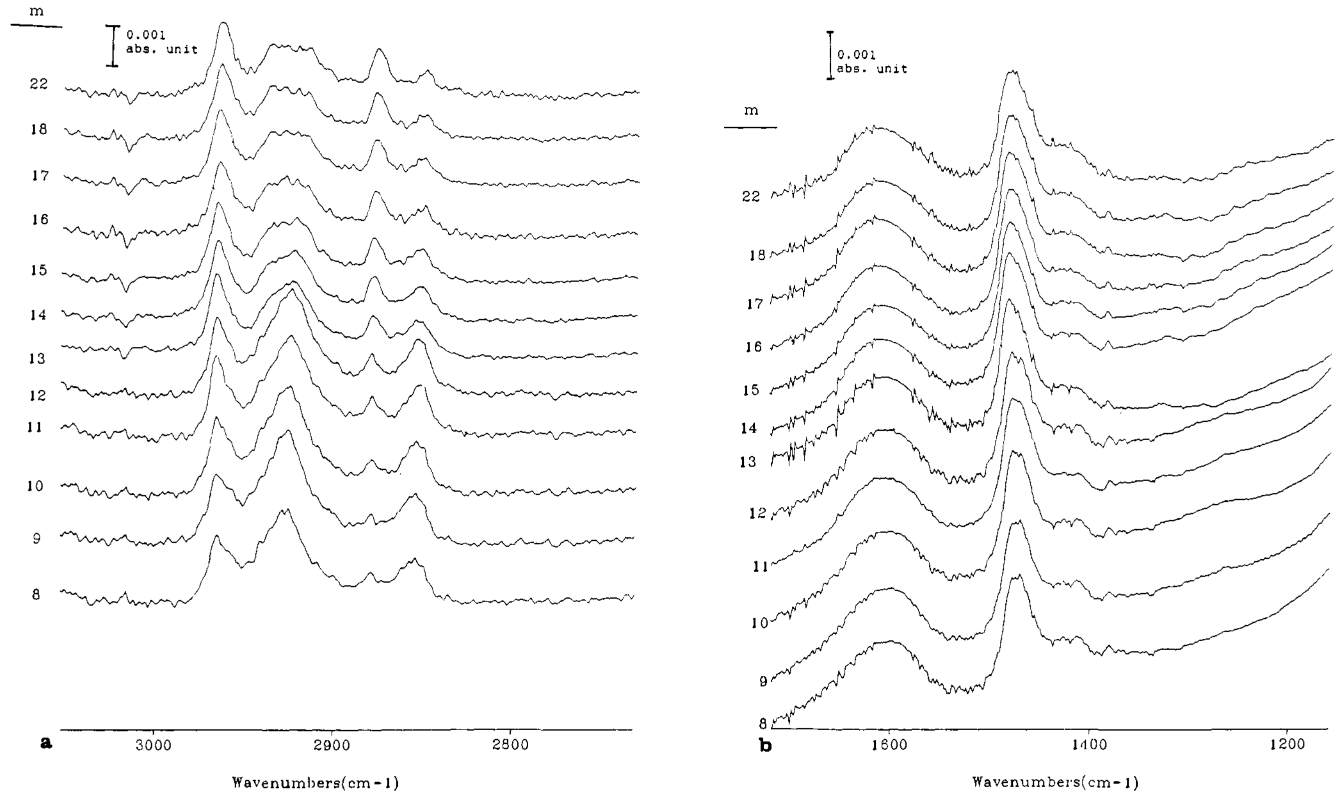

Figure 7. Reflection–absorption IR spectra for a monolayer of *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, on Al. (a) High-frequency region. (b) Low-frequency region.

proposition that a similar packing density resulted for both long and short chain acids. Such a packing density leaves little room for molecular chains to flop around even if the interchain interaction is believed to be insignificant. A similar chain tilt develops from such a conformation. The odd–even effect in IR data and contact angle are rather consistent and explicable by the orientation of the terminal methyl group: for an even carbon chain, the terminal methyl points closer to the surface normal, so that the symmetric vibration mode for the methyl group is stronger and the asymmetric vibration mode is weaker. The contact angle (for hydrocarbon liquids in particular) on such a "methyl" surface is higher. With an odd carbon chain, the

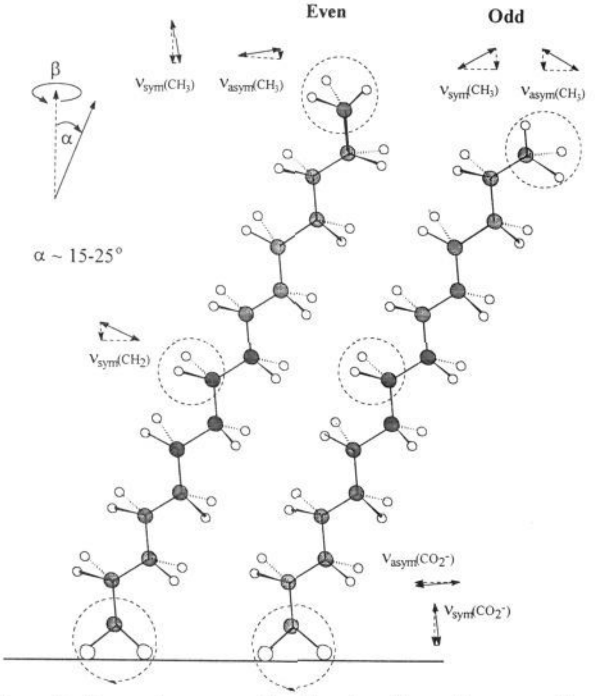

Figure 8. Proposed structure of *n*-alkanoic acid monolayer on a silver surface.

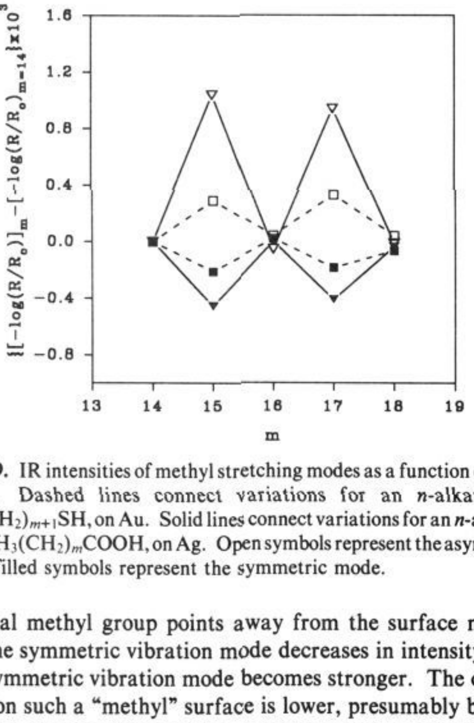

Figure 9. IR intensities of methyl stretching modes as a function of chain length. Dashed lines connect variations for an *n*-alkanethiol, $CH_3(CH_2)_{m+1}SH$, on Au. Solid lines connect variations for an *n*-alkanoic acid, $CH_3(CH_2)_mCOOH$, on Ag. Open symbols represent the asymmetric mode; filled symbols represent the symmetric mode.

terminal methyl group points away from the surface normal, thus the symmetric vibration mode decreases in intensity while the asymmetric vibration mode becomes stronger. The contact angle on such a "methyl" surface is lower, presumably because of more exposure of the methylene unit next to the methyl group. For acids of sufficient length ($m > 11$), the wetting liquid senses an identical structure for all the even chain acids and a slightly different structure for all the odd chain acids.

An interesting contrast between the acid/Ag system and thiol/Au system exist. A similar odd–even effect of the methyl vibrational modes was observed in the thiol/Au system but it is much less pronounced than that in the *n*-alkanoic acid/Ag system (Figure 9). In the thiol on Au system, the asymetric vibration mode varied by a factor of 1.3 (I_{odd}/I_{even}) and the symmetric vibration mode varied by a factor of 1.4 (I_{even}/I_{odd}). For the *n*-alkanoic acid/Ag system, the asymmetric mode varied by a factor of 2.2 and symmetric mode by a factor of 2. The contact angle alternation with chain length was hardly observed on the thiol/Au system.[39] IR spectra simulation performed on a thiol/Au system[17] indicated that the extent of the odd–even effect in methyl vibration modes was far less than the calculated value and a considerable population of gauche conformations has to be invoked to get a "better" fit but still not a "close fit" of the observed methyl intensities. Since an odd–even effect was expected to be more significant as the chain tilt increased, the IR results observed for the acid/Ag system suggest that either the acid adsorbed on Ag was significantly more tilted than thiol on a Au system or the acid on Ag system was no more tilted but much more ordered than the thiol on Au system, with little gauche interaction along the chain. Several factors suggest that the latter should be the case. While a linear correlation between peak intensities for the $\nu_s(CH_2)$ mode was found for acid/Ag, thiol/Au, and thiol/Ag systems, the slope (i.e., the average intensity per methylene unit) for the acid/Ag system (9×10^{-5} absorbance units) lies between that for thiol/Au (1.45×10^{-4} AU) and thiol/Ag (5×10^{-5} AU). This suggests that the average tilt is in the same order. Based on an all-trans zigzag model, the expected ratio of I_{odd}/I_{even} (equivalent to the ratio of the transition dipole along the surface normal) for methyl vibration modes can be estimated as a function of chain orientation. A chain tilt of 25° was suggested if comparing the observed and expected ratio of $\nu_s(CH_3)$ or 15° if comparing the ratio of $\nu_a(CH_3)$. The discrepancy implies that the all-trans zigzag model is oversimplified. Rotation of the molecular plane should be involved.

Further comment regards the methylene deformation mode, $\delta(CH_2)$. A temperature dependence study[40] of the IR spectra for docosylthiol/Au suggested that as the temperature decreases, the molecular chains becomes more ordered and at temperatures below 200 K, the system adopts an orthorhombic or monoclinic state with two chains per unit cell, leading to a splitting of a CH_2 deformation band. Such a result was also predicted by molecular dynamic simulation[41] and supported by a He diffraction study.[42] These results led to the conclusion that ***at room temperature***, there is substantial disorder, at least near the chain ends, for C22 thiol on gold.

In the case of an acid/Ag system, the trigonal-shaped head group binds to the surface through two oxygen atoms. The alignment of the carboxylate group dictates the conformation of CH_2 next to it (the lower energy conformation is that with C_2–C_3 bond eclipsing the C–O bond[43]) and so the rest of the polymethylene chain. Intuitively, if the head group can not rotate, the polymethylene chain can not rotate either. Such constrain does not exist in a thiol/Au system since sulfur binds to gold through a S–Au single bond. However, this rotational barrier can be removed by introducing a rodlike section between the head group and the polymethylene chain. In fact, factor group splitting of the CH_2 deformation band was indeed observed (at 1460 and 1471 cm^{-1}) at *room temperature* when there is a diacetylene unit inserted between a carboxyl and a C16 polymethylene chain.[44] The unsplit CH_2 deformation[45] observed for *n*-alkanoic acid on silver might as well suggest that at room temperature a crystalline monolayer describable by a one chain model such as triclinic packing results.

On the surface of copper and aluminum, *n*-alkanoic acid also completely dissociates but the head group carboxylate coordinates to the surface in a tilt way, as suggested by IR. For shorter chain

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(39) Careful examination of the wetting properties on this system showed a slight alternation (~2°), too close to the typical experimental error in the current measurement (±1°). However, Porter et al. claims an odd–even effect in the wetting of alkanethiolate on Au(111): Porter, M. D. Private communication.

(40) Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, *93*, 767–773.

(41) Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1989**, *91*, 4994–5001.

(42) Chidsey, C. E. D.; Liu, G. Y.; Rowntree, P.; Scoles, G. J. *J. Chem. Phys.* **1989**, *91*, 4421–4423.

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(44) Results to be published in a separate paper.

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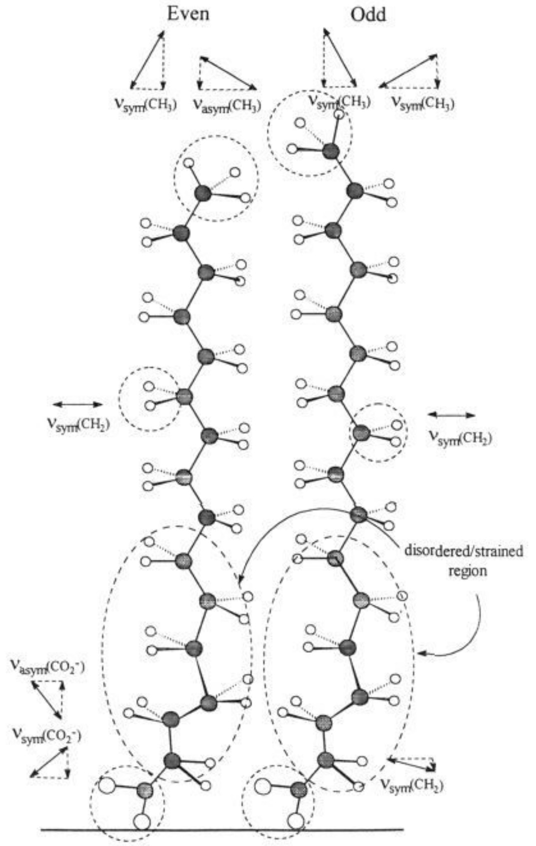

Figure 10. Proposed structure of *n*-alkanoic acid monolayer on copper and aluminum surfaces.

acids, the film is disordered for lack of enough cohesive interaction and a less dense film then results. As the chain length increases, the cohesive force becomes strong enough to pull up the molecular chains into "normal" orientation, for optimal interaction energy.[46] The normal orientation is in harmony with an invariance of intensity for all the methyl vibrational modes and contact angles for hydrocarbon liquids, whether the chain is odd or even, since for normal orientation, the methyls have the same "outer surface structure" as well as the same transition dipole component along the surface normal. Theoretically, a perpendicular chain would also have CH_2 mode intensities independent of the chain length, i.e., at zero intensity. The observed IR intensity for $\nu_s(CH_2)$ is indeed independent of chain length, nevertheless, not at zero. A possible interpretation is that in achieving the ultimate perpendicular orientation, some twisting or strain has to develop (in order to compromise between head group binding geometry and optimal packing orientation for a long polymethylene chain) near the head group. These several methylene units near the head group contribute to all (or most of) the absorption intensity observed for methylene modes. The rest of the methylenes have little or no contribution because of perpendicular orientation. Thus, the chains stand straight up beyond a certain length. This "disordered" section may change depending upon how strong the cohesive interaction is. Since the progressional band is the result of coupling between twisting and wagging of CH_2 units trans to each other and a polar head group is known to enhance the intensity,[35,36,44] a skewed conformation near the head group may "insulate" the head group from the rest of the polymethylene chain conformationally and thus "turn-off" or diminish the progressional band. The situation is depicted in Figure 10.

While it has been suggested that chains are aligned normal on both copper and aluminum surfaces for higher acids, closer examination of the band shape for the methylene stretches $\nu_a(CH_2)$ and $\nu_s(CH_2)$ indicates that there are differences. On copper, the $\nu_a(CH_2)$ band around 2917 cm^{-1} and the $\nu_s(CH_2)$ band at 2849 cm^{-1} are more or less symmetrically shaped. On aluminum, the $\nu_a(CH_2)$ band has multiple peaks or, say, is spread in a broader range. The $\nu_s(CH_2)$ band at 2850 cm^{-1} was also shifted to a higher frequency relative to that on copper. It is proposed that on an aluminum surface, the strain or twist of the molecular chain is more serious than on copper, i.e., the *n*-alkanoic acid/Cu system is more ordered than the *n*-alkanoic acid/Al system.

Then what makes these systems behave differently? The answer might lie in the binding geometry/binding strength of carboxylate on each metal as well as the surface lattice of the metal oxides. All three metal surfaces form oxides when exposed to the ambient laboratory atmosphere. The IR also clearly indicates the presence of an oxide layer under the monolayer film, but these oxides apparently have different basicities. The isoelectric points increase in the order $Al_2O_3 < Cu_2O < AgO$, with silver oxide being most basic.[8(b),47] It was pointed out earlier that the peak frequency for symmetric carboxylate shifted from 1402 cm^{-1} on silver to 1440 cm^{-1} on copper and to 1478 cm^{-1} on aluminum. This shift parallels the strength of the basicity and reflects the coordination strength when bound to the respective surface. It is interesting to note that the direction of shift also coincides with the apparent stability: the monolayer on Ag resists organic solvent rinsing, while the monolayer on Al is not stable to solvent rinsing. A carboxylate can coordinate to a metal ion in various configurations, from bridging bidentate ligand to chelating ligand to unidentate ligand (or pseudo ester). The increasing separation between the symmetric and asymmetric carboxylate vibration mode, $\Delta(\nu_a(CO_2^-) - \nu_s(CO_2^-))$, in going from Ag surface[48] ($\sim$110 cm^{-1}) and Cu surface ($\sim$111 cm^{-1}) to Al surface ($\sim$133 cm^{-1}) might also imply the trend toward an unsymmetric carboxyl configuration,[49-51] i.e., from unidentate ligand to bridging to ester-like structure.

The acid on copper and aluminum systems are interesting in contrast with an alkanethiol on silver system. To explain the invariance of intensities for methyl vibration modes, it was proposed that the chain tilts either in a positive or negative direction depending on whether it is an even or odd carbon chain.[17] A mixed domain system consisting of zero tilt and larger tilt chain assemblies was also proposed.[16] The former interpretation would imply that the interfacial energy between the methyl surface and the ambient environment plays an important role in determining the tilt. However, this factor is known to be small (energy involved a few kT, several tenths of a kcal) compared to the binding energy (tens of kcal) and chain–chain interaction (several kcal). This interpretation also requires a different binding geometry for the head group for the odd and even chain. The latter explanation did not answer the absence of an odd–even effect on methyl vibration modes. Examination of the IR and contact angle data in the thiol on Ag system[16] indicated that an odd–even effect was observed for a short chain thiol and vanished with a longer thiol. An alternative interpretation is that the structure/orientation for alkanethiol on silver depends on the chain length. The shorter chain maintains a tilt orientation. As the chain lengthens, significant chain–chain interactions come into play and the molecular chains adopt normal orientation, accompanied by restructuring of the binding layer as well as some strained segments near the head group. That this does not happen on the surface

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(48) The asymmetric vibration mode for carboxylate is hardly detected in our spectra, while in a previous report[8a] of arachidic acid on Ag, a weak peak at 1514 cm^{-1} was assigned as the $\nu_a(CO_2^-)$.

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(50) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Organometallic Compounds*; Wiley: New York, 1986.

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of gold might have to do with some intrinsic difference in the binding configuration on the two surfaces.[52,53]

Conclusion

In this paper, it was demonstrated that the structures for SAMs of *n*-alkanoic acid on copper, aluminum, and silver surfaces are dominated by the substrates as well as chain length. A spectrum of structures were suggested. The silver provides a unique setting for the carboxyl groups to bind in an highly ordered array. All available sites are occupied by the carboxyl head groups, and they pack in such a density that even for chains as short as C5, the molecular chain extends trans zigzag, forming a tilt angle between 15 and 25°. Increasing the chain length results in crystalline packing, while maintaining the same binding geometry and similar chain tilt. On the surface of copper as well as aluminum, the binding geometry precludes an ordered molecular chain for shorter chain length acids, thus leading to less densely packed film. As the chain lengthens, the cohesive interaction pulls up the chains into normal orientation while causing some strain or twisting near the head group. The strain is most serious on the surface of aluminum and less so on the surface of copper, due to a conformational mismatch between the asymmetrically bound carboxylate group and the perpendicularly oriented hydrocarbon tail.

Acknowledgment. Financial support of this work from the National Science Council of Republic of China is gratefully acknowledged.

Supplementary Material Available: Tables of peak positions for vibration modes of monolayers of $CH_3(CH_2)_mCOOH$ adsorbed on silver, copper, and aluminum as well as progressional bands (7 pages). Ordering information is given on any current masthead page.

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