

Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 5. Acid-Base Interactions

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Received February 18, 1993. In Final Form: May 3, 1993

Interactions between self-assembled monolayers containing carboxylic or sulfonic acid terminal groups, and vapor-phase *n*-alkylamine probe molecules, have been studied using FTIR-external reflectance spectroscopy, mass-sensitive surface acoustic wave devices, and ellipsometry. The results indicate that proton transfer from the surface-acid group to the amine-functionalized probe is controlled by both the proton affinity and the degree of structural ordering of the surface-acid groups. In contrast to bilayers formed by hydrogen bonding between carboxylic acid-terminated monolayers, the bilayer structures that result from proton transfer are stable for periods of many hours.

Introduction

Self-assembled monolayers (SAMs) are versatile model systems for studying interfacial electron transfer, biological interactions, molecular recognition, double-layer structure, adhesion, and other interfacial phenomena.¹ Of fundamental importance to these studies are the physical and chemical interactions between SAMs and their surrounding media. To address this issue, the general approach illustrated in Scheme I has been used to investigate electrostatic (ion-ion) binding interactions,² covalent bonding,³ and hydrogen bonding⁴ between ambient-phase molecules and SAMs. In this paper, we expand our previous study of hydrogen bonding⁴ to include acid-base interactions that occur between carboxylic and sulfonic acid-functionalized SAMs and vapor-phase probe molecules containing a terminal amine group. Results obtained from FTIR external reflectance spectroscopy (FTIR-ERS), surface acoustic wave (SAW) measurements, and ellipsometry indicate that proton transfer from the surface-acid groups to the amine-functionalized probe is controlled by the relative proton affinity and the degree of structural ordering of the surface-confined acid groups. The results reported here for SAMs are intended to complement previously reported studies of structurally related Langmuir-Blodgett multilayers, which were found to have interesting pyroelectric characteristics.⁵

Experimental Section

All chemicals were used as received from Aldrich Chemical Co., except NH₃ which was obtained from a concentrated solution

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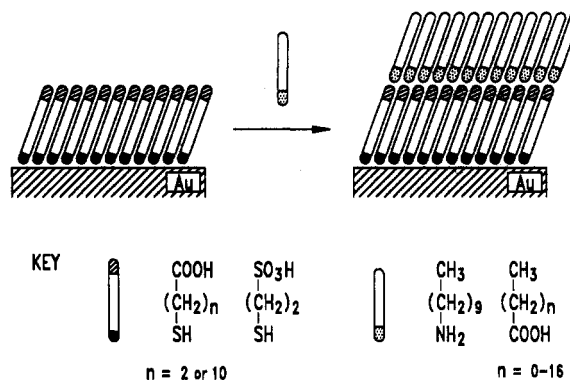
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Scheme I



of NH₄OH (J. T. Baker). Au substrates were prepared by e-beam or thermal deposition of about 200 nm of Au onto polished single crystalline Si wafers, which were previously coated with an adhesion layer of 10 nm of Cr or Ti. Au substrates for SAW measurements were similarly prepared, but the substrates were ST-cut quartz. Before metalization, the quartz surface of the SAW devices was passivated by vapor-phase silanization with (CH₃)₂HSiCl. We found that this treatment significantly reduces adsorption of the *n*-alkylamine probe molecules on the portion of the SAW device not covered with Au.

Au-coated substrates were cleaned in freshly prepared "piranha" solution (Caution: Piranha solution, 1:3 H₂O₂:H₂SO₄, reacts violently with many organic materials and should be used with extreme care, and it should not be stored in sealed containers) for about 10 s, rinsed with deionized water, and dried under N₂ gas. Long-chain carboxylic acid-terminated SAMs and methyl-terminated SAMs were prepared by soaking the freshly cleaned Au substrates in 0.5-1.0 mM ethanol solutions of HS(CH₂)₁₀-COOH or HS(CH₂)₁₁-CH₃ for at least 10 h. Au/HS(CH₂)₂-COOH substrates were prepared by vapor-phase deposition. The carboxylic acid and methyl surfaces were rinsed with 100% ethanol and then with deionized water (Milli-Q, Millipore). The water rinse ensures complete conversion of Au/HS(CH₂)_n-COO⁻ to Au/HS(CH₂)_n-COOH, since the pK_a values of close-packed surface-confined acid groups shift up relative to their bulk-phase

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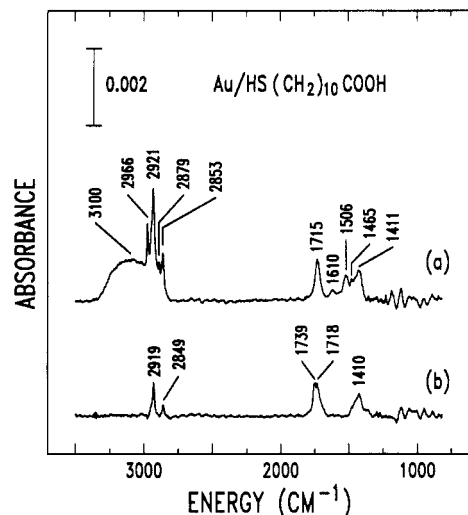


Figure 1. FTIR-ERS spectra of an Au/HS(CH₂)₁₀COOH monolayer (b) before and (a) after exposure to vapor-phase CH₃(CH₂)₉NH₂.

analogs as a result of intramonomer hydrogen bonding and electrostatic repulsion of the charged carboxylate groups.^{4,6} SAMs of Au/HS(CH₂)₂SO₃H were prepared by soaking clean Au substrates in a 5 mM aqueous solution of HS(CH₂)₂SO₃Na for at least 10 h and then rinsing the substrate with 0.2 M H₂SO₄ and water to protonate the terminal SO₃⁻ groups.

For FTIR-ERS and ellipsometry experiments, binding of *n*-alkylamine probe molecules to functionalized SAMs was carried out by exposing the monolayer-modified Au substrates to a saturated vapor of an amine at room temperature for 10 min. Binding experiments involving NH₃ were carried out by suspending SAM-modified Au substrates above a concentrated aqueous solution of NH₄OH. The substrates were then purged with flowing N₂ for at least 2 min to remove condensed amine multilayers that might have formed during the previous step.^{3a,7a} A somewhat different procedure, which is described in the text, was used for the SAW experiments. The binding process was monitored by *ex situ* FTIR-ERS and ellipsometry and *in situ* SAW measurements.

The FTIR, ellipsometry, and SAW apparatuses have been described previously.^{3a,4,7} Briefly, all FTIR-ERS data were acquired using the following parameters: p-polarized light at an 85° angle of incidence relative to the surface normal, 256 scans at 2 cm⁻¹ resolution, and box-car apodization with minimal baseline correction applied to spectra. For calculating monolayer thicknesses from the ellipsometry data, we assumed a SAM refractive index of 1.45. For SAW experiments, the relationship between the frequency change (Δf) and mass-per-area (m_A) is given by eq 1. Here, κ is the fraction of the center-to-center distance between the transducers covered by the Au film.

$$\Delta f/f_0 = -\kappa c_m f_0 m_A \quad (1)$$

In the present case, its value is 0.57. The mass sensitivity, c_m , is 1.33 cm²/g-MHz for ST-quartz; f_0 is the oscillator frequency, 98 MHz.⁷

All experiments were performed between 20 and 25 °C.

Results and Discussion

Figure 1 shows FTIR-ERS spectra for a Au/HS(CH₂)₁₀COOH SAM before and after exposure to a saturated vapor of CH₃(CH₂)₉NH₂. Before amine exposure (Figure 1b), the asymmetric and symmetric C-H stretching vibrations, which result from the methylene groups in the Au/HS(CH₂)₁₀COOH monolayer, are present at 2919 and 2849

cm⁻¹, respectively. The positions of these bands indicate that the methylene chains are mostly ordered and closely-packed in a solidlike environment, since disordered methylene chains usually exhibit stretching vibrations 5–10 cm⁻¹ higher in frequency.^{4,8} The bands at 1739 and 1718 cm⁻¹ are due to the C=O stretching vibrations of non-hydrogen-bonded and laterally hydrogen-bonded COOH terminal groups, respectively.^{4,5d,8b,c,9} The structure of the hydrogen-bonded surface which gives rise to the band around 1718 cm⁻¹ is uncertain at the present time, but steric constraints suggest that it arises from linearly hydrogen-bonded oligomers, probably dimers or short sequences.^{8b,c} The broad band centered at 1410 cm⁻¹ arises mainly from an enhancement of the C-H bending (scissors) mode in α -CH₂ groups, but it probably also includes an unresolved contribution from interacting C-O stretching and C-O-H in-plane bending modes that should be present around 1431 cm⁻¹.^{8b,10} The absence of a high-energy O-H stretching band is consistent with prior studies of acids in solid state environments,^{8b,10} and the effect may be compounded in the present case by the surface infrared selection rule.¹¹

After the COOH-terminated monolayer surface is exposed to CH₃(CH₂)₉NH₂ vapor, a layer of CH₃(CH₂)₉NH₂ adsorbs, as indicated in Figure 1a by the increased intensity of the methylene stretching bands at 2921 and 2853 cm⁻¹, and the appearance of the asymmetric and symmetric methyl vibrations at 2966 and 2879 cm⁻¹, respectively.^{8b,10} Importantly, the C=O band at 1739 cm⁻¹ (Figure 1b), which corresponds to non-hydrogen-bonded COOH groups, disappears after amine exposure while most of the C=O band intensity at 1718 cm⁻¹, which corresponds to laterally hydrogen-bonded COOH groups, remains and shifts slightly to 1715 cm⁻¹. We assign the band at 1506 cm⁻¹ (Figure 1b) to the N-H symmetric bending mode of the NH₃⁺ groups, which are formed by the vapor-phase acid-base reaction between COOH and NH₂ groups.¹⁰ The N-H asymmetric bending mode corresponding to NH₃⁺ groups is not observed, at least partially as a result of an orientation effect: NH₃⁺ groups with their 3-fold symmetry axis aligned perpendicular to the substrate surface have their asymmetric bending dipoles parallel to the surface and thus inaccessible for surface infrared excitation.¹¹ The new band centered at 3100 cm⁻¹, which is broadened by intramonomer hydrogen bonding, corresponds to the N-H stretching modes of NH₃⁺.¹⁰ The band at 1610 cm⁻¹ is assigned to the asymmetric stretching vibration of COO⁻.¹⁰ The bands at 1465 and 1411 cm⁻¹ are difficult to assign with a great deal of certainty, and the tentative assignments given here should be viewed with caution. The 1411-cm⁻¹ band probably corresponds to the α -CH₂ bending (scissors) mode, and the band at 1465 cm⁻¹ may arise from either an enhancement of the remaining CH₂ scissors modes or the COO⁻ symmetric stretching mode or a superposition of both.^{8b,10} The FTIR-ERS spectrum shown in Figure 1a does not exhibit noticeable change for at least 10 h, indicating that the bilayer structure formed after amine exposure is quite stable.

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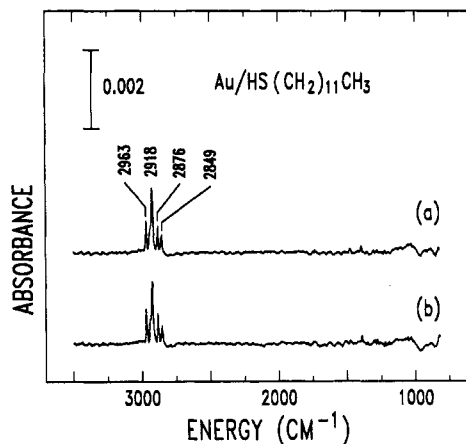


Figure 2. FTIR-ERS spectra of an Au/HS(CH₂)₁₁CH₃ monolayer (b) before and (a) after exposure to vapor-phase CH₃(CH₂)₉NH₂.

Ellipsometric measurements indicate that the thicknesses of the Au/HS(CH₂)₁₀COOH monolayer and the Au/HS(CH₂)₁₀COO⁻/NH₃⁺(CH₂)₉CH₃ bilayer are 13 ± 2 and 23 ± 2 Å, respectively. Since both the naked Au surface and the Au/HS(CH₂)₁₀COOH monolayer are high-energy surfaces,^{16,12} they are prone to contamination by the laboratory ambient. Therefore, the accuracy of the absolute thickness values may have an uncertainty greater than the ± 2 Å precision of the measurement. Additionally, the COOH and the NH₂ groups might cause the film refractive index to deviate significantly from the value of 1.45 used to calculate the thicknesses. Regardless of these relatively minor factors, however, the important point is that multilayer condensation does not occur; rather, a specific proton-transfer interaction is responsible for stable bilayer formation.

To test the possibility of CH₃(CH₂)₉NH₂ being adsorbed onto the Au/HS(CH₂)₁₀COOH monolayer surface by means other than an acid-base interaction,¹³ a control experiment was performed by dosing a Au/HS(CH₂)₁₁CH₃ SAM with CH₃(CH₂)₉NH₂. This process resulted in no detectable change in the FTIR-ERS spectrum (Figure 2). This FTIR-ERS result was confirmed by ellipsometric measurements: the thickness of the acid surface was 10 ± 2 Å before and after amine exposure.

FTIR-ERS results provide a high degree of chemical information about organic monolayers, but they do not yield reliable quantitative information about surface coverage. To determine the fractional extent of bilayer coverage, we used mass-sensitive surface acoustic wave (SAW) devices to measure adsorption and desorption in real time.^{3a,4b,7} Figure 3 shows *in situ* SAW data obtained when Au/HS(CH₂)₁₁CH₃ and Au/HS(CH₂)₁₀COOH surfaces were simultaneously dosed with a 50% -of-saturation CH₃(CH₂)₉NH₂-in-N₂ vapor stream. Vapor-phase SAW experiments of self-assembly processes nearly always result in the general trends shown in Figure 3: rapid condensation of adsorbate multilayers, in this case the amine, followed by surface saturation, and, finally, desorption of all but about one monolayer upon N₂ purging. The frequency change at the end of the experiment indicates that the methyl-terminated control surface tenaciously binds about 0.33 nmol/cm² of CH₃(CH₂)₉NH₂, eq 1. Assuming an Au roughness factor of 1.8,^{3a} this coverage corresponds to about 0.2 monolayer of CH₃(CH₂)₉NH₂. In contrast to these SAW data, the FTIR-ERS data indicated no adsorption

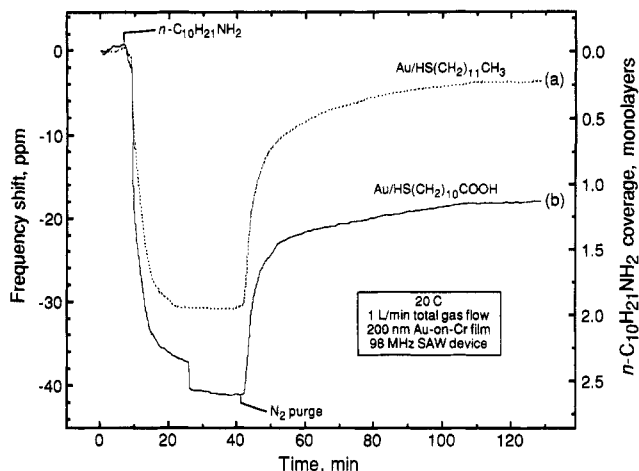


Figure 3. Response of SAW oscillation frequency to vapor-phase CH₃(CH₂)₉NH₂. The active area of the SAW device was modified with (a) a Au/HS(CH₂)₁₁CH₃ SAM and (b) a Au/HS(CH₂)₁₀COOH SAM. The difference between curves b and a at steady state corresponds to persistent adsorption of 0.9 monolayer of CH₃(CH₂)₉NH₂ on the carboxylic acid-terminated SAM.

of CH₃(CH₂)₉NH₂ onto the methyl-terminated surface. We reconcile these observations by noting that the amine will bind to portions of the quartz SAW device surface that are neither covered by Au nor completely passivated by the silanization treatment described in the Experimental Section.¹⁴

The mass of CH₃(CH₂)₉NH₂ irreversibly bound to the Au/HS(CH₂)₁₀COOH surface is much larger than that measured for the methyl surface (Figure 3). After correcting for surface roughness and the mass adsorbed to the control SAW device, we find that 0.9 ± 0.1 monolayer of amine adsorbs to the acid surface. In short, the SAW data are consistent with the FTIR-ERS and ellipsometry data presented earlier and strongly suggest that one monolayer of CH₃(CH₂)₉NH₂ tenaciously adsorbs to a Au/HS(CH₂)₁₀COOH surface. An interesting feature present in the data for the acid-terminated monolayer is the abrupt drop in frequency of about 3.5 ppm that occurs 24 min after the start of the experiment. We believe this feature results from a conformational reorganization of the growing bilayer, which makes space for additional CH₃(CH₂)₉NH₂. Although this explanation is conjectural, we are certain that this feature is not the result of a SAW device or instrumentation artifact.¹⁵

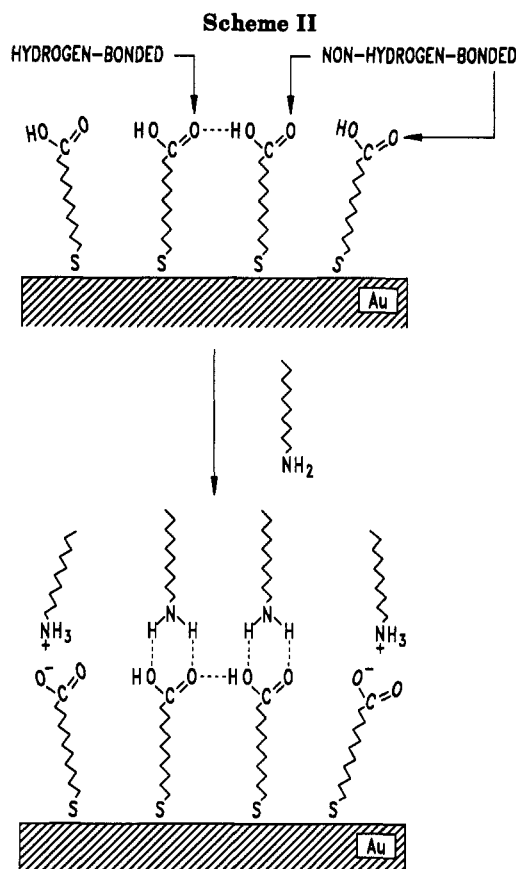
Based on the FTIR-ERS, ellipsometry, and SAW data, we suggest the model for the vapor-phase acid-base reaction between Au/HS(CH₂)₁₀COOH and CH₃(CH₂)₉NH₂ illustrated in Scheme II. After initial CH₃(CH₂)₉NH₂ adsorption, non-hydrogen-bonded C=O groups undergo either a proton transfer reaction or a hydrogen bonding interaction with NH₂ groups; this conclusion is

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(15) The transient, which occurs 24 min into the experiment shown in Figure 3, is not due to a SAW device or instrumentation artifact for the following reasons: (1) although not apparent in the figure, this "transient" actually occurred over a period of approximately 40 s, during which time four data points were acquired: this observation rules out a single-point device- or oscillator-related transient; (2) there is no similar, concurrent shift in the data for the methyl-terminated surface, which excludes the possibility of pressure or temperature transients; (3) the slope of the curve following the transient is very different than that preceding the transient, indicating a markedly slower net adsorption rate, which is consistent with the notion that the adsorbed amine monolayer "completed itself" during the transient; (4) we have previously observed and published similar SAW frequency transients associated with monolayer self-assembly (see ref 7a).

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(13) Kallury, K. M. R.; Thompson, M.; Tripp, C. P.; Hair, M. L. *Langmuir* 1992, 8, 947.



supported by the disappearance of the C=O stretching band at 1739 cm^{-1} and the bands traceable to COO⁻ and NH₃⁺ groups in Figure 1a. Since the surface coverage of CH₃(CH₂)₉NH₂ is about one monolayer, laterally hydrogen-bonded COOH groups, which are represented by the band at 1718 cm^{-1} , must also hydrogen bond to CH₃(CH₂)₉NH₂, probably through lone pairs of electrons on one or both of the acid-group oxygen atoms. This conclusion is supported by the slight decrease in the C=O stretching frequency noted for hydrogen-bonded COOH groups after amine exposure (1715 cm^{-1} in Figure 1a vs 1718 cm^{-1} in Figure 1b).^{4a,16}

It is somewhat surprising that a significant portion of the surface COOH groups can survive attack by the amine, since this type of reaction proceeds quantitatively in the liquid phase. We believe there are two reasons for this behavior that are direct consequences of the two-dimensional molecular organization of the surface-confined COOH groups. First, closely-packed methylene chains in the Au/HS(CH₂)₁₀COOH layer significantly reduce the motional freedom (entropy) of surface COOH groups; therefore, breaking lateral hydrogen bonds within the acid monolayer is thermodynamically less favorable than it is in a bulk liquid phase. In other words, the effective pK_a of a lateral hydrogen-bonded surface COOH group is higher than it is for identical molecules in bulk liquid phases.¹⁷ Second, if every surface COOH group undergoes a proton transfer reaction with a NH₂ group, then two layers of

(16) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: New York, 1971; p 74.

(17) We recently showed that solution-phase and bulk-phase pK_a values can be different by several pH units (ref 1c). Whitesides has reported data that indicate the same trend (ref 6). For surface-confined acids, there are two reasons for this behavior. First, the acidic protons are tied up in hydrogen-bonded dimers (and perhaps oligomers) and are therefore more difficult to remove. Second, removal of acidic protons results in a close-packed monolayer of negative charge, a thermodynamically unfavorable situation.

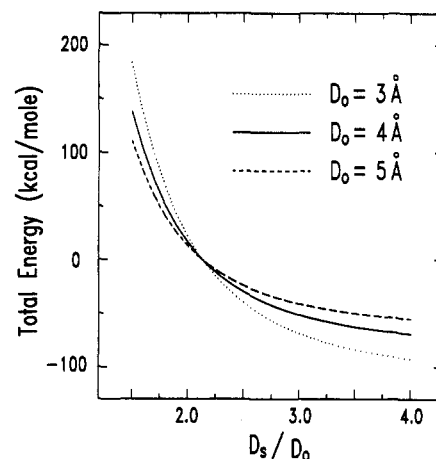
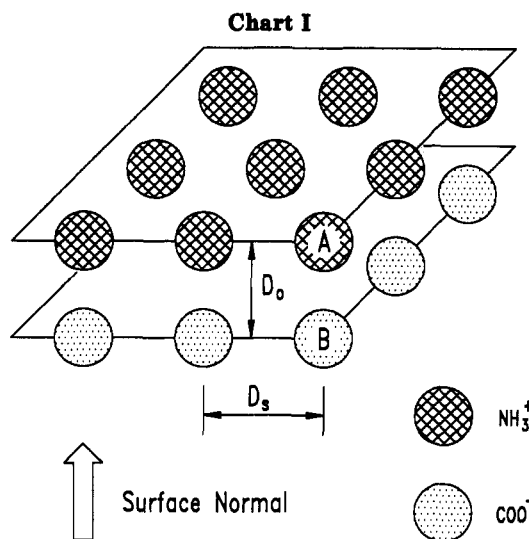


Figure 4. Calculated total binding energies for an electrostatically bound, hexagonal bilayer.



surface charge will result: one that is positively charged and one that is negatively charged, Chart I.

A simple Coulomb's law calculation indicates that the total electrostatic energy for such a segregated bilayer system is positive when the distance between two nearest neighbors that possess the same charge, D_s , is comparable to the distance between two nearest neighbors of opposite charge, D_0 . This result obtains because the repulsive Coulomb energy, which originates from same-charge nearest neighbor pairs, is larger than the attractive Coulomb energy, which originates from opposite-charge nearest neighbor pairs, because atoms in different planes are, on the average, further away from their neighbors than atoms in the same plane. However, the total energy becomes negative if the ratio, D_s/D_0 , is larger than a critical value that depends on the lattice type of each charged ionic layer.

For a hexagonal close-packed bilayer lattice, this ratio is about 2.14 (Figure 4). We made this calculation by summing the energy terms that arise from the electrostatic interactions between atom A (Chart I) and its 1450 nearest intraplane neighbors, atom B and its 1450 nearest intraplane neighbors, atom A and its 1450 nearest interplane neighbors, and atom B and its 1451 nearest interplane neighbors. Note that we include 1451 interactions in the latter case to avoid counting the attractive interaction between atoms A and B twice.¹⁸ On the basis of the van der Waals radii,¹⁹ we estimate an interplane distance between C and N atoms of 4.3 Å. Since the centers of charge may not coincide with the centers of these atoms,

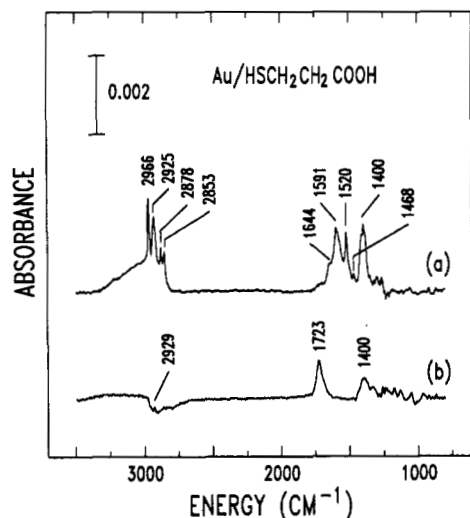


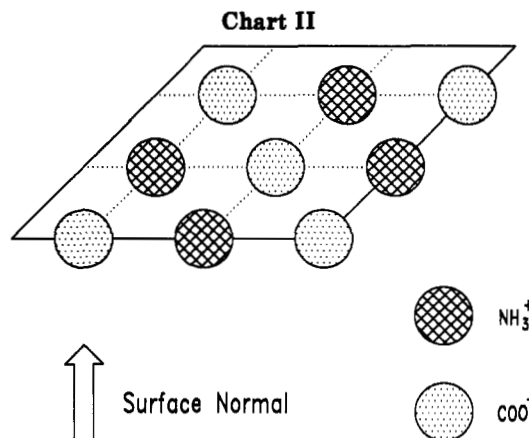
Figure 5. FTIR-ERS spectra of an Au/HS(CH₂)₂COOH monolayer (b) before and (a) after exposure to vapor-phase CH₃(CH₂)₉NH₂.

the true value of D_0 may deviate somewhat from this value. However, the calculation indicates that over the range 3–5 Å the same general trends in total energy obtain.

In our system, sites of proton transfer reactions between pairs of COOH and NH₂ groups are probably separated by regions where laterally hydrogen-bonded COOH groups form ordered domains that are not reactive toward NH₂ groups (Scheme II). This situation is equivalent to having a large D_0/D_0 ratio so that the total Coulomb energy is dominated by the attractive term from each ion pair. Sites of COO⁻ and NH₃⁺ pairs are likely to be located at less-ordered domain boundaries or at defect sites within each domain, where OH moieties in COOH groups do not undergo hydrogen bonding and therefore react with NH₂ groups without the extra energy cost associated with breaking intramonolayer hydrogen bonds.

To test the importance of chain length on surface acid/base chemistry, we also examined the interaction between a Au/HS(CH₂)₂COOH SAM and vapor-phase CH₃(CH₂)₉NH₂. Prior to reaction with the amine, we observed a strong C=O stretching vibration at 1723 cm⁻¹ (Figure 5b), but after exposure to the amine (Figure 5a) this peak completely disappears and is replaced with absorbances traceable to the asymmetric and symmetric NH₃⁺ bending modes at 1644 and 1520 cm⁻¹, respectively, and the COO⁻ asymmetric stretching mode at 1591 cm⁻¹. The band at 1400 cm⁻¹, which is present in both parts of Figure 1, probably arises from the enhanced α -CH₂ bending (scissors) mode. The band at 1468 cm⁻¹ (Figure 1a) is likely to be a superposition of absorptions from the remaining CH₂ scissors modes and the symmetric COO⁻ stretching mode.^{9b,10} In contrast to the incomplete proton exchange reaction between the longer-chain COOH-terminated SAM and the amine, we interpret the data for the short-chained SAM as resulting from complete proton transfer.

The differences in the extent of the surface reactions between the long- and short-chained carboxylic acid-terminated monolayers and the amine-terminated, vapor-phase reactant arises from differences in monolayer



acidities (surface pK_a values), which are brought about by van der Waals-induced ordering effects and the chain-length-dependent stability of the carboxylic acid-terminated monolayer. Reactions between disordered surface-confined COOH groups and the probe-molecule NH₂ groups are possible because the resulting NH₃⁺ and COO⁻ groups have the structural freedom to arrange themselves in low-energy configurations, which reduces the effects of the repulsive electrostatic interactions discussed earlier. For example, NH₃⁺ groups may penetrate the SAM layer slightly to enhance their interactions with the surface-confined anions. The necessary free volume that such a configuration implies may arise from partial surface displacement of HS(CH₂)₂COOH by the amine. We have previously observed that amine-terminated alkanes undergo self-assembly onto Au from the vapor phase, and that *n*-alkylamines are capable of displacing surface-confined HS(CH₂)₂CH₃.¹⁴ A configuration involving interpenetration of acid and amine groups will result in an energetically stable network in which positive and negative ions are arranged in a configuration analogous to that of the (100) plane of NaCl, Chart II. Such a configuration is not possible in a close-packed monolayer, which forms an effective barrier to NH₃⁺ interpenetration. From the data discussed here, we conclude that surface pK_a values for carboxylic acid-terminated monolayers, and therefore their likelihood of participating in proton transfer reactions, are strongly chain-length dependent.

To learn more about the acid-base characteristics of functionalized organic monolayer surfaces, we exposed a Au/HS(CH₂)₂SO₃H SAM to vapor-phase CH₃(CH₂)₉NH₂. Before reaction (Figure 6b), the presence of surface-confined SO₃H groups is supported by asymmetric and symmetric O=S=O stretching vibrations at 1394 and 1172 cm⁻¹, respectively.¹⁰ The two-carbon methylene chains are represented by the just-visible peak corresponding to the asymmetric C-H stretching vibration at 2925 cm⁻¹, which emerges from a broad negative band centered at 2900 cm⁻¹. The broad feature probably results from slight contamination of the Au reference substrate. After reaction (Figure 6a), all surface SO₃H groups are converted to SO₃⁻ groups, as indicated by the disappearance of the 1394-cm⁻¹ band and the appearance of the 1215- and 1048-cm⁻¹ bands, which originate from the asymmetric and symmetric O=S=O stretching modes of SO₃⁻ groups, respectively.¹⁰ Complete proton transfer from Au/HS(CH₂)₂SO₃H to CH₃(CH₂)₉NH₂ is also supported by the symmetric bending mode of the NH₃⁺ groups present at 1536 cm⁻¹. Evidence of stable CH₃(CH₂)₉NH₂ adsorption can also be inferred from the appearance of bands near 2900 cm⁻¹, which result from asymmetric and symmetric C-H stretching vibrations of the methyl and

(18) It is important to include the same number of negative and positive ions in the calculation, since neither the repulsive nor the attractive energy sum converges. The validity of our numerical approach was confirmed by calculating the Madelung constant of the NaCl lattice: the calculated value is 1.7475, which is very close to the literature value of 1.7476 (ref 19).

(19) CRC Handbook of Chemistry and Physics, 70th ed.; Weast, R. C., Lide, D. R., Eds.; Chemical Rubber Corporation: Boca Raton, FL, 1989.

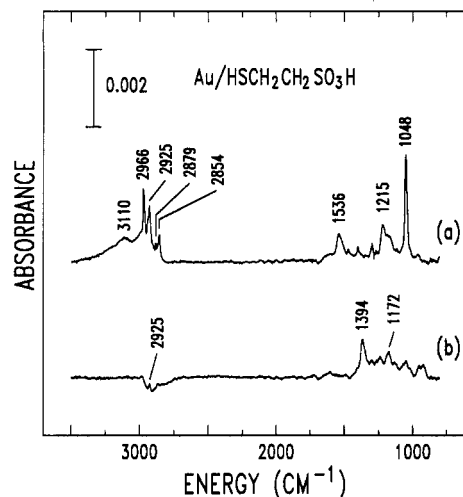


Figure 6. FTIR-ERS spectra of an Au/HS(CH₂)₂SO₃H monolayer (b) before and (a) after exposure to vapor-phase CH₃(CH₂)₉NH₂.

methylene groups in CH₃(CH₂)₉NH₂. On the basis of the data shown in Figure 6, we conclude that surface-confined sulfonic acid groups are at least as acidic as the corresponding carboxylic acid groups. This result is, of course, in accord with expectations based on bulk-phase chemistry.

We have found that bilayer stability is a function of the length of the hydrocarbon chain of the vapor-phase, amine-terminated probe molecule. For example, we find that NH₃ does not irreversibly adsorb to a COOH-terminated surface, while the stability of a bilayer capped with CH₃(CH₂)₅NH₂ is roughly midway between that of NH₃ and CH₃(CH₂)₉NH₂. In a previous paper relating to hydrogen bonding interactions,^{4a} we used acidic probe molecules and found that the lightest *n*-alkanoic acid that adsorbed onto a COOH-terminated surface for more than a few minutes was CH₃(CH₂)₉COOH. Applying the simple model we used to analyze the previously reported data,^{4a} we conclude that interactions between surface COOH groups and NH₂ probe groups are stronger than those

between surface COOH groups and COOH-terminated probe molecules. This conclusion is also supported by the methylene C–H stretching frequencies shown in Figure 1a, which are shifted to lower energies by about 5–8 cm⁻¹ compared to those found for the COOH-capped bilayers.^{4a} This shift suggests a higher degree of stability and order for bilayers that rely at least in part on proton transfer reactions.

Conclusions

To summarize, we have interpreted interactions between self-assembled monolayers terminated with COOH and SO₃H groups and vapor-phase *n*-alkylamine probe molecules on the basis of FTIR-ERS, SAW measurements, and ellipsometry. We find that both hydrogen-bonding and Coulomb interactions are responsible for the adsorption of the amine probe molecules on the acid surface. Moreover, the degree of structural ordering of the terminal acid groups strongly influences the interaction mode. Hydrogen bonding is significant only when the surface-acid groups are well ordered, while Coulomb interactions dominate when the surface-acid groups are disordered or loosely-packed. The acidity of the surface-confined and vapor-phase reactants is also important. When the relative acidities are matched, only hydrogen bonding interactions occur,^{4a} but as the difference in acidities becomes greater, the likelihood of proton transfer is enhanced.

Acknowledgment. R.M.C. and L.S. gratefully acknowledge the National Science Foundation (CHE-90146566) for partial support of this research. Work at Sandia National Laboratories is supported by the U.S. Department of Energy under Contract DE-AC04-76DP00789. The excellent technical assistance of Mary Anne Mitchell is acknowledged by A.J.R. We are also grateful to one of the reviewers for clarifying the low-energy IR band assignments for the carboxylic acids and for providing insight and guidance with regard to the electrostatic binding-energy calculations.