

Probing Adhesion Forces at the Molecular Scale

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Abstract: Adhesion forces between well-ordered organomercaptan monolayer films strongly bound to both a Au substrate and a microscopic Au probe were measured over separations ranging from ~ 10 nm to repulsive contact and probe radii from 50 nm to 60 μm using interfacial force microscopy. Films terminated with methyl groups (CH_3 vs CH_3) were examined and these results are contrasted with hydrogen-bonding (NH_2 vs NH_2 and COOH vs COOH) and acid–base (NH_2 vs COOH) combinations. From the peak value of the adhesive pull-off force, we calculate interfacial bond energies using a model that has been shown to be applicable in such situations. These values qualitatively scale with those expected for van der Waals, hydrogen-bonding, and acid–base interactions. The force-versus-displacement behavior, which has not previously been measured, is suggested to be dominated by the distinctive mechanical properties of the films.

Introduction

Measurements of adhesion forces at the molecular scale, such as those discussed here, are necessary to understand macroscopic boundary-layer behavior such as adhesion, friction, wear, lubrication, and many other important phenomena.¹ Our recent interfacial force microscopy (IFM) studies have provided detailed information about the mechanical response of both self-assembling monolayer (SAM) films and the underlying substrates.^{2–4} In addition, we recently demonstrated that the IFM is useful for studying the chemical nature of such films.⁵ In this report, we discuss a new method for studying surface interactions and chemical reactions using the IFM.⁶ To quantitatively measure the work of adhesion and bond energies between two organic thin films, we modify both a Au substrate and a Au probe with self-assembling organomercaptan molecules having either the same or different end groups (CH_3 , NH_2 , and COOH) (Figure 1) and then analyze the force-versus-displacement curves (force profiles) that result from the approach to contact of the two surfaces.⁷ Our results show that the magnitude of the adhesive forces measured between methyl–methyl interactions are in excellent agreement with van der

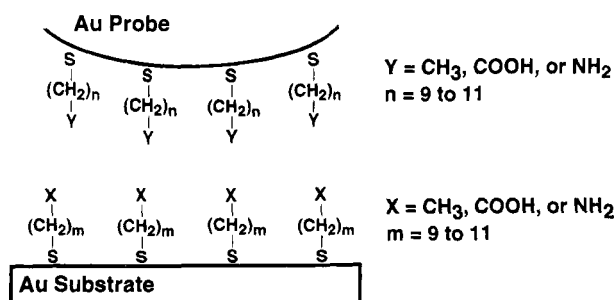


Figure 1. Schematic illustration of the experimental configuration. An Au probe and an Au substrate are covered by self-assembled monolayers of *n*-alkanethiol molecules with different combinations of end groups. The force of interaction between these films is recorded as a function of relative separation up to repulsive contact.

Waals calculations using Lifshitz theory^{8,9} and previous experimentally determined values.^{10,11} Moreover, the measured peak adhesive forces scale as expected for van der Waals, hydrogen-bonding, and acid–base interactions.

Over the past few years there have been several surface forces apparatus (SFA)^{12,13} and atomic force microscopy (AFM)^{14–20} studies probing specific chemical and mechanical interactions between surfaces. However, SFA and AFM necessitate the use of deflection-based force sensors, which are mechanically unstable when the force gradient between the probe and substrate

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exceeds the sensor force constant, k . This instability causes the SFA or AFM probe to "jump" into contact with the substrate at surface separations ranging from a few angstroms up to hundreds of angstroms depending on the stiffness of the sensor spring and the nature of the interfacial forces. Jump-to-contact complicates data interpretation since it causes discontinuities in the force data and, more importantly, can generate large contact stresses that physically damage the surface where adhesive bonding is being probed. The IFM uses a self-balancing force-feedback system to avoid this instability, which allows us to controllably form and measure the mechanical stability of the adhesive interface over a large range of separations including repulsive contact.⁶ The IFM force-feedback approach also decouples the sensor and substrate responses so that force measurements are not dominated by the elastic compliance of the sensor.⁶ In addition, a broad range of well-defined tip and substrate surfaces can be readily accommodated with virtually no materials constraints.

Experimental Section

We use SAM films adsorbed on Au substrates because of their well-understood structure and easily tailored chemical properties.⁷ Monolayer films were prepared by soaking Au probes and Au substrates in ~ 0.5 mM ethanolic solutions of a specific n -alkanethiol ($\text{HS}(\text{CH}_2)_n\text{X}$, where $n = 9$ to 11 and $\text{X} = \text{CH}_3$, NH_2 , or COOH) for a minimum of 24 h. The substrates were prepared by room-temperature electron-beam deposition of 200 nm of Au over a Ti-primed (20 nm) Si(100) wafer. We have previously used AFM to measure the rms surface roughness (1.8 nm) and crystallite size (60 nm) of these substrates; results from others indicate that the crystallite orientation at the surface is primarily (111). The Au IFM probes were fabricated by (i) electrochemically etching 50- μm -diameter Au wires in a freshly prepared piranha solution (3:1 concentrated H_2SO_4 :30% H_2O_2 . **Cauti-**on: piranha solution is a powerful oxidizing agent and reacts violently with organic compounds. It should be discarded immediately after use in a waste container with a loosely fitting lid.), (ii) flame annealing 50- μm -diameter Au wire, or (iii) combining these two methods (e.g., the Au wire was etched followed by annealing only the end of the tip). The probes were characterized by scanning electron microscopy (SEM) after IFM measurements and found to have a parabolic or spherical shape with apex radii of curvature ranging from 50 nm to 60 μm .²¹ We have previously shown that stable SAMs reproducibly adsorb to Au probes.⁵

The IFM measurements were carried out in a low-pressure chamber that was evacuated to 10^{-4} mmHg and then back-filled with dry N_2 . Measurements such as those we describe here are often carried out in liquids to minimize the effects of jump-to-contact, but as discussed earlier the IFM is not subject to this instability. This is a distinct advantage since complications arising from solvents and solvent-borne contaminants are eliminated. We locate the surface by controllably bringing the probe tip into the proximity of the substrate surface by sensing the first detectable contact load (< 50 nN). After the surface was located in this manner, the force profile was measured by moving the two surfaces apart a fixed distance before ramping the probe toward the specimen at a rate of 8 nm/s until we detect zero force after contact. At this point the probe was separated from the specimen surface at the same rate. We typically measured two to three force profiles with a particular probe. Adhesion measurements for each film combination were obtained with at least three different probes. We examined only a small number of adhesive events per probe because multiple contacts

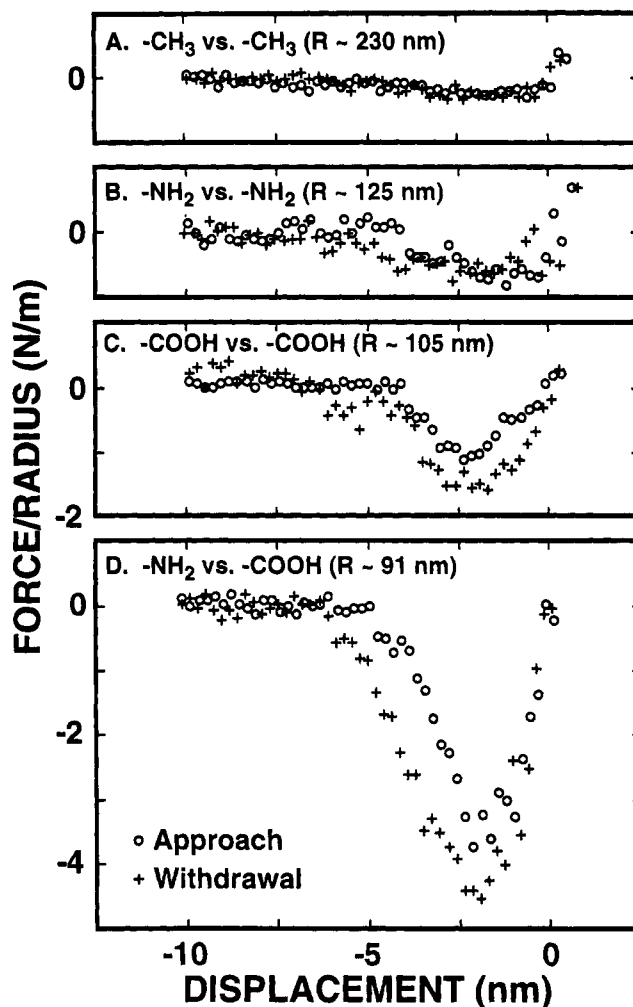


Figure 2. Force-versus-displacement curves taken between (A) two methyl-terminated SAMs, (B) two amine-terminated SAMs, (C) two carboxylic acid-terminated SAMs, and (D) an amine- and a carboxylic acid-terminated SAM. The force axis is normalized to the probe radius, and force data are plotted on the same scale to facilitate direct comparison between different chemical interactions. Zero displacement is arbitrarily chosen to represent the point where the force goes through zero while the probe is in contact with the sample. For clarity, only 20% of the data points for both the approach ($\circ$) and withdrawal ($+$) curves are plotted.

yielded adhesive forces that are substantially different from the initial force data, suggesting progressive damage to the SAM films.²²

Results and Discussion

Representative force profiles for SAMs having the terminal-group combinations indicated are shown in Figure 2. The force axis is normalized to the probe radius, and all of the force data are plotted on the same scale to facilitate direct comparison of the different chemical interactions. We arbitrarily chose zero displacement to represent the point where the interaction force goes through zero while the probe is in contact with the sample (i.e., zero applied force). Within the noise limitations, the force curves are continuous, which indicates that no jump-to-contact occurs between the probe and substrate.

Work of Adhesion. We use the peak value of the attractive force from the unloading curve (pull-off force) along with established adhesion models to evaluate the work of adhesion for the various film combinations. We considered two quantitative adhesion models that differ in the way in which they handle the range of attractive forces and the elastic compliance of the

(21) We examine each probe by SEM after IFM measurements to normalize the magnitude of the force results with respect to its radius and to critically evaluate its parabolic or spherical shape.

(22) We observe several effects between the different combinations of SAMs that result from repetitive force-versus-displacement measurements taken in the same substrate location. For example, the magnitude of the adhesive forces can vary by factors of ~ 2 compared with initial force data. We also observe hysteresis in some of the force profiles, which is not initially present.

Table 1. Summary of Statistics on Adhesion Experiments

interaction couple	F/R (N/m)	W (mJ/m ²) ^a	γ (mJ/m ²) ^b	bond energy (kcal/mol) ^c
CH ₃ vs CH ₃	0.4 ± 0.2	60 ± 32	30 ± 16	<i>d</i>
NH ₂ vs NH ₂	0.7 ± 0.2	100 ± 24	50 ± 12	1.3 ± 0.7
COOH vs COOH	1.4 ± 0.3	228 ± 54	114 ± 27	5 ± 2
NH ₂ vs COOH	4.3 ± 0.4	680 ± 62	-516 ± 69 (γ_{12})	16 ± 2

^a The peak value of the attractive force from the unloading curve (pull-off force) and the DMT model²⁴ were used to estimate the work of adhesion, W . These values were converted to (b) surface energies, γ , by using eq 3 and (c) bond energies by converting the value of the pair-wise component from an energy per area (mJ/m²) to an energy per mole (kcal/mol) using the molecular packing density of the SAM.²⁷

^b Since the van der Waals interaction is not a "two-center" bond under the experimental conditions described, the bond energy value is not meaningful.

interfacial materials. The JKR model²³ includes only zero-range surface forces but explicitly treats the effect of adhesive bonding on the contact deformation, while the DMT model²⁴ includes long-range interactions but does not accurately address adhesion-controlled compliance effects. Past studies have found that the JKR model underestimates the work of adhesion but reasonably predicts the contact area at pull off.²³ In contrast, the DMT model accurately estimates the work of adhesion but predicts zero contact area at pull off.²⁴

As in previous SFA studies,²⁵ we have used the DMT model²⁴ to calculate the work of adhesion, W , for a sphere interacting with a flat surface (eq 1). Here F is the pull-off force of the

$$W = \frac{F}{2\pi R} \quad (1)$$

unloading curve and R is the probe radius. (We have also calculated W by integrating the area under the unloading curve and estimating the contact area at zero load using the JKR model. Within the limitation imposed by the noise level of the experiments, the results are indistinguishable from those listed in Table 1.) For interactions between two identical surfaces, W is equal to twice the value of the surface energy, γ , of the material being studied.²⁶ Table 1 summarizes pull-off force measurements for several film combinations. These data include the statistical variation of the initial force-versus-displacement measurement for a minimum of three different probe radii.²² Table 1 also includes values for the surface energies (determined for symmetric combinations), interfacial energy (determined for the asymmetric combination), and the bond energies. We calculated the bond energies by converting the pairwise component of the surface energy, which we defined as the total energy minus the van der Waals contribution that we assume is equal to the surface energy for the methyl-methyl case, from an energy per area (mJ/m²) to an energy per mole (kcal/mol) using the molecular packing density of the SAM (21.4 Å²/molecule).²⁷

From the measured pull-off force between two methyl-terminated SAMs, we determine a surface energy of 30 mJ/m², which is in excellent agreement with results obtained from SFA measurements of crystalline-monolayer hydrocarbon films, 28 mJ/m²,¹⁰ and from bulk contact-angle measurements of similar low-energy hydrocarbon molecules, 23–31 mJ/m².¹¹ Since our

measured surface energy is consistent with results from Lifshitz theory,^{8,9} we conclude that the adhesive forces for this film combination can be attributed solely to van der Waals forces.²⁸

Our pull-off force measurements for two amine-terminated SAMs yield a work of adhesion of 100 mJ/m². When considering molecular species that can form hydrogen bonds across an adhesive interface, Fowkes²⁹ has suggested that the surface energy can be resolved into a component due to van der Waals forces, γ_{vdw} , and a component due to pairwise interactions such as hydrogen bonding, $\gamma_{\text{H-bond}}$ (eq 2). Since the

$$W = 2\gamma_{\text{vdw}} + 2\gamma_{\text{H-bond}} \quad (2)$$

van der Waals component for the amine-terminated film will be nearly identical to the methyl-terminated SAM, we can use eq 2 to estimate a hydrogen-bonding component of the adhesion energy to be 40 mJ/m². From this result we estimate that the hydrogen bonds formed across the interface have a bond energy of 1.3 kcal/mol. In the gas phase, methylamine is found to dimerize by the formation of one hydrogen bond per molecule having a bond energy of 3.4 kcal/mol.³⁰

Since carboxylic acid groups can also form intermolecular hydrogen bonds, we analyzed the force profiles for carboxylic acid-carboxylic acid interfaces using the same procedure described for the amine-amine adhesion pair. Beginning with the measured adhesion energy of 228 mJ/m², we attributed 60 mJ/m² to van der Waals interactions leaving 170 mJ/m² attributable to interfacial hydrogen-bonding interactions. (In order to verify that the van der Waals component was not strongly affected by the functional groups, we measured the adhesion force for a carboxylic acid-methyl pair and found it to be indistinguishable from the strength of the methyl-methyl van der Waals interaction.) The hydrogen-bond component of the surface energy for the carboxylic acid-carboxylic acid pair that was determined in this way corresponds to 5 kcal/mol. The measured dimerization energy of formic acid in the vapor phase involves two hydrogen bonds per dimer pair and is 14 kcal/mol.³⁰

For both the amine-amine and the carboxylic acid-carboxylic acid pairs, the magnitude of the interfacial hydrogen-bond energy estimated from the adhesion force is smaller than the value obtained from gas-phase experiments. The weakened interfacial hydrogen bond, especially for the carboxylic acid-terminated SAMs, may result from competition with intramonomer lateral hydrogen bonds that form within SAMs or steric restrictions associated with the close-packed film structure that prevent formation of the most favorable bonding configuration.^{31–33} Regardless of these differences in absolute energies, the important point is that the relative interfacial bonding strengths determined from the force profiles are of the appropriate magnitude in going from the methyl-methyl pair, which form no hydrogen bonds, to the amine-amine pair, which form

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one hydrogen bond per molecule, to the carboxylic acid–carboxylic acid interface, which can form two hydrogen bonds per molecule.

The measured value for the work of adhesion between carboxylic acid- and amine-terminated SAMs is 680 mJ/m². Since we are now considering adhesion between dissimilar materials, we must account for the additional contribution of the interfacial energy to the work of adhesion (eq 3).²⁶ In eq 3,

$$W_{12} = \frac{1}{2}(W_1 + W_2) - \gamma_{12} \quad (3)$$

γ_{12} is the interfacial energy (subscripts 1 and 2 refer to the carboxylic acid- and amine-terminated SAMs, respectively). Although γ_{12} could also be resolved into van der Waals and pairwise components, we have assumed that the van der Waals contribution is negligible compared to the value determined for the symmetric combinations, which are included in W_1 and W_2 . Using the values of W_1 and W_2 determined from adhesion measurements on like combinations, we calculate an interfacial energy of -516 mJ/m² or a bond energy of 16 kcal/mol. The negative sign for interfacial energy indicates that stronger bonds are formed at the acid–base interface compared to the acid–acid or base–base interface,³⁴ which is in accord with chemical intuition. Calorimetry studies that measure the enthalpy of complexation for a primary amine added to a pure solution of a carboxylic acid yield interaction energies that range up to 23 kcal/mol.^{35,36} However, caution must be used in directly applying these values to estimate the interfacial adhesive bond since the magnitude of the enthalpy change depends upon the degree of complexation, which is sensitive to the relative concentrations of the acid and base components. Nonetheless, the measured interaction energy is certainly in a range that is consistent with the value that we determine from the adhesion measurements.

In addition to hydrogen bonding, the acid–base SAMs interact by proton transfer from the carboxylic acid to the amine terminal group.³⁷ Although we do not know the exact amount of charge transferred between the two surfaces, previous studies of vapor-phase *n*-alkylamine probe molecules interacting with carboxylic acid-terminated SAMs suggest that proton transfer is controlled by both the proton affinity and the structural ordering of the reactive end groups.³⁷ We do not observe any evidence that charge remains on either the amine or carboxylic acid surface after the IFM measurements, which is in contrast to recent SFA studies where an electrical discharge was observed between silica and aminosilane-covered silica surfaces.^{13b} However, the insulating substrate used in this study may have supported some of the charge transferred between the two dissimilar surfaces prior to separation.

Unlike the methyl–methyl case, the SAM films with carboxylic acid and amine end groups are not hydrophobic and can be expected to adsorb at least a submonolayer quantity of water from the environment. Adsorbed water will reduce their surface energies,³⁸ but we can rewrite eq 3 to account for the difference (eq 4). Here, Δ_1 and Δ_2 are the amounts that the

$$W_{12} = \frac{1}{2}W_1 - \Delta_1 + \frac{1}{2}W_2 - \Delta_2 - \gamma_{12} \quad (4)$$

adsorbates reduce the surface energy of the carboxylic acid-

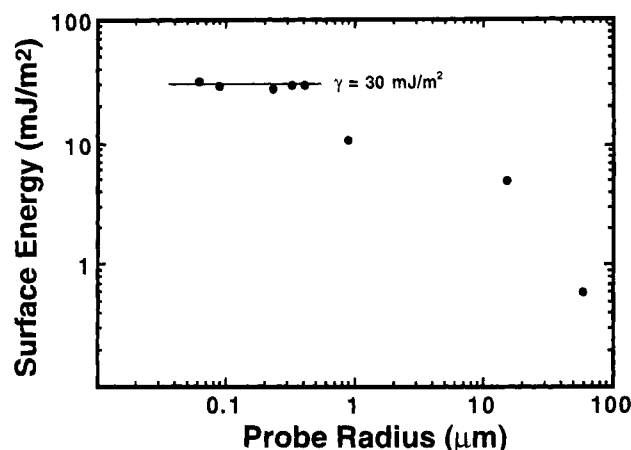


Figure 3. Surface energy, γ , versus probe radius between two methyl-terminated SAMs. γ was determined using the DMT model for interfacial adhesion.²⁴

and amine-terminated SAMs, respectively. These effects are illustrated by contrasting the measured surface energy of mica cleaved in a vacuum, ~ 4500 mJ/m², to the value obtained in air, ~ 300 mJ/m².³⁸ Thus, the actual values of W for combinations other than the two methyl-terminated SAMs are likely to be even larger than those in Table 1.

Even in the absence of extrinsic effects such as impurity adsorption, the bond energies determined from solid–solid adhesion measurements may never be as high as those estimated from either solution- or vapor-phase analogs. At a solid–solid interface, hydrogen-bond and acid–base interactions can be sterically hindered from forming their optimum bonding configuration. In contrast, adhesion energies that are due solely to van der Waals interactions should be easier to predict since they are not influenced by steric constraints of the end groups. Although our data for methyl–methyl and carboxylic acid–carboxylic acid interactions are consistent with this line of reasoning, we cannot quantitatively address the effect of functional group orientation on interfacial bonding until we perform these measurements in ultrahigh vacuum (UHV) conditions where the influence of impurities on the surface can be controlled.

Adhesion measurements can also be affected by the shape of the probe. For example, Burnham et al. measured the pull-off force between a tungsten probe and a methyl-terminated monolayer film in air.¹⁶ The monolayer films in these experiments were bound to an oxidized Al substrate through a carboxylic acid head group. Using a 2-μm radius probe tip, they measured a pull-off force of 35 nN which, using eq 3, corresponds to a surface energy of 1.4 mJ/m². Their results are far below our measured value for van der Waals forces or that expected from Lifshitz theory. They suggested, however, that this value was low because their tip had asperities which reduced the contact area. Since this study used a probe with a much larger radius than ours, we investigated the effect of probe size on the measured pull-off force. We performed adhesion measurements between methyl-terminated SAMs while varying the probe radius from 50 nm to 60 μm. The data shown in Figure 3 are plotted in terms of the surface energy determined from eq 3. The magnitude of the normalized adhesive interaction remains constant with the size of the probe until tip radii exceed ~ 400 nm, decreasing strongly for larger probe radii. We also attribute the smaller adhesion values measured with Au probes of larger radius to poor contact between the two

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surfaces due to asperities on the probe tip (macroscopic faceting). Recent molecular dynamic simulations of SAMs under compression have shown that such tip asperities can greatly influence the contact loads applied to the monolayer films.³⁹ Previous AFM studies also suggest that small asperities on the probe would significantly influence the magnitude of the measured adhesion forces.^{16,17} The surface roughness of the Au substrate could also affect the contact area for probes having large radii.

Force-versus-Displacement Measurements. Because of the instrumental jump-to-contact phenomenon,¹ only a few force profiles conducted in air or dry nitrogen have been published. Thus, there is little precedent for analyzing the shape of the force profiles shown in Figure 2. As discussed previously, Burnham et al.¹⁶ reported behavior similar to that shown in Figure 2C using an AFM with a cantilever having a spring constant of 50 N/m. However, as mentioned earlier, the maximum adhesive force was found to be much smaller than expected. Moreover, the range of interaction extended to approximately 20 nm. Since these measurements were conducted in air, the tungsten probe was probably covered with a contamination layer, which would account for the long-range interaction.

We can obtain an approximate value for the expected range of interaction for our simplest adhesion couple (i.e., CH₃ vs CH₃) by assuming that the films are rigid and that adhesive interactions only arise from van der Waals forces. For a sphere of radius R interacting with a flat substrate, the force of interaction is given by the expression $F(d) = \text{constant}/d^2$, where d is the separation between the surfaces of the films.⁴⁰ The peak attractive force will occur at contact when d reaches its minimum value d_0 . This value has been found to be near 0.16 nm for a wide variety of materials including hydrocarbons.⁴¹ Thus, for a separation d of 1.6 nm, the interaction force is reduced by a factor of 100. This separation is considerably less than the apparent threshold for the CH₃ vs CH₃ interaction shown in Figure 2A, which occurs at a value near 5 nm relative to the equilibrium point where the force equals zero. In fact, this ~5 nm threshold is found for all of the combinations shown in Figure 2.

We do not fully understand the origin of the force-versus-displacement behavior shown in Figure 2 at the present time. However, it seems clear that they must be dominated by the unique mechanical properties of the SAMs. For example, in their normal configuration the SAM films tilt by about 30° to maximize their lateral van der Waals interactions. Under the

influence of interfilm forces, the films could stand erect, which would increase their range of interaction but would decrease their interaction strength (because of the decreased packing density). Increasing the contact area between the two films would increase the packing density until it is balanced by the repulsive interfilm interaction (which has been found to be highly nonlinear^{4,39}). Such behavior is not addressed by either the JKR or DMT models and would have the effect of greatly increasing the apparent range of the interfacial interaction. An additional feature of the SAMs having reactive end groups is the appearance of hysteresis in the force-versus-displacement data. Our measurements are transient in nature, and this "adhesive hysteresis" occurs because of the time required to fully form the interfacial bonds.⁴² Further force-versus-displacement data taken in more carefully controlled environments, at various rates, and for a variety of film lengths should be revealing in this regard.

Conclusions

In summary, we have used the IFM to measure the magnitude of the adhesion forces for chemical interactions between well-ordered SAMs having either the same or different terminal groups. Using the pull-off force and the DMT adhesion model, we calculate the effective surface energies for the various end-group combinations. Although adsorbed water may affect our measured values, the work-of-adhesion values qualitatively scale as expected for van der Waals, hydrogen-bonding, and acid-base interactions, and the methyl-methyl value agrees with those previously found for similar hydrocarbons. These experiments are an important step toward future UHV experiments that should provide more accurate values of interfilm bond energies. The details of the force profiles, which have not previously been available for analysis, are not consistent with either the JKR or DMT models for interfacial adhesion, and we believe they require consideration of the distinctive chemical and mechanical properties of the films. We suggest that the long-range interaction between the two surfaces is dominated by the films' ability to change configuration as the surfaces are brought into near contact. We observe considerable adhesive hysteresis for the chemically active film combinations, which is due to the time dependence of the interfilm bonding.⁴²

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