Low-Energy Ion−Surface Reactions of Pyrazine with Two Classes of Self-Assembled Monolayers: Influence of Alkyl Chain Orientation

Vincent J. Angelico, Scott A. Mitchell,[†] and Vicki H. Wysocki*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Collisions of pyrazine with two classes of self-assembled monolayer (SAM) films are employed to determine whether surface confinement and the resulting alkyl chain orientation, influences low-energy ion−surface reactions. SAM films formed from *n*-alkanethiols ($CH_3(CH_2)_n$−S−Au, *n* = 14−17) and 4-(4-alkoxyphenylbenzenethiols (4-(4-$CH_3(CH_2)_mOC_6H_4$)−C_6H_4−S−Au, *m* = 14−17) chemisorbed onto Au (111) substrates are known to exhibit a chain-length-dependent odd−even effect that places the terminal C−C bond into different orientations. Ion−surface collisions (20 eV) of pyrazine molecular ion (M = *m/z* 80) with these surfaces yield reaction product ions corresponding to the addition of hydrogen atoms ([M + H]$^+$ = *m/z* 81) and methyl groups ([M + CH_3]$^+$ = *m/z* 95) from the surface to the probe ion. Differences in the relative abundance of the reaction product ions are measured as a function of chain length for both classes of SAM film. SAM films with odd chain lengths (*n*, *m* = 14 and 16) have a consistently higher abundance of H addition product ions than SAM films with even chain lengths (*n*, *m* = 15 and 17). Alternating reactivity is also observed for the addition of CH_3, with methyl addition occurring more readily on even-chain-length films. The variations are consistent with the well-characterized orientation differences known to exist for films of this type. Specifically, odd-chain-length films are oriented such that the last C−C bond is more parallel to the plane of the surface than it is for even-chain-length films. The critical element of the parallel orientation is that it leaves, on average, one hydrogen atom on the terminal methyl and both hydrogen atoms on the first underlying methylene in more reactive positions compared to even chain lengths. Conversely, the trend in the relative abundance of CH_3 addition indicates that the orientation produced by an even-chain-length film, with the last C−C bond more perpendicular to the surface, allows the probe ion better access to the methyl carbon. Reflection absorption IR spectroscopy (RAIRS) data independently confirm the orientational disposition of the films. The RAIRS data show that the odd−even effect is less dramatic for the *n*-alkanethiols when compared to 4-(4-alkoxyphenyl)-benzenethiols. A smaller difference in ion−surface reactivity is measured for *n*-alkanethiols, demonstrating that ion−surface reactions can distinguish subtle differences

in average orientation. In short, we report that the extent of ion−surface reactions of pyrazine ion with two classes of SAM films is directed by the spatial orientation of the surface-confined species that participate in the reaction.

Proposed uses of self-assembled organic thin films range from molecular-based electronic and optical devices to biorecognition sensors.[1−6] There are a variety of self-assembling systems, but some of the most extensively studied are the thiol-based self-assembled monolayers (SAMs) on gold.[7−10] Various techniques, including FT-IR, Raman spectroscopy, XPS, contact angle measurements, ellipsometry, STM, FFM, and AFM, have been used to describe the chemistry and molecular architecture of these films.[11−16] These techniques are often used in a complementary fashion to characterize a given thin film.[17−19] Accelerating the development of applications based on thin films will depend on

† Present address: Pharm-eco Laboratories, 128 Spring St., Lexington, MA 02421.

(1) Tamada, K.; Nagasawa, J.; Nakanishi, F.; Abe, K.; Hara, M.; Knoll, W.; Ishida, T.; Fukushima, H.; Miyashita, S.; Usui, T.; Koini, T.; Lee, T. R. *Thin Solid Films* **1998,** *329,* 150−155.

(2) Allara, D. L.; Dunbar, T. D.; Weiss, P. S.; Bumm, L. A.; Cygan, M. T.; Tour, J. M.; Reinerth, W. A.; Yao, Y.; Kozaki, M.; Jones, L. In *Molecular Electronics: Science and Technology;* Aviram, A., Ratner, M., Eds.; Annals of the New York Academy of Sciences 852; New York Academy of Sciences: New York, 1998; pp 349−370.

(3) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J Am. Chem. Soc.* **1995,** *117,* 9529−9534.

(4) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996,** *271,* 1705−1707.

(5) Gupta, V. K.; Abbott, N. L. *Science* **1997,** *276,* 1533−1536.

(6) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1999,** *398,* 495−498.

(7) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J Am. Chem. Soc.* **1987,** *109,* 3559−3568.

(8) Bain, C. D.; Troughton, E. B.; Tao, Y.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989,** *111,* 321−335.

(9) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987,** *109,* 733−740.

(10) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J Am. Chem. Soc.* **1991,** *113,* 7152−7167.

(11) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E. *Adv Colloid Interface Sci.* **1992,** *39,* 175−224.

(12) Wong, S. S.; Takano, H.; Porter, M. D. *Anal. Chem.* **1998,** *70,* 5209−5212.

(13) Pemberton, J. E.; Bryant, M. A.; Sobocinski, R. L.; Joa, S. L. *J. Phys. Chem.* **1992,** *96,* 3776−3782.

(14) Widrig, C. A.; Alves, C. A.; Porter, M. D. *J Am. Chem. Soc.* **1991,** *113,* 2805−2810.

(15) Alves, C. A.; Smith, E. L.; Porter, M. D. *J Am. Chem. Soc.* **1992,** *114,* 1222−1227.

(16) Bertilsson, L.; Liedberg, B. *Langmuir* **1993,** *9,* 141−149.

(17) Alves, C. A.; Porter, M. D. *Langmuir* **1993,** *9,* 3507−3512.

(18) Kumar, A.; Biebuyck, H. A.; Abbott, N. L.; Whitesides, G. M. *J Am. Chem. Soc.* **1992,** *114,* 9188−9189.

the ability of researchers to more accurately characterize the physical and chemical properties of these systems.

In 1991, the use of SAM films on gold as targets for low-energy (10−200 eV) ion−surface collisions in a tandem mass spectrometer was first reported.[20,21] In these experiments, ions are mass-selected by the first mass analyzer and potentials are adjusted to cause the selected ions to collide into the thin film. The products of the collision are then focused into and analyzed by the second mass analyzer of the tandem system. When polyatomic ions are collided into the films at low energy (<100 eV), the product ions that are observed in the spectra can arise from fragmentation of the projectile (surface-induced dissociation (SID)) or a chemical reaction between the projectile and the film. A considerable amount of work has been reported in the literature that illustrates the use of SID to investigate the energetic requirements and mechanisms for fragmentation of protonated peptide ions produced by electrospray ionization.[22−28] In these studies, the surface functions primarily as a collision target to facilitate fragmentation. However, early studies focused on using ion−surface reaction products as a means of characterizing the surface rather than the projectile.[20,21,29] An initial rationale for using SAM films in SID studies was to increase signal throughput by providing a barrier to neutralization of the ion beam, often a dominant pathway when the target is bare metal. In later experiments, the films were exploited as model systems that provided a highly organized target surface to investigate the fundamental processes that occurred during low-energy ion−surface collisions.[30−40] It was noted that certain projectiles react with films to provide spectral peaks
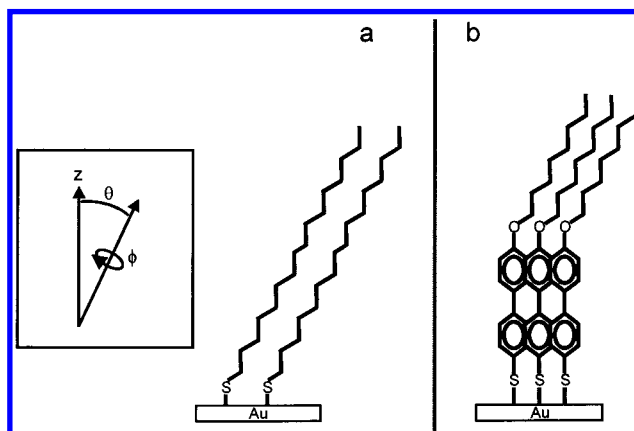

Figure 1. SAM films composed of (a) *n*-alkanethiol and (b) 4-(4-alkoxyphenyl)benzenethiol bound to polycrystalline gold (111) substrate.

characteristic of film quality. For example, a damaged or contaminated fluorocarbon film can be readily identified by detection of product ions corresponding to H or C_nH_x additions to projectile ions such as acetone or dimethyl sulfoxide.[31] A report by Cooks and coauthors investigated the abstraction of multiple surface atoms from unlabeled and perdeuterated *n*-alkanethiol SAM films by pyrazine and pyrene projectile ions. In that work, they concluded that when reaction product ions are formed that contain more than one atom or group from the surface those atoms or groups originated from the same chain and not adjacent chains.[41]

Recent work with labeled Langmuir−Blodgett (LB) films at low collision energies has shown that the interactions of the projectile ion are predominately with the terminal groups or atoms of a target surface.[42,43] Of particular relevance to the present study is work using LB films formed from stearic acid where the terminal methyl groups are labeled with deuterium or [13]C. A key finding made in this study was that when small organic projectiles (e.g., benzene, pyrazine) react with atoms and groups native to the film, the products formed originate predominately, but not exclusively, from the upper portion of the film and not the underlying methylenes.[43] This was observed as a one mass unit shift in the hydrogen addition (H → D) or formal methyl addition (CH$_3$ → [13]CH$_3$) when the target was changed from an unlabeled to a labeled film.

The goal of the present study is to take advantage of the sensitivity and shallow depth of penetration provided by low-energy ion−surface collisions to investigate the influence of alkyl chain orientation on ion−surface reactions. Two model SAM systems were selected for this study. The first system is a series of simple *n*-alkanethiols of the form $CH_3(CH_2)_nSH$ (*n* = 14−17) (Figure 1a). SAM films of this type have a well-documented orientation difference for the terminal methyl groups.[10,44,45] Dif-

(19) Walczak, M. M.; Chung, C. K.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J Am. Chem. Soc.* **1991**, *113*, 2370−2378.
(20) Winger, B. E.; Julian, R. K.; Cooks, R. G.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1991**, *113*, 8967−8969.
(21) Wysocki, V. H.; Jones, J. L.; Ding, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 8969−8970.
(22) McCormack, A. L.; Jones, J. L.; Wysocki, V. H. *J Am. Soc. Mass Spectrom.* **1992**, *3*, 859−862.
(23) Jones, J. L.; Dongré, A. R.; Somogyi, Á.; Wysocki, V. H. *J. Am. Chem. Soc.* **1994**, *116*, 8368−8369.
(24) Dongre, A. R.; Jones, J. L.; Somogyi, A.; Wysocki, V. H. *J. Am. Chem. Soc.* **1996**, *118*, 8365−8374.
(25) Dongre, A. R.; Somogyi, A.; Wysocki, V. H. *J. Mass Spectrom.* **1996**, *31*, 339−350.
(26) Gu, C. G.; Somogyi, A.; Wysocki, V. H.; Medzihradszky, K. F. *Anal. Chim. Acta* **1999**, *397*, 247−256.
(27) Tsaprailis, G.; Nair, H.; Somogyi, Á.; Wysocki, V. H.; Zhong, W.; Futrell, J. H.; Summerfield, S. G.; Gaskell, S. J., *J. Am. Chem. Soc.* **1999**, *121*, 5142−5154.
(28) Tsaprailis, G.; Nair, H.; Somogyi, A.; Wysocki, V. H.; Zhong, W.; Futrell, J. H.; Summerfield, S. G.; Gaskell, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 5142−5154.
(29) Morris, M. R.; Riederer, D. E.; Winger, B. E.; Cooks, R. G.; Ast, T.; Chidsey, C. E. D. *Int. J. Mass Spectrom. Ion Process.* **1992**, *122*, 181−217.
(30) Somogyi, A.; Kane, T. E.; Ding, J. M.; Wysocki, V. H. *J. Am. Chem. Soc.* **1993**, *115*, 5275−5283.
(31) Kane, T. E.; Somogyi, A.; Wysocki, V. H. *Org. Mass Spectrom.* **1993**, *28*, 1665−1673.
(32) Callahan, J. H.; Somogyi, A.; Wysocki, V. H. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 693−699.
(33) Dejarme, L. E.; Cooks, R. G.; Ast, T. *Org. Mass Spectrom.* **1992**, *27*, 667−676.
(34) Ast, T.; Riederer, D. E.; Miller, S. A.; Morris, M.; Cooks, R. G. *Org. Mass Spectrom.* **1993**, *28*, 1021−1033.
(35) Riederer, D. E.; Miller, S. A.; Ast, T.; Cooks, R. G. *J Am. Soc. Mass Spectrom.* **1993**, *4*, 938−942.
(36) Pradeep, T.; Ast, T.; Cooks, R. G.; Feng, B. *J. Phys. Chem.* **1994**, *98*, 9301−9311.
(37) Pradeep, T.; Riederer, D. E.; Hoke, S. H.; Ast, T.; Cooks, R. G.; Linford, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 8658−8665.
(38) Burroughs, J. A.; Hanley, L. *Anal. Chem.* **1994**, *66*, 3644−3650.

(39) Wainhaus, S. B.; Burroughs, J. A.; Wu, Q. Y.; Hanley, L. *Anal. Chem.* **1994**, *66*, 1038−1043.
(40) Burroughs, J. A.; Wainhaus, S. B.; Hanley, L. *J. Chem. Phys.* **1995**, *103*, 6706−6715.
(41) Riederer, D. E.; Cooks, R. G.; Linford, M. R. *J. Mass Spectrom.* **1995**, *30*, 241−246.
(42) Gu, C. G.; Wysocki, V. H.; Harada, A.; Takaya, H.; Kumadaki, I. *J Am. Chem. Soc.* **1999**, *121*, 10554−10562.
(43) Gu, C.; Wysocki, V. H. *J. Am. Chem. Soc.* **1997**, *119*, 12010−12011.
(44) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J Am. Chem. Soc.* **1990**, *112*, 558−569.
(45) Bryant, M. A.; Pemberton, J. E. *J Am. Chem. Soc.* **1991**, *113*, 8284−8293.
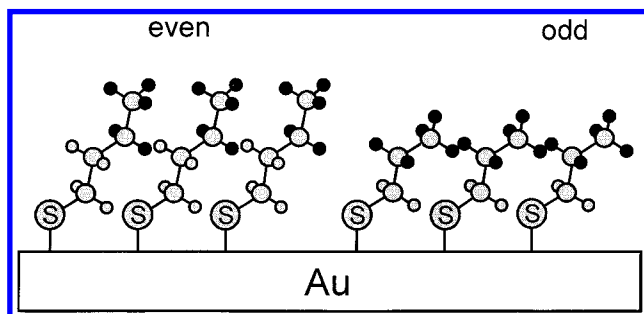
Figure 2. Idealized structure for *n*-alkanethiols with an odd (right) number of carbons and even (left) number of carbons. The odd alkyl chain length positions the terminal C—C bound more parallel to the plane of the surface compared to the even alkyl chain length. The parallel orientation places the terminal hydrogen atoms in a more favorable position to react with impinging ion beam while hindering access to the terminal carbon.

ferences in orientation of the terminal groups have been reported experimentally by FT-IR, Raman, and wetting studies and most recently by friction force microscopy.[12,44–46] This so-called "odd–even" effect arises from a tilt angle (θ) of ~24° with respect to the surface normal for the all-trans alkyl chains, resulting in different cant angles versus the surface normal for the terminal methyl group of odd versus even chain length films (Figure 2).[45] The second system of thiols investigated is composed of a rigid biphenyl mercaptan headgroup with a long-chain alkoxy substituent ($4\text{-}(4\text{-}(CH_2)_mOC_6H_4)\text{-}C_6H_4\text{-}SH$, $m = 14–17$) (Figure 1b). The odd–even effect reported for these compounds measured by FT-IR and contact angle is enhanced[47,48] over that of simple *n*-alkanethiols due to steric constraints imposed by the aromatic headgroups that limit chain twisting. Pyrazine is used as the probe ion in all experiments. This compound is selected because at low collision energies (≤ 100 eV) with hydrocarbon-containing films the molecular ion is moderately reactive, with a little over half the detected ions reacting with the film.

EXPERIMENTAL SECTION

Materials. Four alkanethiols, $CH_3(CH_2)_nSH$ ($n = 14–17$) were used in these experiments. $CH_3(CH_2)_{15}SH$ and $CH_3(CH_2)_{17}SH$ were used as purchased from Aldrich (99%). $CH_3(CH_2)_{14}SH$ and $CH_3(CH_2)_{16}SH$ were synthesized, as previously described,[30] from the corresponding alkyl iodides ($CH_3(CH_2)_{14}I$, Aldrich (98%) and $CH_3(CH_2)_{16}I$, Fluka (97%)). The 4-(4-alkoxyphenyl)benzenethiols, $4\text{-}(4\text{-}CH_3(CH_2)_mOC_6H_4)\text{-}C_6H_4SH$ ($m = 14–17$), were prepared by the synthetic route outlined in Scheme 1 , and a more detailed description of the synthesis is provided as Supporting Information.

Scheme 1
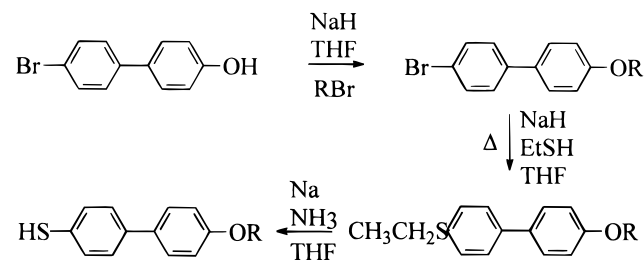
Substrate Preparation. All SAM films were formed on vapor-deposited gold surfaces obtained from Evaporated Metal Films

(Ithaca, NY). The surfaces are 17 mm × 13 mm (0.5-mm silica base) and have a 5-nm underlayer of titanium that is covered with 100 nm of vapor-deposited gold. Before immersion in the thiol solution, the surfaces were UV cleaned for 10 min (Boekel UV cleaner model 135500, Boekel Industries Inc.).

Monolayer Preparation. Alkanethiolate surfaces were prepared by immersing freshly cleaned gold substrates into a ~20 mM ethanol solution of a given thiol and allowing them to react for 72 h. The films were then rinsed 4–6 times by sonication in ethanol, dried, immediately inserted into the fast entry lock on the mass spectrometer, and put under vacuum or into the dry air-purged FT-IR chamber. The 4-(4-alkoxyphenyl)benzenethiolate surfaces were prepared in a similar fashion in ~20 mM THF/EtOH (1:1 v/v) solution of a given 4-(4-alkoxyphenyl)benzenethiol.

RAIRS Measurements. Reflection absorption IR measurements were collected on a Nicolet Magna 550. The spectrometer was equipped with a Spectra Tech FT-80 grazing angle accessory (80° incident angle). p-Polarization was used for all measurements. A freshly UV cleaned gold surface was used as the background for all spectra. The spectrometer was set up to collect 400 scans at a resolution of 4 cm^{-1}.

Mass Spectrometric Measurements. The tandem MS system consists of two Extrel 2000 u quadrupoles arranged in a 90° geometry with a surface intersecting the ion optical path. Experiments are carried out with the surface at a 45° angle relative to the ion beam exiting from the first quadrupole. The collision energy is determined by the potential difference between the ion source and the surface (for singly charged ions). Increasing the ion source potential relative to the surface potential varies the collision energy. A detailed description of the basic tandem system is published elsewhere,[49] and only new design features are described below. A multiple surface holder has been constructed which allows up to four surfaces to be positioned in the vacuum chamber. The holder is an 18 mm × 140 mm Kel-f strip connected to the end of a magnetically coupled movable rod that allows precise linear movement of the surface holder in the *z* direction and full rotation in the *x, y* plane. The holder is positioned perpendicular to the ion beam exiting the first quadrupole, allowing any of the four surfaces to be positioned into the path of the ion beam. Surfaces are inserted into the instrument through a fast-entry apparatus constructed from a stainless steel cube that can be isolated from the main vacuum system via a gate valve. The surfaces are electrically linked via the back of the holder, and a single power supply is used to apply an equivalent potential to each of the surfaces. The base pressure in the main chamber is $\leq 2 \times 10^{-7}$ Torr with a sample pressure of ~6 × 10^{-7} Torr. Results indicate that the pressure and general instrument conditions do not change significantly from surface to surface or sample set to sample set. All data points represent the average of at least three independent measurements.

RESULTS AND DISCUSSION

Ion–Surface Reactions. Figure 3 shows the tandem mass spectrum for a 20-eV collision of pyrazine molecular ion M$^{•+}$ (*m/z*

(46) Tao, Y.-T. *J. Am. Chem. Soc.* **1993**, *115*, 4350–4358.
(47) Tao, Y. T.; Lee, M. T.; Chang, S. C. *J. Am. Chem. Soc.* **1993**, *115*, 9547–9555.
(48) Li, T. W.; Chao, I.; Tao, Y. T. *J. Phys. Chem. B* **1998**, *102*, 2935–2946.
(49) Wysocki, V. H.; Ding, J. M.; Jones, J. L.; Callahan, J. H.; King, F. L. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 27–32.
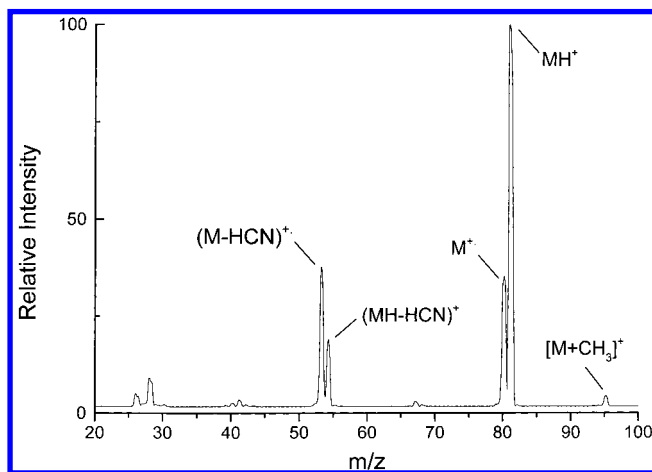
Figure 3. The 20 eV collision of pyrazine ion $M^{\bullet+}$ (m/z 80) with a $CH_3(CH_2)_{17}-S-Au$ SAM film. The base peak in the spectrum MH^+ (m/z 81) represents a reaction of the probe ion and a hydrogen atom from the SAM film. The peak at m/z 95 is the formal addition of methyl to the $M^{\bullet+}$ ion. The two most abundant fragment ions at m/z 53 and 54 represent $[M - HCN]^{\bullet+}$ and $[MH - HCN]^+$.
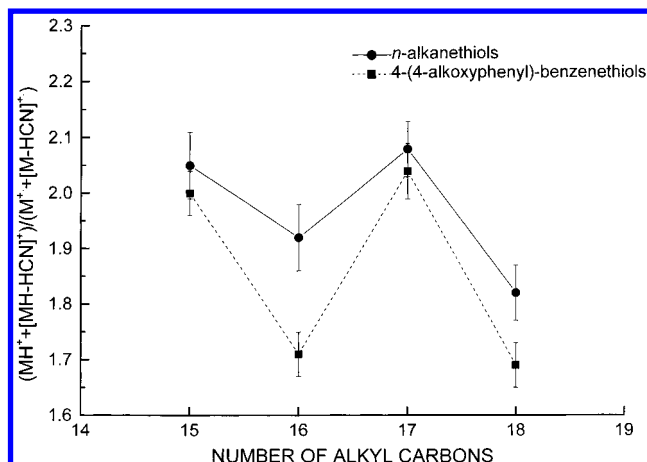

Figure 4. Reaction peak intensities presented as a ratio of $(MH^+ + [MH - HCN]^+)/(M^{\bullet+} + [M - HCN]^{\bullet+})$ plotted versus chain length for n-alkanethiols and 4-(4-alkoxyphenyl)benzenethiols. Larger values for the quotient indicate more H addition.

80) with a $CH_3(CH_2)_{17}-S-Au$ surface. Two reaction products can be observed in the spectrum. The peak at m/z 81 labeled MH^+ represents a reaction between the $M^{\bullet+}$ ion and the SAM film resulting in the addition of a hydrogen atom to the projectile. The peak at m/z 95 corresponds to the addition of CH_3 to the $M^{\bullet+}$ ion. At this collision energy, the $M^{\bullet+}$ and MH^+ ions acquire adequate internal energy to fragment. Two dominant fragment ions corresponding to loss of a neutral HCN appear at m/z 53 $[M - HCN]^{\bullet+}$ and m/z 54 $[MH - HCN]^+$. The integration of the normalized peak areas followed by the summation of the contributions from unreacted pyrazine, H addition, and CH_3 addition ions provides a means to plot and track changes in the abundance of these species for a series of films.

Figure 4 is a plot tracking the relative H addition where the y axis is the quotient $(MH^+ + [MH - HCN]^+)/(M^{\bullet+} + [M - HCN]^+)$ and is plotted versus the total number of alkyl carbons. The solid line represents the data collected for the n-alkanethiol system and the dashed line represents the data collected for the 4-(4-alkoxyphenyl)benzenethiols. A clear odd−even effect can be
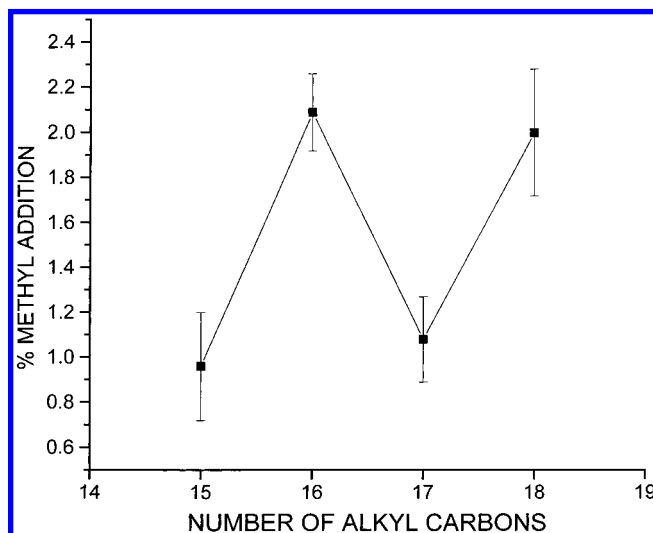
Figure 5. Percentage of the total ion current that corresponds to methyl addition plotted versus total number of alkyl carbons.

observed for both systems with the odd-chain-length analogues leading to a greater abundance of H addition product ions. Each point represents an average of the measurements taken on three different SAM films. The variation in reaction quotient for each point reflected by the error bars is likely due to small changes in instrument conditions and the reproducibility of substrate and film quality. A similar plot for methyl addition is presented in Figure 5 for the 4-(4-alkoxyphenyl)benzenethiols. In this case, the y axis represents percentage of the total ion current that corresponds to methyl addition. An alternating reactivity is again observed, however, in contrast to hydrogen addition results, methyl addition occurs more readily on even chain length films.

The variations in reactivity for odd versus even chain lengths are consistent with chain-length-dependent differences in terminal group orientation.[10,44,45] Specifically, the difference in cant of the terminal methyl groups produced by the chain tilt (θ) (Figure 1) results in subtle differences in the position of the terminal C−C bond with respect to the surface normal.[50] When the chain length is odd, the terminal C−C bond is more parallel to the surface than when the chain length is even. These orientations present the incoming ion with two spatially distinct environments each with a different set of steric requirements that must be met for an ion−surface reaction to take place. The parallel orientation adopted by the final C−C bond of the odd-chain-length films places one terminal hydrogen atom, on average, slightly above the plane of the chain termini and also allows the impinging ion more ready access to the hydrogen atoms bound to the first underlying methylene (Figure 2). The exposed hydrogen atoms are not only likely to be more reactive but they also inhibit access to the terminal carbon. Conversely, the perpendicular orientation adopted by the even chain lengths exposes the terminal carbon, places the terminal hydrogen atoms in equivalent but less exposed orientations, and hinders access to the first underlying methylene.

***n*-Alkanethiols versus 4-(4-Alkoxyphenyl)benzenethiols.** A comparison of the plots in Figure 4 shows that the 4-(4-alkoxyphenyl)benzenethiols have a larger variation in reactivity quotient than do the n-alkanethiols. Parts a and b of Figure 6 show

(50) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927−945.
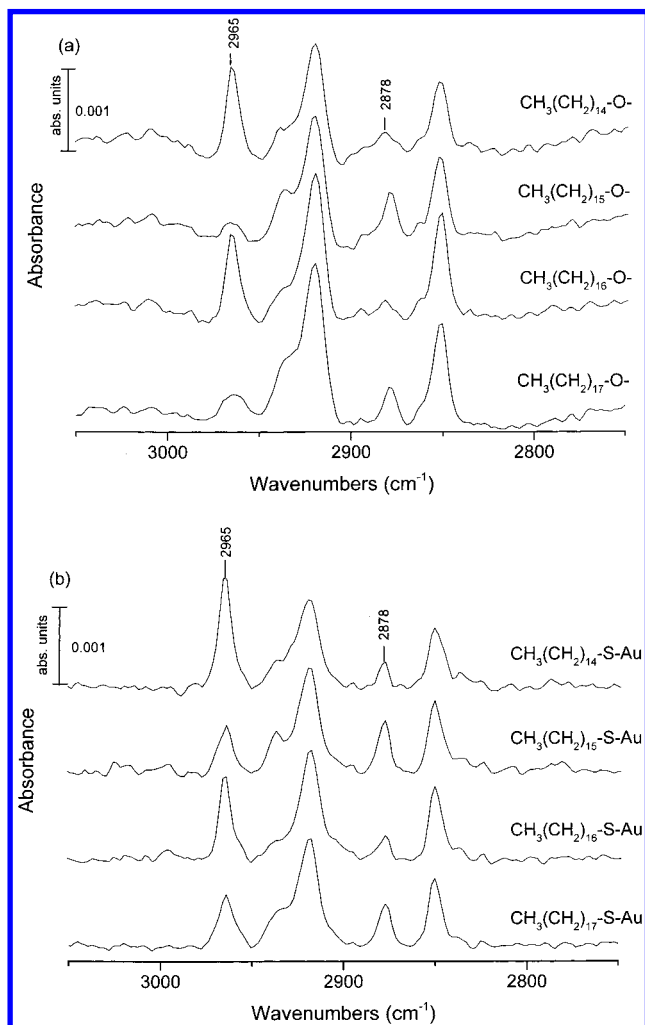
Figure 6. Methyl and methylene stretching region of the reflection absorption IR spectra of (a) 4-(4-alkoxyphenyl)benzenethiols and (b) *n*-alkanethiols.

the RAIR spectra for films composed of 4-(4-$CH_3(CH_2)_mOC_6H_4$)−C_6H_4SH ($m = 14-17$) and $CH_3(CH_2)SH$ ($n = 14-17$), respectively. The RAIRS data are shown here as an independent measure of our monolayer structures. The peaks of interest occur at 2878 and 2965 cm^{-1} corresponding to the $\nu_s(CH_3)$ and $\nu_a(CH_3$, ip) stretches respectively, with the methylene stretching modes $\nu_s(CH_2)$ and $\nu_a(CH_2)$ appearing at 2850 and 2919 cm^{-1}.[10] For 4-(4-alkoxyphenyl)benzenethiols films with R groups containing an even number of carbons ($m = 15, 17$), the intensity of the ν_s-(CH_3) stretching mode for the terminal methyl group is enhanced and the intensity of the $\nu_a(CH_3$, ip) stretching mode is diminished while the reverse is observed for films with R groups containing an odd number of carbons ($m = 14, 16$). Figure 6b is the same spectral region for the series of *n*-alkanethiols. When compared to that for the 4-(4-alkoxyphenyl)benzenethiols, the odd−even effect for the *n*-alkanethiol system is diminished.[51] The reactivity data in Figure 4 are clearly mirroring the same trend seen in Figures 6, both in odd−even effect and in the intensity of the effect.

The basis for the enhanced odd−even effect in the RAIRS data for the SAM films composed of 4-(4-alkoxyphenyl)benzenethiols

(51) Chang, S. C.; Chao, I.; Tao, Y. T. *J Am. Chem. Soc.* **1994**, *116*, 6792−6805.

is the different conformational constraints imposed on the alkyl moiety by the aromatic headgroup versus the *n*-alkanethiols.[48] The maximum effect is observed in RAIR spectra for an odd−even pair when the chain twist angle (ϕ) is minimized (Figure 1). As a consequence of the available stable packing arrangements and the decrease in rotational freedom, films formed from 4-(4-alkoxyphenyl)benzenethiols have a larger portion of the terminal methyl group population in the optimum position (small twist angle) versus *n*-alkanethiols.[48] The increased degree of variation of the reactivity quotient for odd versus even for the 4-(4-alkoxyphenyl)benzenethiols (Figure 4) is consistent with this explanation. The significant new result presented here is that small differences in the average orientation of the film can be detected by ion−surface reactions.

Effects of Film Order and Substrate Topography. Another general observation that can be made when comparing the data plots in Figure 4 is an overall decrease in the H-addition intensity for the 4-(4-alkoxyphenyl)benzenethiols. The reaction quotient values for the *n*-alkanethiols vary from 1.82 to 2.08 and those for the 4-(4-alkoxyphenyl)benzenethiols range from 1.65 to 2.05. We speculate that differences in film order and the effects of using a polycrystalline gold substrate are influencing the degree of hydrogen addition. It has been shown that the 4-(4-alkoxyphenyl)-benzenethiols tend to form more ordered films than the *n*-alkanethiols primarily due to constraints imposed by the rigid aromatic headgroup.[48] Another possible contributing factor is the increased thickness of 4-(4-alkoxyphenyl)benzenethiols. The aromatic headgroups add ∼12 Å to the thickness of each SAM film. The added film thickness could compensate for edge effects and other heterogeneities in the polycrystalline Au substrate by bridging the defect sites and allowing more chain−chain interactions to occur. Earlier work published by this group highlighted the potential effects of film order on reaction intensity by comparing short- (1-butanethiol) and long- (1-octadecanethiol) chain *n*-alkanethiols.[30] The short-chain films were consistently better hydrogen donors. The conclusion drawn in that research was that the short-chain film was less ordered, leaving more of the underlying methylenes exposed and/or more susceptible to adsorption or insertion of hydrocarbon contaminants.[30] In separate but related work that is part of an ongoing study, results for CH_3-$(CH_2)_{19}$−S−Au, $CD_3(CD_2)_{19}$−S−Au, and $CD_3(CH_2)_{19}$−S−Au SAM films are used to evaluate and separate the contribution of all possible sources of hydrogen to the total hydrogen addition ion current. During a 20 eV collision of pyrazine with the hydrocarbon SAM films, ∼65% of the total ion current measured at the detector is observed as H addition ions. We have calculated that of the total ion population that reacts to form hydrogen adducts, ∼70% originate from the terminal methyl group, 21% from the underlying methylenes, and 9% from hydrocarbon contaminants. Clearly, these numbers are controlled by a combination of the quality of the film that can be formed from a particular compound and the topography of the substrate onto which it is deposited. The substrate used in these experiments is a silica slide with a 5 nm underlayer of titanium onto which 100 nm of gold is deposited. The morphology of the gold is not consistently smooth at the atomic level but is known to have a "hill-like" landscape with crystalline-like features ∼0.01 μm² and an average height variation in the 5−10 nm range (unpublished result). We acknowledge that

the topography of the gold can introduce a degree of nonuniformity to the film orientation and order that is sufficient to expose some underlying methylenes to the colliding projectile. However, the results indicate that the size of the ion beam used in these experiments ($\sim 6 \times 8$ mm)[52] is sufficient to ensure a valid average sampling of the film. Despite irregularities in the film and substrate, it is still possible to observe that the orientation of these surface-confined species influences the extent of ion−surface reaction.

CONCLUSIONS

We report that low-energy (20 eV) ion−surface reactions of pyrazine ions are remarkably sensitive to small differences in the orientation of alkyl-based SAM films. The intensity of hydrogen and methyl addition ions is shown to vary for odd versus even chain lengths for two different SAM systems. The variation of the intensity of the reaction product ions is attributed to subtle differences in the position of the terminal C−C bond. The orientation of the odd-chain-length films allows better access to a terminal hydrogen atom while hindering access to the terminal carbon. The even-chain-length orientation limits access to the hydrogen atoms but better exposes the terminal carbon. The sensitivity of the process is underscored by comparing the data collected for the *n*-alkanethiol system and the 4-(4-alkoxyphenyl)-benzenethiol system where reactions of pyrazine ion with hydrogen atoms native to the films are discriminating enough to distinguish small differences in the average orientation. The difference in *reactivity* of surface-confined alkyl chains with different numbers of carbons seems somewhat remarkable, at first consideration, because polycrystalline vapor-deposited gold and a standard SAM surface preparation is used with no annealing of the gold or the SAM film. However, if one considers that each probe of the surface is a single ionized molecule, the results are reasonable since even relatively small ordered domains on the surface present a relatively large ordered domain to the ionic probe molecule and provide an average result that is consistently different for odd versus even chain lengths.

SUPPORTING INFORMATION AVAILABLE

Detailed procedures for the synthesis of 4-(4-alkoxyphenyl)-benzenethiols, including summaries of NMR and mass spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

(52) Kane, T. E.; Angelico, V. J.; Wysocki, V. H. *Anal. Chem.* **1994**, *66*, 3733−3736.