havior is believed to be general for this class of intermediates.

Characterization of Thiol Self-Assembled Films by Laser Desorption Fourier Transform Mass Spectrometry

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Abstract: Self-assembled alkanethiol monolayers on gold films have been studied using the technique of laser desorption coupled with Fourier transform mass spectrometry. We demonstrate that thiol molecules can be desorbed intact using 193-nm laser radiation. Information on the self-assembled films at a molecular level is achieved. In addition to the well-known thiolate species, alkane sulfonates resulting from air exposure of the self-assembled film are also detected. No phase segregation ≥30 μm is observed from the laser desorption of self-assembled films made of alkanethiol mixtures.

Introduction

Self-assembled monolayer films have recently been the subject of intense study. The self-assembled films that have been studied most are the self-assembled thiol or disulfide on a gold surface with the techniques of infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD), wetting chemistry, optical ellipsometry, electrochemistry, electron diffraction, He diffraction, ³He⁺ diffraction, X-ray diffraction, and scanning tunneling microscopy.[1-33] The XPS data indicate that monolayers of thiols are formed on gold surfaces. The ellipsometry and IR measurements indicate that the hydrocarbon chain of the thiol is tilted away from the perpendicular to the gold surface. The He and electron diffraction experiments show that the hydrocarbon chains are ordered and that less ordered films are formed as the carbon chain length decreases. Electrochemistry studies exhibit no pinholes in the films. On the basis of these studies, a picture has emerged in which a well-ordered monolayer of thiolate covers the Au surface such that all sulfur atoms are bonded to Au with the carbon chain uniformly oriented at a tilt angle from the surface normal. A variety of self-assembled films have been studied using the different techniques described above, but information on the molecular composition of the films is obtained from indirect observations. For example, more direct evidence is required to definitively conclude whether thiolates or thiols are formed on the self-assembled films, and little is known about molecular impurities.

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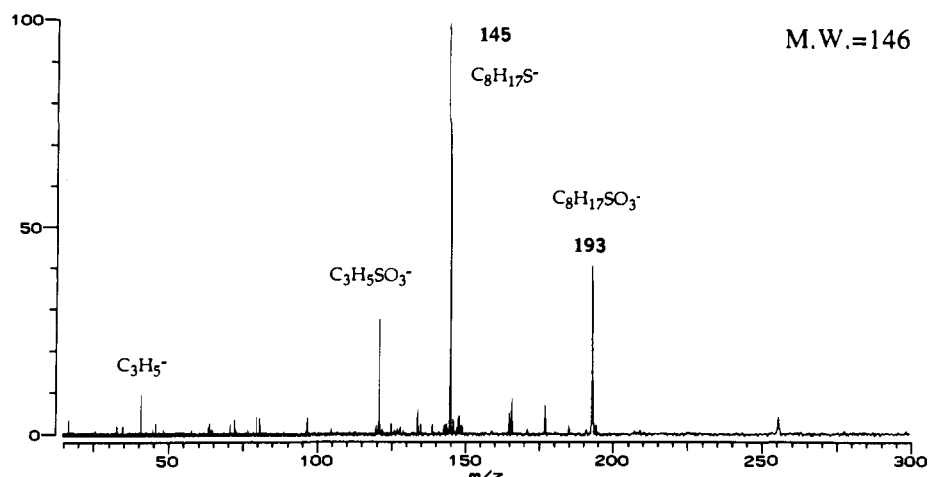
Figure 1. The negative ion mass spectrum obtained by laser desorption from a self-assembled film of $CH_3(CH_2)_7SH$ on gold with a single laser pulse at 193 nm.

Characterization of organic self-assembled films is more difficult than that of inorganic surfaces because organic materials often exhibit radiation damage during scattering and diffraction experiments. Molecular desorption of methanethiol has been observed,[2] but the long-chain thiols decompose during thermal desorption experiments.[5] The laser desorption Fourier transform mass spectrometry (FTMS) method[34] avoids this problem by causing sudden desorption, which leads to the desorption channel prevailing over the competing surface decomposition channel. In our experiments described here, 193-nm laser radiation is used to desorb the alkanethiol molecules from Au surfaces into the gas phase and negative ions are detected by FTMS. Molecular negative ions RS⁻ of the parent thiols are observed from the laser desorption at this wavelength.

Experimental Section

Laser Desorption and Fourier Transform Mass Spectrometry. All experiments were conducted on a Fourier transform mass spectrometer constructed in our laboratory.[35] The instrument consists of an ion cyclotron resonance mass analyzer cell and a 0.9-T Varian electromagnet, an IonSpec Model 2000 data system, and a vacuum chamber that is pumped to a base pressure of 5×10^{-10} Torr by a 150-L/s ion pump and a 330-L/s turbomolecular pump. Samples of alkanethiols on gold were mounted on the end of a stainless steel probe which was inserted into the chamber through a vacuum lock and placed 1 cm in front of a hole in one of the plates of the analyzer cell. A focused laser beam was directed into the cell through a hole opposite the samples and irradiated the samples at near normal incidence. The laser used in these experiments was a Lambda Physik EMG 103 MSC excimer laser operating at 193 nm (ArF*). The laser energy used for the desorption (deposited onto the surface) was in the $\sim$110-μJ range, which corresponds to a power density of 3×10^8 W/cm². This is very close to the threshold for ablation of the gold substrate. When gold ablation occurs we directly observe this by the observation of Au⁻ and Au⁺ in the negative ion and positive ion spectra, respectively. All of the spectra presented here were obtained with power densities below that required for the observation of Au⁻ and Au⁺. The laser pulse duration was 20 ns. The laser was focused 5 mm behind the sample. The spot sizes were measured by increasing the laser energy and ablating the thin gold film. Measuring the resulting crater with an optical microscope typically showed a spot size of 50 μm in diameter. Negative ions formed directly from the laser desorption were trapped in the mass analyzer cell using -3 V trapping potentials. Mass spectra were obtained with a single laser shot. No signal averaging was necessary.

We have studied the mechanism of laser desorption of peptide adsorbates from Au films with different thicknesses using different laser wavelengths. Our results indicate that laser desorption mechanisms can be divided into thermal mechanisms and nonthermal mechanisms. The thermal mechanism tends to dominate when longer wavelengths are used, whereas short-wavelength laser pulses can result in desorption via a nonthermal pathway (charge transfer or photochemical).[36] Less frag-

mentation and a strong negative ion signal are observed during the nonthermal laser desorption using 193 or 248 nm laser radiation, and more fragmentation is observed due to the high-temperature jumps at metal surfaces during the thermal laser desorption using 351-nm laser radiation. According to this understanding, the highly energetic photons (248 or 193 nm) may not introduce damage in organic surfaces and can result in desorption of intact adsorbate molecules.

Materials. 1-Butanethiol (99%), 1-hexanethiol (95%), 1-octanethiol (97+%), nonyl mercaptan (98%), 1-dodecanethiol (98%), hexadecyl mercaptan (92%), and octadecyl mercaptan (98%) were purchased from Aldrich chemical company and used as received. Completely deuterated octadecyl mercaptan is a gift from Professor Whitesides' group in the chemistry department of Harvard University. Ethanol (Gold Shield Chemical Co.) served as a solvent for the thiols and was deoxygenated with bubbling nitrogen for 1 h before use.

Sample Preparation. Gold substrates were prepared by thermal evaporation of gold (99.999%, Aldrich) onto well-polished Macor tips (final polishing stage 0.05 μm) which had been precoated with chromium to improve adhesion (10 nm of Cr followed by 200 nm of Au). Evaporation was accomplished in an Edwards E306A coating system at 5×10^{-6} Torr. The gold film thickness was measured by a quartz crystal thickness monitor. Self-assembled thiol samples were prepared by putting fresh gold films into 1 mmol thiol/ethanol solutions overnight and then rinsed with copious amounts of ethanol followed by air drying. The monolayer thiol samples were then inserted into the laser desorption FTMS instrument for analysis. Comparison samples provided by Whitesides' group consisted of thiol monolayers adsorbed on gold films which had been evaporated onto Cr-coated Si substrates.

Results and Discussion

Experiments have been conducted for $C_nH_{2n+1}SH$ ($n = 4, 6, 8, 9, 12, 16,$ and 18) adsorbed on the Au films. Mass spectra from the laser desorption of thiols ($n = 8, 9, 12, 16,$ and 18) are shown in Figures 1–5. Laser desorption of thiols with $n > 8$ yields strong negative ion signals for the deprotonated molecular ions. These results strongly support the picture that thiolates instead of thiols are actually formed on the self-assembled films. In addition to the thiolate, another species 48 mass units higher than the thiolate is observed in all of the spectra for $n \geq 8$. An internal calibration of these spectra can be accomplished by identifying well-known strong negative ion peaks such as S⁻ and HS⁻. By using this calibration, the high mass peak can be assigned to the corresponding sulfonate species. The measured difference between the RS⁻ peak and the peak we assign to the sulfonate agrees with the expected value within 0.005 amu in all cases. A sample film of the completely deuterated C_{18} thiol was obtained from Whitesides' group at Harvard. Spectra obtained from this sample show the thiolate and sulfonate peak with the correct 48-amu mass separation, which helps confirm our assignment. Oxidation of the adsorbed thiolates to sulfonates has been observed in self-assembled thiol films on copper and silver.[37] The desorption of thiols with

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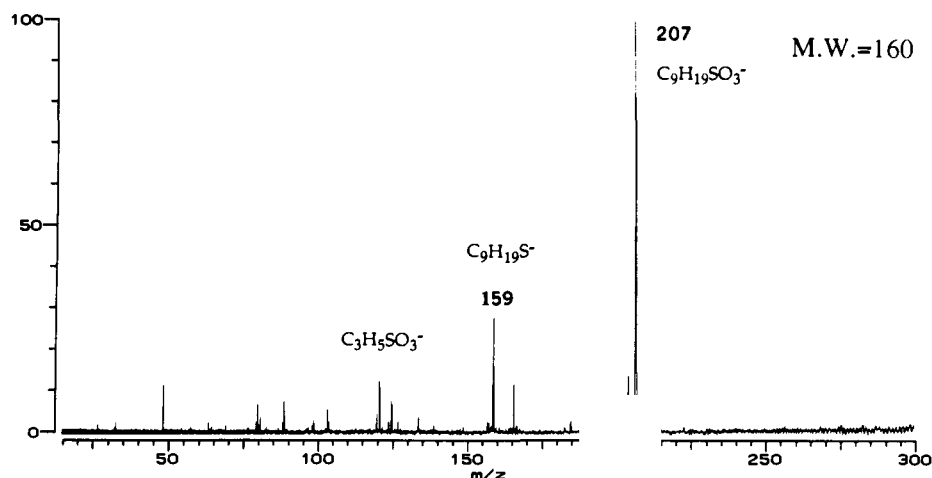(36) Li, Y.; McIver, R. T., Jr.; Hemminger, J. C. *J. Chem. Phys.* **1990**, *93*, 4719–4723.

Figure 2. The negative ion mass spectrum obtained by laser desorption from a self-assembled film of $CH_3(CH_2)_8SH$ on gold with a single laser pulse at 193 nm.

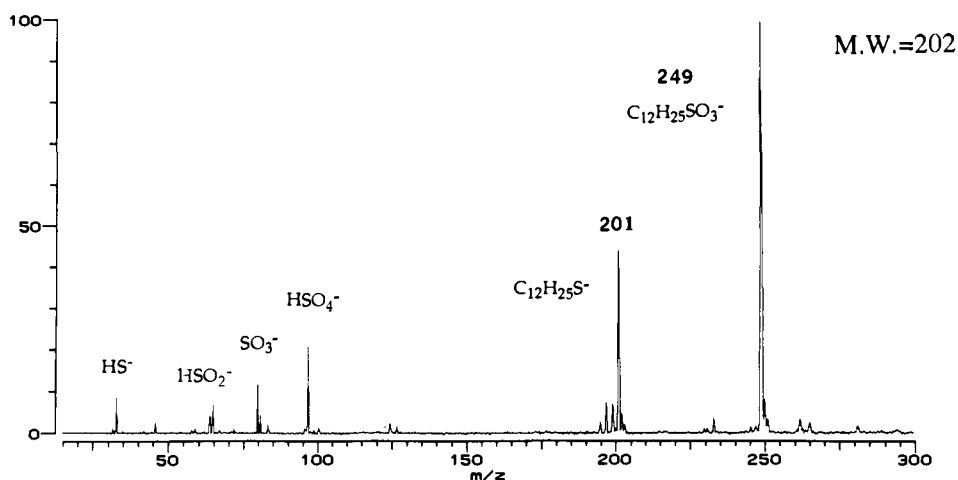**Figure 3.** The negative ion mass spectrum obtained by laser desorption from a self-assembled film of $CH_3(CH_2)_{11}SH$ on gold with a single laser pulse at 193 nm.
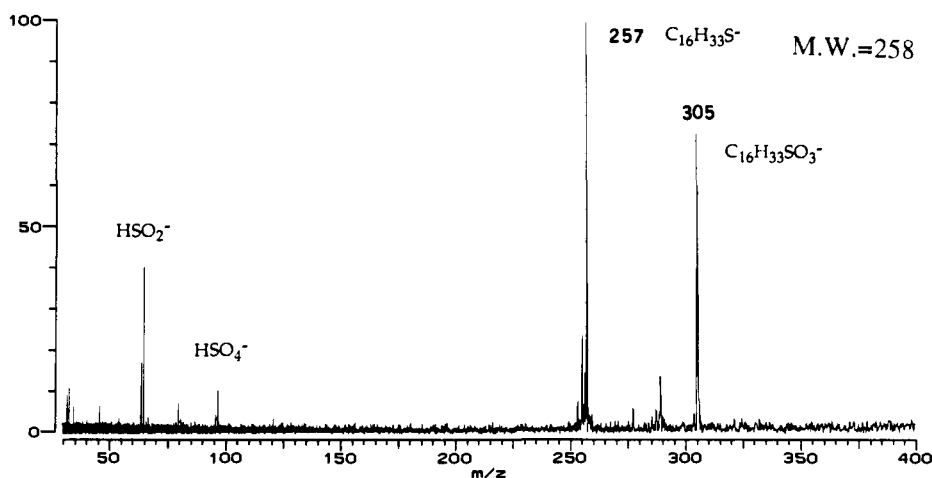

Figure 4. The negative ion mass spectrum obtained by laser desorption from a self-assembled film of $CH_3(CH_2)_{15}SH$ on gold with a single laser pulse at 193 nm.

$n < 6$ produces a strong molecular ion signal for the sulfonate while the thiolate molecular ion is hardly detectable. While it is reasonable to suggest that oxidation may occur more readily when the carbon chain is shorter, we cannot at this time directly

compare signal intensities from the two species. The purity of the thiol compounds received from Aldrich was examined using GC/MS, and no sulfonates were detected from the thiols, which indicates that thiols have not been substantially oxidized before use.

Air oxidation of the self-assembled film appears to be the primary mechanism for production of the sulfonate from the

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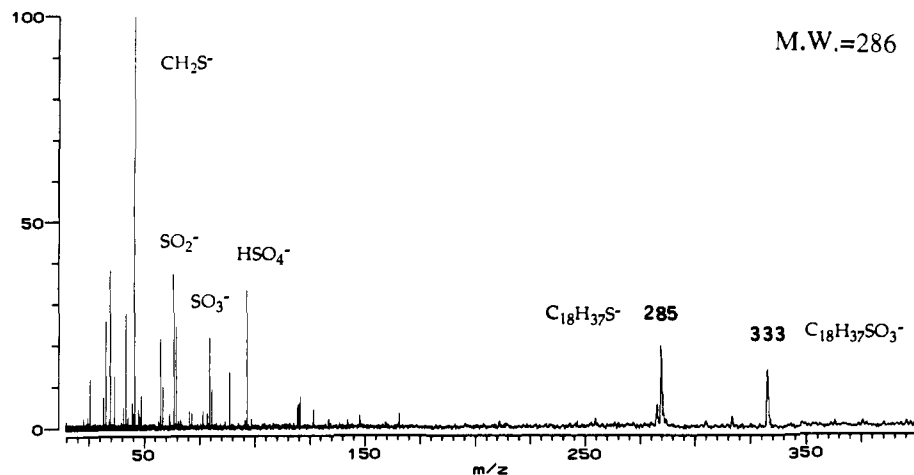
Figure 5. The negative ion mass spectrum obtained by laser desorption from a self-assembled film of $CH_3(CH_2)_{17}SH$ on gold with a single laser pulse at 193 nm.

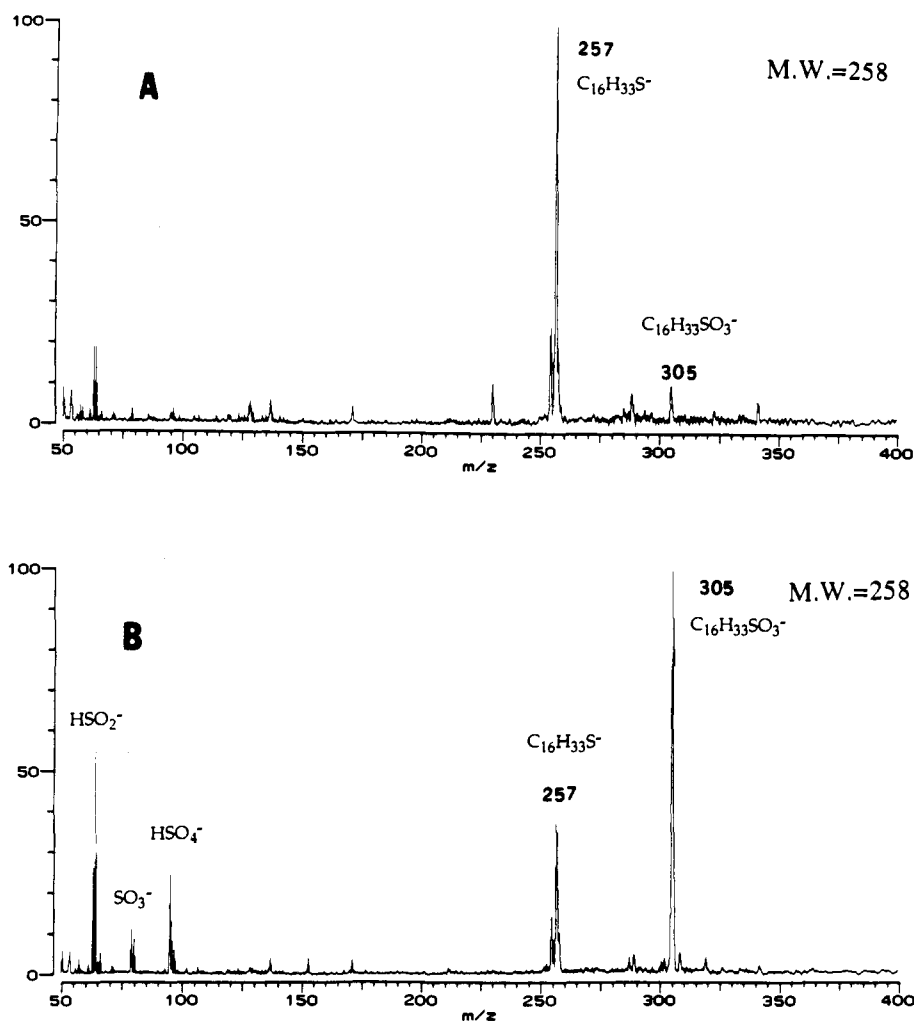**Figure 6.** (A) The negative ion mass spectrum obtained by laser desorption from a freshly prepared self-assembled film of $CH_3(CH_2)_{15}SH$ on gold with a single laser pulse at 193 nm. (B) The negative ion mass spectrum obtained, using the same conditions as in part A, from a sample which was prepared at the same time as the sample in A and allowed to sit in air for 6 days prior to analysis.

thiolate. Figure 6A shows a representative laser desorption mass spectrum obtained from a freshly made C_{16} thiol film with only a small sulfonate peak. Figure 6B shows a representative spectrum from a film which was made at the same time with the same thiol solution and then allowed to sit in air for 6 days prior to analysis. Dramatic growth of the sulfonate species is obtained due to the air exposure.

Comparison experiments were conducted on samples from Whitesides' lab using the laser desorption technique and XPS.

Both techniques generate the same results for the samples from the two different sources. Although XPS experiments indicate that there is <2% oxgyen on the surfaces, the laser desorption experiments show substantial signal for oxidized species on the surfaces. This seeming disparity points at the fact that we do not at this point know the relative sensitivity of the laser desorption experiment when ions are produced directly by the desorption event. Since the gas-phase acidity of sulfonic acids ($\Delta G° \sim 314$ kcal/mol for $RSO_3H = RSO_3^- + H^+$) is much higher than that
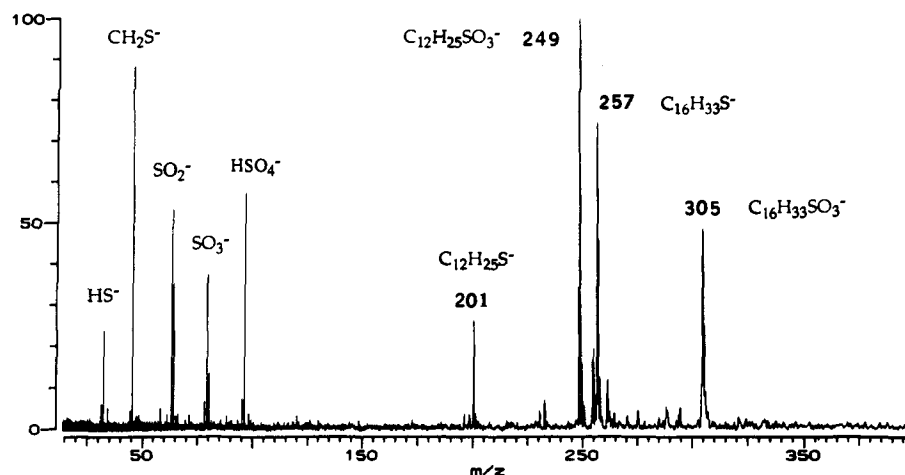
Figure 7. The negative ion mass spectrum obtained by laser desorption from a self-assembled film of a $CH_3(CH_2)_{15}SH$ and $CH_3(CH_2)_{11}SH$ mixture on gold with a single laser pulse at 193 nm.
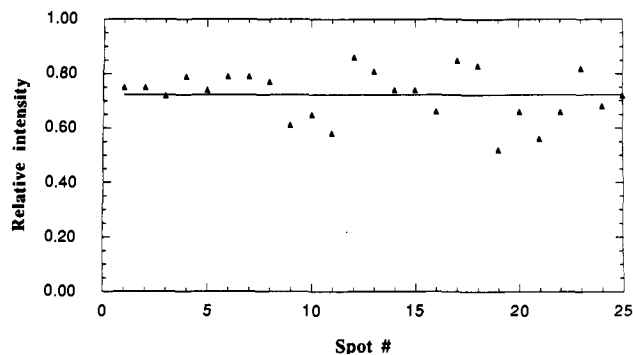
Figure 8. The relative intensity of $(C_{16}H_{33}S^-/(C_{12}H_{25}S^- + C_{16}H_{33}S^-))$ from the laser desorption across a self-assembled film produced from a mixed solution of the two thiols. The horizontal solid line shows the average of all the data points.

of the corresponding thiols (~ 350 kcal/mol), the sensitivity for production of sulfonates is expected to be much higher than for that of thiolates.

Laser desorption results in molecular identification for films made of not only pure thiols but also a thiol mixture. The laser desorption mass spectrum of the film made from a mixture of hexadecyl mercaptan (C_{16}) and 1-dodecanethiol (C_{12}) (1:1 mole ratio) is shown in Figure 7. The mass spectrum contains all the characteristic peaks corresponding to thiolates and sulfonates of the two chain lengths (compare with Figures 3 and 4).

Whether or not phase segregation islands are formed from the films made of two thiols has been studied by chemical wetting methods. The laser desorption method provides an alternative means to explore the homogeneity of the self-assembled surfaces because the laser beam with a spot size of 50 μm can serve as a probe to scan across the surface. If a phase segregation island is formed and the laser beam is overlapping it during the desorption, only the thiol in the island would be desorbed and detected by the mass spectrometer. If the thiols are formed in a well-mixed form on gold, desorption products should always consist of the two thiols. Laser desorption of the self-assembled film from the mixture of C_{16} and C_{12} thiols by scanning the laser beam (a spot size 50 μm in diameter) across the sample was carried out, and desorption products were detected from 25 different laser shots by FTMS. All individual mass spectra contained the molecular peaks of C_{16} and C_{12} thiolates. The maximum fluctuation of the

relative intensity of the two thiol molecular peaks, defined as the ratio of the intensity of a specific ion to the total ion intensity, is 20% as shown in Figure 8. If one assumes that all of the signal fluctuation were due to inhomogeneity of the formation of the thiol mixture within the laser spot, an upper bound of 30 μm can be set on the size of phase segregation islands.

Conclusions

These first demonstration experiments have shown that laser desorption/FTMS provides a convenient way to identify the molecular components of self-assembled thiol films. In addition, our data provide new information and confirmation of ideas about thiol films.

(1) Thiolates instead of thiols are formed on the self-assembled films.

(2) In addition to thiolates, sulfonates, formed by air oxidation of the films, are observed. The signal of the sulfonate species is more intense for the lower molecular weight alkanethiols.

(3) An upper bound on the size of phase segregation islands in films of mixed alkanethiols is established as around 30 μm.

Clearly, many new experiments can now be envisioned in which the adsorbed thiol films are chemically modified after adsorption with the use of laser desorption/FTMS as a probe of the subsequent species that are formed.

Note Added in Proof. We have learned of recent SIMS experiments by M. Tarlov and co-workers, which also show RSO_3^- species from alkylthio monolayers on gold which have been exposed to air for several days. A description of their work has been submitted to *Langmuir*.