

Nondissociative Chemisorption of Methanethiol on Ag(110): A Critical Result for Self-Assembled Monolayers

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The alkanethiol self-assembled monolayers (SAMs) have been extensively studied because of their technological applications in various fields, such as corrosion inhibition, wetting, lubrication, sensors, and molecular electronics.^{1–5} Notably, the interaction of alkanethiols with gold has been used to prepare molecule–metal junctions in molecular electronic devices.^{6–10} However, the key question of whether S–H bond scission occurs upon adsorption of alkanethiols on noble metal surfaces remains controversial.^{11–13} Vibrational and X-ray photoelectron spectroscopy (XPS) studies indicate that on Au(111), CH₃SH does not dissociate by S–H bond scission.¹²

There is a general belief that the S–H bond of alkanethiols dissociates on Ag and Au surfaces to form an alkanethiolate species, which can strongly attach by chemisorption to the metal surface through the S atom as an anchor. In contrast to this common assumption, in this communication, we present evidence for nondissociative adsorption of the simplest alkanethiol, methanethiol, on the clean Ag(110) surface. Three definitive experiments have been performed to prove the nondissociative adsorption of CH₃SH on clean Ag(110) by using temperature-programmed desorption (TPD), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES). (1) On the clean Ag(110) surface, we observe that molecular adsorption in the first layer (0.5 ML) occurs, producing a (2 × 1) overlayer structure. The methanethiol molecule desorbs at ~140 K, and only tiny quantities of other products such as CH₄ are observed. In addition, appreciable coverages of residual S are not observed by Auger spectroscopy following CH₃SH desorption. (2) Using a 50:50 isotopomer mixture of CH₃SD and CD₃SH, we demonstrate that no S–H or S–D bond scission followed by recombination occurs upon desorption. (3) We find that when the CH₃SH molecule is incident on the clean Ag(110) surface in the temperature range from 230 to 400 K, less than 1% of the incident molecules dissociate to produce an adsorbed sulfur-containing species.

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a typical operating pressure of 3 × 10⁻¹¹ Torr, and excellent vacuum conditions below 1 × 10⁻¹⁰ Torr exist during gas dosing. A clean Ag(110) surface at 25 K was exposed to methanethiol using a collimated molecular beam doser delivering a known flux to the crystal.¹⁴ Figure 1 shows the TPD spectra of adsorbed methanethiol on the clean Ag(110) surface at different exposures. To eliminate the influence of sulfur impurity as a result of a very minor amount of methanethiol decomposition during TPD measurements, each TPD spectrum was obtained after cleaning the surface by argon ion sputtering, followed by annealing to 773 K. The clean desorption of CH₃SH without appreciable desorption of products such as CH₄ and H₂S indicates that CH₃SH does not dissociate on the clean Ag(110) surface. In addition, Auger spectroscopic studies show that <0.3% of a monolayer of S remains after ~0.5 ML of CH₃SH has desorbed below 300 K (not shown).

To investigate whether a recombinative reaction occurs during methanethiol desorption, we performed TPD experiments using a

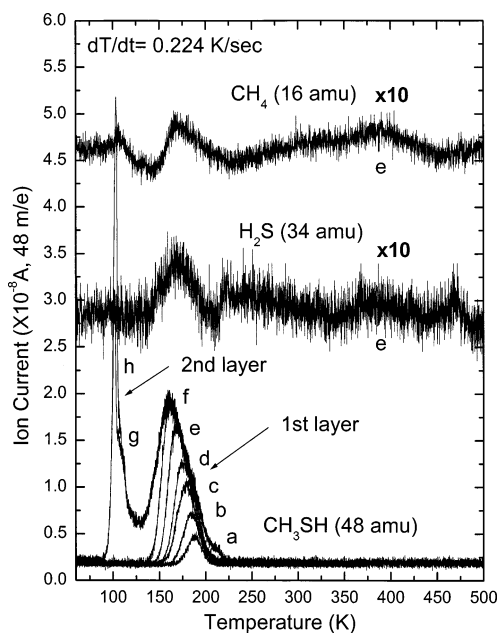


Figure 1. TPD spectra of methanethiol on the clean Ag(110) surface at different exposures. Only tiny quantities of CH₄ and H₂S accompanied the CH₃SH desorption. Tiny quantities of adsorbed S remained after CH₃SH desorption (not shown). Exposures: (a) 3.1 × 10¹³, (b) 6.3 × 10¹³, (c) 1.1 × 10¹⁴, (d) 1.6 × 10¹⁴, (e) 2.3 × 10¹⁴, (f) 3.1 × 10¹⁴, (g) 5.5 × 10¹⁴, and (h) 6.2 × 10¹⁴ molecules/cm².

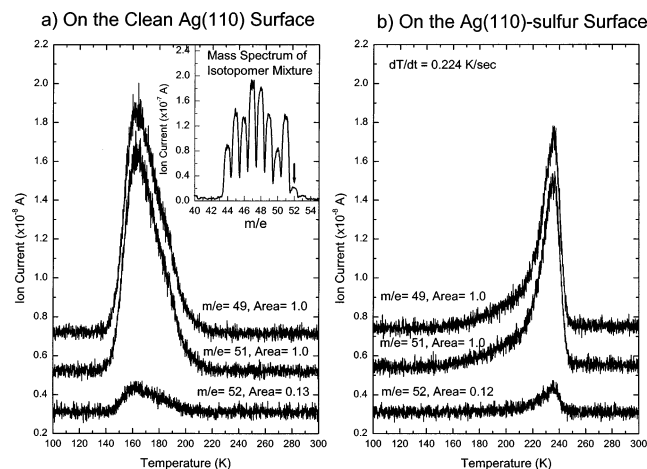


Figure 2. TPD spectra of a 50:50 isotopomer mixture of methanethiols (CD₃SH and CH₃SD). (a) On the clean Ag(110) surface. (b) On the Ag(110)–S surface.

50:50 isotopomer mixture of CD₃SH (51 amu) and CH₃SD (49 amu). Any formation of CD₃SD by isotopic mixing between the molecules would yield CD₃SD (52 amu). The mass spectrum of the mixture of isotopomers adsorbed is shown in the insert of Figure 2. The ratio of mass intensity of the adsorbed methanethiol isotope

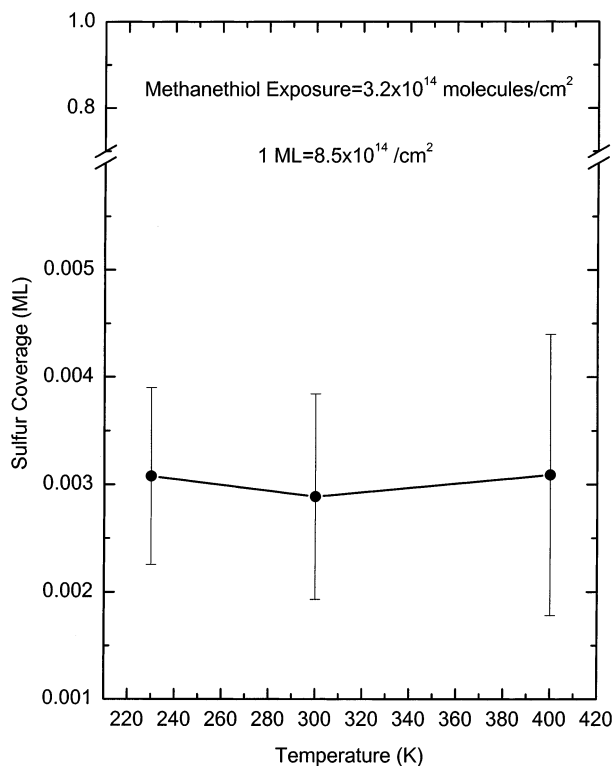


Figure 3. Sulfur accumulation on the clean Ag(110) surface by methanethiol decomposition at elevated temperature. The coverage of the sulfur-containing species was calculated by comparing the intensity of the observed Auger sulfur peak with the intensity of the known small exposure of methanethiol at 25 K, where undissociated $\text{CH}_3\text{SH}(\text{a})$ is produced. The error bars represent the amplitude of the noise in the Auger measurement of the small coverage of S produced.

mixture for 49, 51, and 52 amu is 1.0:1.0:0.13, respectively. It is expected that the ratio of isotopomer yields would change for these species if S–H and S–D bond cleavage occurred on the silver surface followed by recombination. Figure 2 shows the TPD spectra of the isotope mixture of methanethiol on the silver surface obtained by multiplexing the mass 49, 51, and 52 amu signals. No change in the isotopic ratio was observed when this mixture of isotopomers desorbs from the clean Ag(110) or from a Ag(110) surface containing adsorbed sulfur. The result indicates either that the methanethiol nondissociatively adsorbs on the Ag(110) surface or that recombination of $\text{CH}_3\text{S}(\text{a})$ and $\text{H}(\text{a})$ to produce $\text{CH}_3\text{SH}(\text{g})$ does not occur. In addition, it implies that isotope exchange by means of an elementary step involving associated adsorbed CH_3SH molecules that may undergo H transfer does not occur on the silver surface.

To further investigate whether S–H bond scission occurs in methanethiol on the clean Ag(110) surface at elevated temperatures, the clean Ag(110) surface was exposed to CH_3SH in the temperature

range 230–400 K [total exposure of methanethiol = 3.2×10^{14} molecules/ cm^2 (~ 0.5 ML); exposure time = 100 s]. The coverage of chemisorbed sulfur-containing species (e.g., methanethiolate, sulfur, sulfhydryl species) as a result of the dissociation of methanethiol was monitored by AES. Less than 1% of the incident methanethiol molecules dissociates to produce an adsorbed sulfur-containing species in the temperature range of 230–400 K as shown in Figure 3. This result indicates either that the S–H bond dissociation channel is inefficient due to a very low sticking probability of CH_3SH at these temperatures or that S–H bond cleavage of methanethiol hardly occurs even above room temperature.

In summary, we have performed three definitive experiments designed to detect methanethiol dissociative adsorption on the clean Ag(110) surface. Each experiment shows that the S–H bond of adsorbed methanethiol does not dissociate on the clean Ag(110) surface and that methanethiol cleanly desorbs from the surface. In addition, methanethiol does not produce a sulfur-containing species (e.g., methanethiolate) near room temperature on the clean Ag(110) surface. These results are of importance in understanding the self-assembly of alkanethiol layers on silver where it has been commonly assumed that S–H bond scission occurs at room temperature. Although this study was performed under UHV conditions using the shortest alkyl chain molecule, which differs from the methods used to prepare a SAM in solution, we believe that this result provides an important insight into the surface bonding which takes place during alkanethiol self-assembly on silver surfaces.

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