

# Anomalous XANES Spectra of Octadecanethiol Adsorbed on Ag(111)

E. E. Doomes,<sup>†</sup> P. N. Floriano,<sup>†</sup> R. W. Tittsworth,<sup>‡</sup> R. L. McCarley,<sup>†</sup> and E. D. Poliakoff\*,<sup>†</sup>

Department of Chemistry and Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana 70803

Received: June 28, 2002; In Final Form: January 28, 2003

We report on the sulfur K-edge X-ray absorption near-edge structure (XANES) spectra of self-assembled monolayers for a series of *n*-alkanethiols adsorbed on Ag(111). We investigate the effects of chain length and incidence angle on the XANES spectra of *n*-alkanethiols [CH<sub>3</sub>-(CH<sub>2</sub>)<sub>*x*-1</sub>-SH, *x* = 6, 12, 14, 16, 18, and 22; hereafter referred to as C<sub>*x*</sub>]. Other than that of the C<sub>18</sub> sample, the XANES spectra were similar to one another. The C<sub>18</sub> spectrum displayed an above-threshold feature that was absent in all of the other spectra, and the shape of the principal subthreshold peak is different than that for all of the other compounds. Moreover, the intensities of these features exhibit an atypical angular dependence, as well. These data are consistent with recent EXAFS studies of thiol adsorption on silver, and suggest that the local environment of the sulfur adatom is different for the octadecanethiol adsorbate.

## Introduction

Self-assembled systems have generated a great deal of interest because of their ability to impart selected chemical characteristics to surfaces, and the numerous applications that result.<sup>1–3</sup> A key to the usefulness of alkanethiol monolayers is the ability to fashion specific chemical properties over a large area. The application of alkanethiol-based systems for devices relies on adsorbate layers with well-characterized, reproducible chemical properties. As a result, it is important to understand how monolayers form in such systems, and in particular, how the adsorbed layers are tethered to the underlying substrate. We report sulfur K-edge XANES spectra for a series of *n*-alkanethiols adsorbed on Ag(111) surfaces. XANES spectroscopy is extremely useful for providing information on the oxidation state and local structure of a specific atom in a molecule.<sup>4</sup> Even in the case of a monolayer, XANES is a sensitive indicator of the local environment and electronic character of an adsorbed species.<sup>5</sup>

A central motivation for this study is to determine how the octadecanethiol (C<sub>18</sub>) XANES spectrum compares to the spectra resulting from other thiols. In a previous EXAFS study of alkanethiols adsorbed on metallic surfaces,<sup>6</sup> the results for C<sub>18</sub> adsorbed on Ag(111) were qualitatively different from those obtained from the shorter chain length thiols (C<sub>5</sub> and C<sub>10</sub>, in that study). Specifically, the Fourier transforms of the EXAFS functions were very different for C<sub>18</sub>, and they suggested that the C<sub>18</sub> adsorbate is bound not only on the hollow surface sites but also at the atop surface sites. This result was surprising, so in an effort to further probe these observations, the current study focuses on XANES spectra which have been generated on several alkanethiols adsorbed on Ag(111). One expects that the XANES spectra for the C<sub>18</sub> adsorbates would be different from those of other chain lengths, as the near-edge structure is a sensitive indicator of local structure. By focusing on the XANES measurements, it is possible to compare the behavior of a large

number of chain length thiols and evaluate the trends. On the other hand, such studies are not designed to provide detailed structural data, which would be possible by employing single-crystal systems and a suite of experimental probes, as was demonstrated in a comprehensive study of hexanethiolate SAMs on Cu(100).<sup>7</sup>

In the course of performing these experiments, it was noted that the angular dependence of the XANES spectra for the C<sub>18</sub> adsorbates was markedly different from those of the other thiols, so measurements are also presented on the angular dependence for C<sub>18</sub>. In addition, XANES spectra are presented for non-adsorbed alkanethiols for comparison purposes.

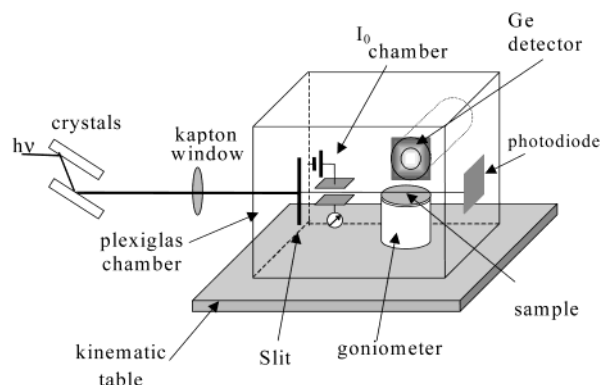
## Experimental Section

Experiments were performed at the X-ray microprobe (XMP) double crystal monochromator beamline at port 5A of the Center for Advanced Microstructures and Devices (CAMD) synchrotron radiation source at Louisiana State University.<sup>8,9</sup> The storage ring was operated at an electron beam energy of 1.3 GeV. The injection current was ca. 200 mA and injections were typically done before the beam decayed below 100 mA. The beamline monochromator was calibrated with the strong absorption resonances observed for zinc sulfate at 2481.44 eV. Si(111) crystals provided monochromatic X-rays in the region of interest. The energy bandwidth for the excitation radiation was approximately 0.5 eV over the range of energies examined. The samples were all prepared in the same manner. A Si(100) wafer was cleaned in a piranha solution (1 to 3 ratio of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>) at 75 °C for at least 30 min. A 2000 Å thick layer of 99.99% Ag was thermally evaporated onto the freshly cleaned wafers as previously reported.<sup>6</sup> All alkanethiol samples were determined to be greater than 99% purity with gas chromatography. The Ag substrate was immersed in a nitrogen-purged 1 mM ethanolic solution of the alkanethiol of interest for at least 12 h. A self-assembled monolayer of the alkanethiol forms on the substrate under these conditions.<sup>10–12</sup> After the assembly process, the samples were rinsed with absolute ethanol and dried under a stream of argon immediately prior to performing the XANES measurements. The endstation consisted of an I<sub>0</sub> monitor, a

\* Address correspondence to this author at the Department of Chemistry, Louisiana State University. E-mail: epoliak@lsu.edu.

<sup>†</sup> Department of Chemistry.

<sup>‡</sup> Center for Advanced Microstructures and Devices.



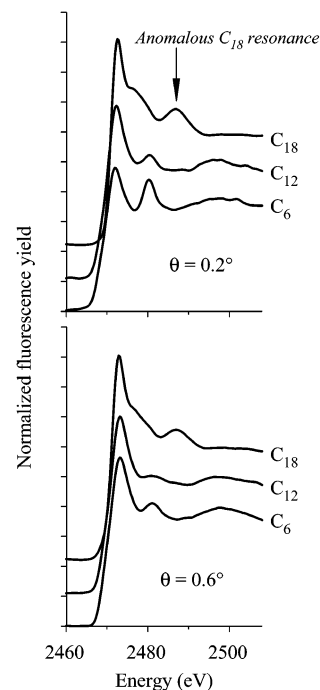
**Figure 1.** Schematic of the endstation used to obtain grazing incidence X-ray spectra.

goniometer, a single element germanium detector, and a photodiode, and was enclosed within a Plexiglas box, as shown in Figure 1. For these experiments, an inert atmosphere was maintained inside the box by flowing helium gas through inlet and outlet valves. The silicon wafer substrate was placed on a goniometer and the zero angle was determined by monitoring the current with ionization chambers placed before and after the sample stage. The beam was collimated with two four-jaw apertures, one before the window of the sample box, and one immediately before the  $I_0$  ionization chamber. Samples were placed on a motorized goniometric sample stage assembly consisting of two translation stages (Newport models UTM25PE.1 and MVN80) and two rotation stages (Newport models URM80PE and BGM50PE). This sample positioner had 0.001 in. precision in the  $x$ ,  $y$ , and  $z$  directions, and a precision of  $0.01^\circ$  for the pitch and yaw. The absolute zero angle and zero height were determined by elevating the sample until the beam intensity behind the sample stage was reduced by 50%, as measured by a photodiode. The stage position was adjusted until the photodiode signal was reduced, regardless of the angle that it was adjusted by. The stage was withdrawn from the beam and the process was performed iteratively until there was good reproduction of the zero angle. All measurements were taken below the critical angle of the silver substrate ( $1.33^\circ$ ) reducing the penetration of incident X-rays into the bulk, suppressing elastic scattering, and reducing background signal.<sup>13</sup> Fluorescence photons were detected at the S  $K\alpha$  peak (2307 eV) with a single element Ge semiconductor detector (Canberra, model GUL01110P). A multichannel analyzer (Canberra acquisition interface module no. 556) was used to window the signal about the sulfur  $K\alpha$  fluorescence transition with a bandwidth  $\Delta E$  of ca. 150 eV. The Ge detector was perpendicular to the sample on an  $xyz$  translator.

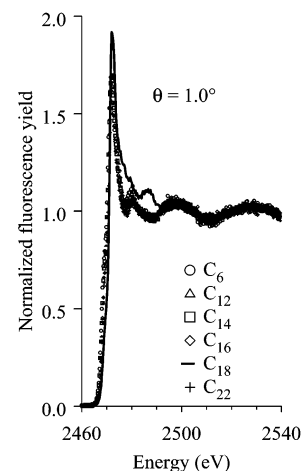
For comparison purposes, fluorescence excitation spectra were obtained for thiols that were not adsorbed on substrates. These spectra were taken to determine which features emerged from interactions following adsorption, and which are intrinsic to the thiol molecules. Spectra were taken for shorter chain thiols ( $C_5$  and  $C_{12}$ ) in solution, and for  $C_{18}$  as a powder. A Lytle-detector<sup>14</sup> was used as a fluorescence-yield detector for these measurements, and the solutions were prepared in ethanol at 0.5 M concentrations. It was not possible to make a sufficiently concentrated solution of the  $C_{18}$  compound, so it was studied as a powder.

## Results

The spectra of all of the samples exhibited angular dependence over a narrow range of shallow angles ( $0.2$ – $1.0^\circ$ ). In

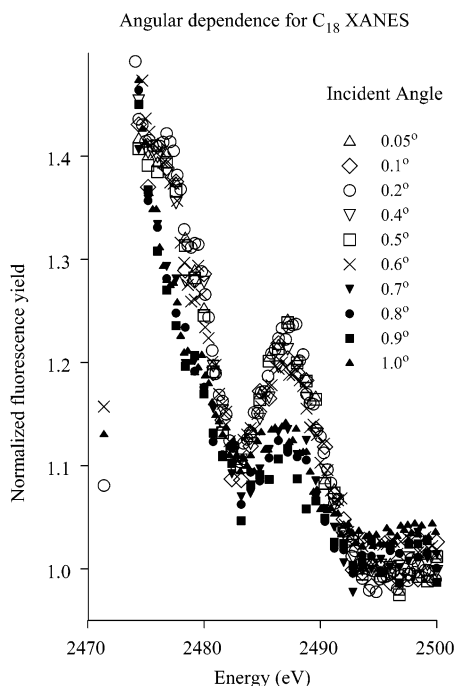


**Figure 2.** Fluorescence excitation spectra of  $C_6$ ,  $C_{12}$ , and  $C_{18}$  monolayers on silver substrate at incidence angles of  $0.2^\circ$  and  $0.6^\circ$ .



**Figure 3.** Fluorescence excitation spectra of a larger subset of the  $n$ -alkanethiols examined at  $1.0^\circ$  incidence angle. The isolated symbols are for all of the compounds other than  $C_{18}$ , while the solid line is the  $C_{18}$  spectrum. All of the thiol spectra track one another except for the  $C_{18}$  spectrum.

Figure 2, some representative spectra are shown for incidence angles of  $0.2^\circ$  and  $0.6^\circ$ . The spectra are normalized to the integrated cross section at the midpoint of the oscillatory structure in the continuum at approximately 2510 eV, where effects due to local structural changes will be relatively small. With the exception of the  $C_{18}$  sample, all of the XANES spectra are similar to one another. While the relative intensities of the features varied somewhat for different thiols, the basic patterns were consistent. The spectra for the chain lengths not shown in Figure 2 ( $C_8$ ,  $C_{10}$ ,  $C_{14}$ ,  $C_{16}$ , and  $C_{22}$ ) are consistent with the spectra of the  $C_6$  and  $C_{12}$  monolayers. In Figure 3, the data for the  $1^\circ$  incidence angle are shown. In this figure, spectra are shown for all of the thiols, and they are not offset. The results underscore the point that the spectra for all of the thiols other than  $C_{18}$  coincide closely.

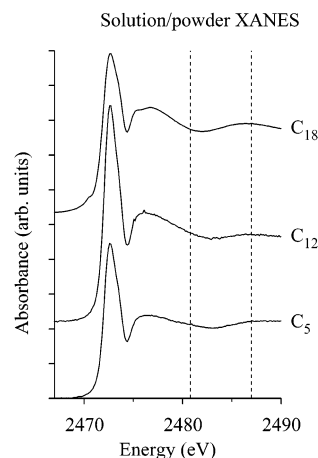


**Figure 4.** Comparison of sulfur K-edge XANES for octadecanethiol-deposited layers on Ag(111) at angles of incidence ranging from 0.05° to 1.0°. The data sets bifurcate into two groups, suggestive of two alternative adsorption sites.

Among the adsorbate results, the  $C_{18}$  data exhibit four noticeable differences from the other samples, and these differences are visible in Figures 2 and 3. First, there is a peak observed at  $h\nu_{\text{exc}} \approx 2487$  eV, which is absent in all of the other thiol spectra (although there may be a hint of this feature in the  $C_{12}$  spectrum). Second, there is a high-energy shoulder ( $h\nu_{\text{exc}} \approx 2477$  eV) on the white line transition that is absent for the other thiols. Third, Figure 3 shows that there is a low-energy shoulder on the white-line feature ( $h\nu_{\text{exc}} \approx 2469$  eV) for all of the thiols other than  $C_{18}$ . Fourth, the peak observed at 2480.8 eV for the other thiols is absent for  $C_{18}$ . The spectra for  $C_{18}$  were taken at different times following preparation, and at different sample positions, to verify that the anomalous behavior was not due to aging of the sample or radiation damage, as has been observed for adsorbed thiols in previous studies.<sup>7,15</sup>

It was noticed that the angular dependence of the  $C_{18}$  results was different than those of the other thiols studied, so a more detailed angular dependence was determined for the  $C_{18}$  adsorbate. The  $C_{18}$  results are shown with an expanded scale in Figure 4. It is striking that both the 2487 eV resonance and the shoulder at 2477 eV are grouped into two distinct families of curves.

Spectra are shown for the solution and powder (i.e., non-adsorbed) thiols in Figure 5. The spectra for all three compounds are very similar. The white-line transition occurs at the same position (2472.7 eV) for all three compounds. There is also a broad peak centered at 2477 eV for all three compounds. The lower energy reference line in Figure 5 is drawn at 2480.8 eV, the position of the resonance observed for all of the thiols other than  $C_{18}$ . There is no resonance visible in the solution phase or powder spectra in Figure 5. Similarly, the other reference line in Figure 5 is drawn at 2487 eV, the resonance position observed for  $C_{18}$ . There is a hint of a peak in the spectra seen in Figure 5, but it is not nearly as pronounced as it is for the  $C_{18}$  adsorbate spectra in Figure 2. The differences between the solution/powder phase spectra and the adsorbate spectra are striking.



**Figure 5.** Spectra taken for nonadsorbate systems. The  $C_5$  and  $C_{12}$  molecules were in solution, and the  $C_{18}$  compound was a powder. The reference lines indicate the positions of strong resonances observed for the adsorbate systems that are largely or completely absent here.

## Discussion

The current results corroborate the results of the previous EXAFS study,<sup>6</sup> in that the XANES spectra for the adsorbed  $C_{18}$  is different from those of the other thiols. To interpret the XANES spectra, we compare the observed spectra to some known sulfur-containing species.<sup>16–18</sup> The portion of the spectrum that lies below the ionization threshold corresponds to transitions from the sulfur 1s orbital to bound electronic states, i.e., unoccupied valence and Rydberg levels. This region of the spectrum is usually dominated by the white-line transition, the most intense feature observed. The primary features observed above threshold are peaks due to shape resonances or double excitations (i.e., nominally forbidden Rydberg levels converging to shake-up states of the ion).<sup>19,20</sup> Both the positions of the resonances and their intensities depend strongly on the oxidation state of the absorber, as well as its local chemical environment. This sensitivity of shape resonances to local environment is one reason XANES spectra are useful for chemical fingerprinting, and why anomalous surface bonding for  $C_{18}$  is expected to show a distinctive fingerprint in its XANES spectrum. There are quite a few sulfur-containing compounds that have been investigated via XANES spectroscopy<sup>16,18,21–25</sup> and this literature provides useful background for interpreting the present results.

The spectra shown in Figure 5 for the nonadsorbate systems are similar to each other, including the spectrum observed for  $C_{18}$ . This is expected if the local environment around the absorbing sulfur atom is similar for those systems,<sup>26</sup> which is the situation for the solution-phase and powder samples. On the other hand, comparison of the adsorbate spectra in Figures 2 and 3 with those in Figure 5 shows that the prominent peaks at 2480.8 and 2487 eV in the adsorbate spectra are essentially absent from the solution and powder samples. Clearly, the introduction of the substrate has influenced the local environment, and hence the sulfur K-edge spectra are different from the nonadsorbate spectra, and different from each other.

Among the adsorbate spectra, the most striking difference between  $C_{18}$  and the other thiols is the feature observed at  $h\nu = 2487$  eV for  $C_{18}$  (see Figure 2). We assign this feature to a shape resonance that results from multiple scattering processes of the photoelectron which involve the Ag substrate. Shape resonances are quasibound continuum states and are known to be sensitive to the local chemical environment.<sup>26</sup> Cross-section enhancements in the continuum (ca. 2–20 eV above the ionization threshold) with widths of several electronvolts are



typical of shape resonances.<sup>26,27</sup> However, an observation of a broad feature above threshold is not sufficient grounds for an assignment as a shape resonance, because nonresonant continuum enhancements are occasionally observed with similar characteristics.<sup>28–30</sup> It is clear that the 2487-eV feature is influenced by the Ag substrate or it would be present for the other thiols studied, which it is not. This provides additional support to the assignment of this feature as a shape resonance, as it is well-known that such continuum resonances are sensitive to subtle geometric changes.<sup>26,27,31–34</sup> The observation of a shape resonance for C<sub>18</sub> that is not observed for the other thiols is consistent with the previous conclusion that a substantial fraction of the C<sub>18</sub> adsorbs differently than the other thiols.<sup>6</sup> Moreover, the present study provides a new result. Namely, the longest chain length examined here, C<sub>22</sub>, returns to the behavior of the shorter alkanethiols. So, the result for C<sub>18</sub> does not indicate a trend that persists for longer chain thiols. It may be that 18 is not a magic number, but rather, thiols with chain lengths of ca. 18 exhibit similar behavior.

Optical methods have also indicated that C<sub>18</sub> adsorption on gold is anomalous. Surface plasmon spectrometry indicates that optical properties of self-assembled monolayers on metal substrates are a function of methylene chain length.<sup>35</sup> In the case of Au(111), the refractive indices gradually increase to an alkyl chain length of 17, where a turning point is reached and the refractive index decreases slightly, indicating that there is a different packing regime in the vicinity of the 18-carbon chain length. However, the results from that study do *not* indicate a similar change in the refractive index of alkanethiol monolayers on silver. Whether this is due to sample preparation or differences between optical and X-ray probes cannot be determined from the present data.

It is possible that the 2487-eV peak is associated with oxidation of the sulfur in the C<sub>18</sub> adsorbate layers, but this interpretation is considered unlikely. Thiols adsorbed on coinage metals undergo oxidation under various conditions,<sup>36</sup> so it is possible that this peak results from an oxidized species. First, the energy of this peak indicates that it must be a continuum feature rather than a subthreshold peak, regardless of whether it is associated with C<sub>18</sub> or a degradation product. Previous XANES results on model compounds containing sulfur indicate that the “white-line” feature ranges from ca. 2471 eV for sulfur in an oxidation state of 0 to ca. 2480 eV for sulfur in the form of sulfate (oxidation state of +6). Thus, because the observed feature is at higher energy than the white-line energy for *any* sulfur-containing compounds, it must be a continuum feature. It is possible that it is a shape resonance associated with an oxidized species, but it would have to be present in *very* high surface concentrations to result in a peak as large as is observed. The reason for this conclusion is that shape resonances do not usually dominate the nonresonant background, so the pronounced resonance observed at 2487 eV is likely due to a species present in very high concentration. Thus, it is most likely that this feature is due to the adsorbed C<sub>18</sub> thiol and not an oxidation product.

Another difference between C<sub>18</sub> and the shorter adsorbed thiols is observed at 2480.8 eV, where a peak is observed for all of the thiols other than C<sub>18</sub>. This peak was observed in a previous XANES study on C<sub>8</sub>,<sup>37</sup> where the spectra were obtained for a sample prepared under UHV conditions. There are a couple of plausible interpretations of this feature. Because these features only emerge for the adsorbed thiols, this structure is probably due to an adsorbate/substrate interaction, as proposed previously.<sup>37</sup> On the other hand, it is possible that this peak arises

from oxidation of the thiols. Indeed, it is known that alkanethiols adsorbed on Ag have a tendency to oxidize and form observable amounts of sulfinates.<sup>15,36,38</sup> So one possibility that was considered was that the observed feature might be the “white-line” feature of an impurity or product associated with C<sub>x</sub> adsorption. In the XANES characterization of sulfur-containing species, it is known that the white-line features of higher oxidation state compounds (sulfinates and sulfonates, specifically) have strong white-line absorptions at this energy.<sup>18</sup> It is expected that longer chain alkanethiols tend to be more resistive to oxidation than short-chain alkanethiols, making C<sub>18</sub> relatively resistant to oxidation. However, it is not likely that oxidation would occur in the UHV study,<sup>37</sup> which would indicate that the assignment by those investigators is correct. X-ray induced chemistry is not out of the question, however, and could lead to results similar to ozonolysis or similar oxidative processes.<sup>39</sup> The assignment of this feature has little direct bearing on the current interpretation, but if it is a result of oxidized thiols, then it would be a useful barometer for the degree of oxidation.

Another difference between the C<sub>18</sub> adsorbate spectrum and others occurs for the white line at 2472.3 eV. For C<sub>18</sub>, this feature was more intense than C<sub>6</sub> or C<sub>12</sub> at each angle that was examined. The white-line transitions are due to transitions to bound states associated with excitation to the LUMO. These transitions involving the 1s electron are governed by the selection rule  $\Delta l = \pm 1$ . Thus, these spectra indicate a reduction in the density of occupied p-states as evident in the diminished intensity of the first component of the white line of the C<sub>18</sub> spectra. This is a sign that the electronic interactions between the C<sub>18</sub> and the substrate are different than those for the other thiols studied, i.e., the different adsorption characteristics for C<sub>18</sub><sup>6</sup> are accompanied by differing electronic interactions. To ascertain a quantitative understanding of the peak intensity for the white-line transition, polarization-dependent measurements are necessary, as described elsewhere.<sup>44</sup> The key point of the present work is that the C<sub>18</sub> peak shapes are qualitatively distinct from those of the other SAMs.

There is evidence from other studies that thiols adsorbed on Ag(111) occupy more than a single binding site. Cyclic voltammetry data exhibited multiple steps, which were interpreted to indicate multiple adsorption sites.<sup>40</sup> Those data were supported by X-ray standing wave measurements for C<sub>8</sub> on Ag(111),<sup>41</sup> as well as by calculational studies which indicated that both atop and hollow site geometries would be observed for Ag(111) surfaces in contrast with Au(111) surfaces.<sup>42</sup> However, the situation is not completely clear for a couple of reasons. First, the voltammetry data can be interpreted differently, as suggested by Wong and Porter.<sup>43</sup> These authors propose that voltammetric fine structure arises from morphological structure of the surface, and not multiple binding geometries on the surface. The current investigation cannot clarify the voltammetric data, but the present study does have some bearing on the previous studies. Specifically, if the 2487-eV peak seen for C<sub>18</sub> is indeed a sign of a new binding geometry (i.e., atop sites<sup>6</sup>), then the current results for all of the other thiols studied suggest that multiple binding sites are not *substantial* components in the SAMs for C<sub>x</sub>,  $x \neq 18$ . This may suggest that the interpretation of multiple voltammetric steps is largely due to effects of surface roughness rather than multiple binding sites, as suggested by Wong and Porter.<sup>43</sup> While atop binding sites may be present for all thiols on Ag(111), the present results indicate that they are less prominent for thiols other than C<sub>18</sub>.

The angular dependence of the XANES provides additional information on the surface binding. The data in Figure 4 clearly

show that the data separate into two sets. The simplest explanation that is consistent with the observed angular dependence is that there are two distinct binding sites for the C<sub>18</sub> adsorbates. The data in Figure 4 are consistent with the EXAFS data<sup>6</sup> which suggested that there were contributions from two adsorption sites for the C<sub>18</sub> SAMs. However, when one performs an EXAFS fit, there is always the question of how the model may bias the results. For example, it may be possible that there are a variety of binding sites, and that the EXAFS data are well represented with a two-state model. However, the angular data shown in Figure 4 suggest that there are two distinct binding sites.

The results obtained here may be dependent on subtle aspects of the preparation methods, which suggest useful directions for further investigation. For example, recent studies have shown that surface annealing processes have time constants that are measured in days, as evidenced by structural and oxidation state changes that occur over a longer time scale than employed for the current study.<sup>7,15</sup> It is possible that the adsorption properties (e.g., percentage of atop sites) are dependent on the finer details of the preparation conditions, such as the annealing time. The current interpretations would similarly benefit from cleaner preparation methods, such as SAM preparation by adsorbate evaporation under UHV conditions, which would not have complications resulting from oxidation contaminants.<sup>44</sup>

## Conclusions

We have obtained XANES spectra at the sulfur K-edge of *n*-alkanethiol monolayers on Ag(111) using fluorescence excitation at grazing incidence. The results show that such spectra are sensitive to changes in bonding between the adsorbed *n*-alkanethiol and the silver substrate. These experiments indicate the presence of an anomalous spectrum for the 18-carbon chain length. Previous EXAFS results indicated that the monolayer structure of octadecanethiol adsorbate was inconsistent with that of shorter chain lengths.<sup>6</sup> Within the scope of the previous study, it was unclear whether the spectrum of the 18-carbon thiol was the beginning of a trend. This study determined that this was in fact not the onset of a trend, but rather a local extremum, as a longer chain length adsorbate (C<sub>22</sub>) was consistent with the spectra of the shorter chain thiols (<C<sub>18</sub>). The C<sub>18</sub> spectra exhibit an anomalous resonance at 2487 eV assigned as a shape resonance that is enhanced by the anomalous binding geometry for C<sub>18</sub>. These results underscore the conclusion that XANES spectroscopy can be a useful probe of the detailed nature of self-assembled monolayer structure, and that chain-length-dependent measurements provide insights into the formation and stability of such adsorbate systems.

**Acknowledgment.** This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. We also acknowledge funding from the U.S. National Science Foundation (R.L.M., CHE-9529770 and CHE-0108961; E.D.P., CHE-9616908). We thank Dr. F. Josef Hormes and the staff of CAMD for experimental support.

## References and Notes

- (1) Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354.
- (2) Zisman, W. A. In *Friction and Wear*; Elsevier: New York, 1959.
- (3) Notoya, T.; Poling, G. W. *Corrosion* **1979**, *35*, 193.
- (4) Hilbrig, F.; Michel, C.; Haller, G. L. *J. Phys. Chem.* **1992**, *96*, 9893.
- (5) Ohta, T. *Physica B* **1995**, *208&209*, 427.
- (6) Floriano, P. N.; Schlieben, O.; Doomes, E. E.; Klein, I.; Janssen, J.; Hormes, J.; Poliakoff, E. D.; McCarley, R. L. *Chem. Phys. Lett.* **2000**, *321*, 175.
- (7) Kondoh, H.; Saito, N.; Matsui, F.; Yokoyama, T.; Ohta, T.; Kuroda, H. *J. Phys. Chem. B* **2001**, *105*, 12870.
- (8) Molders, N.; Dissertation Universität Karlsruhe, 1999.
- (9) Craft, B. C.; Feldman, M.; Morikawa, E.; Poliakoff, E. D.; Saile, V.; Scott, J. D.; Stockbauer, R. L. *Rev. Sci. Instrum.* **1992**, *63*, 1561.
- (10) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
- (11) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.
- (12) Ulman, A. *An Introduction to Ultrathin Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991.
- (13) Terada, S.; Yokoyama, T.; Sakano, M.; Imanishi, A.; Kitajima, Y.; Kiguchi, M.; Okamoto, Y.; Ohta, T. *Surf. Sci.* **1998**, *414*, 107.
- (14) Lytle, F. W.; Greigor, R. B.; Sandstrom, D. R.; Marques, E. C.; Wong, J.; Spiro, C. L.; Huffman, G. P.; Huggins, F. E. *Nucl. Instrum. Methods Phys. Res. Sect. A* **1984**, *226*, 542.
- (15) Schoenfish, M.; Pemberton, J. J. *Am. Chem. Soc.* **1998**, *120*, 4502.
- (16) Sarret, G.; Connan, J.; Kasrai, M.; Eybert-Berard, L.; Bancroft, G. M. *J. Synchrotron Radiat.* **1999**, *6*, 670.
- (17) Kasrai, M.; Brown, J. R.; Bancroft, G. M.; Yin, Z.; Tan, K. H. *Int. J. Coal Geol.* **1996**, *32*, 107.
- (18) Sarret, G.; Connan, J.; Kasrai, M.; Bancroft, G. M.; Charrie-Duhaut, A.; Lemoine, S.; Adam, P.; Albrecht, P.; Eybert-Berard, L. *Geochim. Cosmochim. Acta* **1999**, *63*, 3767.
- (19) Erman, P.; Karawajczyk, A.; Koble, U.; Rachlew, E.; Franzen, K. Y.; Veseth, L. *Phys. Rev. Lett.* **1996**, *76*, 4136.
- (20) Karawajczyk, A.; Erman, P.; Rachlew, E.; Stankiewicz, M.; Franzen, K. Y. *Chem. Phys. Lett.* **1998**, *285*, 373.
- (21) Pavlychev, A. A.; Szargan, R.; Hallmeier, K. H.; Hennig, C.; Franke, A. *Physica B* **1995**, *208&209*, 62.
- (22) Xia, K.; Weesner, F.; Bleam, W.; Bloom, P. R.; Skyllberg, U. L.; Helmke, P. *Soil Sci. Soc. Am. J.* **1998**, *62*, 1240.
- (23) Rose, K.; Shadle, S. E.; Eidsness, M. K.; Kurtz, D. M.; Scott, R. A.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 10743.
- (24) Dezarnaud, C.; Tronc, M.; Modelli, A. *Chem. Phys.* **1991**, *156*, 129.
- (25) Chauvistre, R.; Hormes, J.; Hartmann, E.; Etzenbach, N.; Hosch, R.; Hahn, J. *Chem. Phys.* **1997**, *223*, 293.
- (26) Stohr, J. *NEXAFS Spectroscopy*; Springer-Verlag: Berlin, Germany, 1992.
- (27) Stohr, J.; Sette, F.; Johnson, A. L. *Phys. Rev. Lett.* **1984**, *53*, 1684.
- (28) Kelly, L. A.; Duffy, L. M.; Space, B.; Poliakoff, E. D.; Roy, P.; Southworth, S. H.; White, M. G. *J. Chem. Phys.* **1989**, *90*, 1554.
- (29) Braunstein, M.; McKoy, V. J. *Chem. Phys.* **1989**, *90*, 1535.
- (30) Ferrett, T. A.; Parr, A. C.; Southworth, S. H.; Hardis, J. E.; Dehmer, J. L. *J. Chem. Phys.* **1989**, *90*, 1551.
- (31) Dehmer, J. L. *J. Chem. Phys.* **1972**, *56*, 4496.
- (32) Dehmer, J. L.; Dill, D. J. *Chem. Phys.* **1977**, *65*, 5327.
- (33) Dehmer, J. L.; Dill, D. The Continuum Multiple-Scattering Approach to Electron-Molecule Scattering and Molecular Photoionization. In *Electron-Molecule and Photon-Molecule Collisions*; Rescigno, T., McKoy, V., Schneider, B., Eds.; Plenum Press: New York, 1979; p 225.
- (34) Haack, N.; Ceballos, G.; Wende, H.; Baberschke, K.; Arvanitis, D.; Ankudinov, A. L.; Rehr, J. J. *Phys. Rev. Lett.* **2000**, *84*, 614.
- (35) Ehler, T. T.; Malmberg, N.; Noe, L. J. *J. Phys. Chem. B* **1997**, *1268*.
- (36) Zhang, Y. M.; Terrill, R. H.; Tanzer, T. A.; Bohn, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 2654.
- (37) Rieley, H.; Kendall, G. K. *Langmuir* **1999**, *15*, 8867.
- (38) Chadwick, J. E.; Myles, D. C.; Garrell, R. L. *J. Am. Chem. Soc.* **1992**, *115*, 10364.
- (39) Rieley, H.; Kendall, G. K.; Zemicael, F. W.; Smith, T. L.; Yang, S. H. *Langmuir* **1998**, *14*, 5147.
- (40) Mohtat, N.; Byloos, M.; Soucy, M.; Morin, S.; Morin, M. J. *Electroanal. Chem.* **2000**, *484*, 120.
- (41) Rieley, H.; Kendall, G. K.; Jones, R. G.; Woodruff, D. P. *Langmuir* **1999**, *15*, 8856.
- (42) Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 9389.
- (43) Wong, S.-S.; Porter, M. D. *J. Electroanal. Chem.* **2000**, *485*, 135.
- (44) Kondoh, H.; Tsukabayashi, H.; Yokoyama, T.; Ohta, T. *Surf. Sci.* **2001**, *489*, 20.