

Attenuation of Photoelectrons in Monolayers of *n*-Alkanethiols Adsorbed on Copper, Silver, and Gold¹

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The attenuation length, λ , of photoelectrons with kinetic energies in the range 500–1500 eV in hydrocarbon films was measured with self-assembled monolayers (SAMs) of *n*-alkanethiols adsorbed on copper and silver surfaces. This work extends a previous study using SAMs on gold. The following values were determined for λ : on Ag, 37 Å at 1390 eV, 36 Å at 1119 eV, 35 Å at 1113 eV, 30 Å at 914 eV, 29 Å at 883 eV, and 24 Å at 768 eV; on Cu, 40 Å at 1410 and 1364 eV, 28 Å at 918 eV, and 22 Å at 554 eV. Estimates of λ obtained by using SAMs as scattering layers are more consistent than those obtained by using thin organic films fabricated by other methods. The relationship between λ and the kinetic energy (KE) of photoelectrons, over the energy range studied by using SAMs, can be fit equally well by the expressions $\lambda = 9.0 + 0.022\text{KE}$ or $\lambda \propto \text{KE}^p$ where $p = 0.67 \pm 0.11$. Bethe's equation for electron scattering in matter also relates λ to KE.

Introduction

Accurate values of attenuation lengths³ of electrons (λ), as a function of kinetic energy (KE) and of medium, are crucial in using electron spectroscopies in quantitative analysis.⁴ The most common method of determining λ is the substrate/overlayer technique.⁵ This technique requires formation of thin (10 to ~100 Å), homogeneous films—a difficult requirement, particularly for organic films. *n*-Alkanethiols, $\text{CH}_3(\text{CH}_2)_n\text{SH}$, adsorb from solution onto the surfaces of copper, silver, and gold and form densely packed, oriented monolayer films (self-assembled monolayers, SAMs).^{6–10} The thickness of these films can be easily controlled on the scale of angstroms by varying the chain length of the adsorbate.^{7–10} In this paper we have determined λ for photoelectrons of KE \approx 500–1500 eV in SAMs on copper and silver. This work extends previous work¹¹ with SAMs on gold: the effect of the structure of the SAM is considered; the range of kinetic energies is expanded; the systematic and random errors are estimated.

The attenuation length, λ , is defined by

$$I(\tau) = I_0 \exp(-\tau/\lambda) \quad (1)$$

Direct measurement of λ is accomplished experimentally by varying the thickness, τ , of an overlayer covering a semiinfinite substrate. Previous measurements^{11–21} of attenuation lengths in organic materials, made by a variety of methods, gave widely scattered values (Figure 1). Thin films used to determine λ have been prepared by evaporation of carbon-containing material—graphite,¹² hexatriacontane,¹³ polymerizable monomer ([2.2]p-cyclophane)¹⁴—or use of the Langmuir–Blodgett method.^{17–21} Thin films prepared by evaporation have yielded very large discrepancies in the value of λ —for example, at KE \approx 1200 eV, λ has been determined to range from ~20 to ~80 Å^{13,14}—largely due to difficulties, we believe, in forming homogeneous films and in determining and controlling the thicknesses of these films accurately. The Langmuir–Blodgett technique²² provides greater control over the thickness of an organic film than evaporation but is still not ideal. For example, Brundle et al.¹⁷ acknowledged the presence of “patches” of uncovered substrate and corrected the values of λ they measured by ~20% to accommodate this problem in fabrication.

Self-assembled monolayers (SAMs)²³ provide a method for the preparation of thin, homogeneous, organic films whose thickness is easily controlled on the scale of angstroms.^{7–10} Long-chain *n*-alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$) spontaneously assemble from solution onto copper, silver, and gold surfaces and reproducibly form oriented monolayer films.^{6–10} The structures of these films have been characterized by IR and found to be highly crystalline; the hydrocarbon chains are predominantly trans-extended.^{7,9,10}

The monolayers formed on copper and silver are, however, structurally different from those formed on gold: on gold, the hydrocarbon chain is canted $\sim 30^\circ$ from the surface normal,^{7,9}

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(2) Shell Foundation Pre-doctoral Fellow, 1987–88.

(3) Attenuation length—the thickness of material required to reduce the flux of generated electrons to $1/e$ —should not be confused with inelastic mean free path. Only in the absence of elastic scattering, which is not negligible (Tougaard, S.; Sigmund, P. *Phys. Rev. B* **1982**, *25*, 4452–4466. Jablonski, A.; Ebel, H. *Surf. Interface Anal.* **1988**, *11*, 627–632 and references therein), are the two terms equivalent. Attenuation length and escape depth are interchangeable terms.

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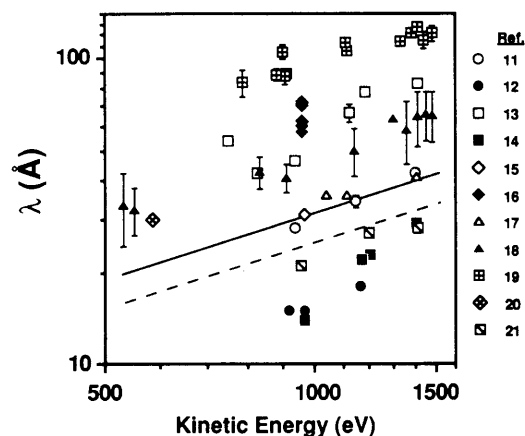


Figure 1. Double-log plot of attenuation lengths, λ , in carbon-based materials as a function of the kinetic energy of the photoelectron. The data were taken from the literature;^{11–21} λ 's from refs 12–14 and 17–21 were obtained by the substrate/overlayer technique using evaporated and Langmuir–Blodgett films, respectively. Data from refs 12 and 15 are for graphite and may not be directly comparable to the data obtained using hydrocarbons. The solid line summarizes our data and is taken from Figure 4; the dashed line represent calculated inelastic mean free paths (IMFPs) through glassy carbon.³⁷

on silver and copper, the cant angle (ϕ) is smaller ($\phi \approx 12^\circ$).^{9,10}

To generate films of different thicknesses, we varied the length of the chain of the adsorbate. This length could be correlated with the thickness of the monolayer, using the cant angle of the chains (determined by IR).^{7,9,10} We measured the intensities of photoelectrons originating in the substrate and compared the intensities for SAMs of different lengths. The structural differences that exist between SAMs formed on copper, silver, and gold should have, in theory, no effect on λ beyond those due to thickness.²⁴

In a previous paper using *n*-alkanethiolate monolayers on gold,¹¹ we found that, over the range KE = 1000–1400 eV, λ could be described by Wagner's empirical expression²⁵

$$\lambda = k(\text{KE})^p \quad (2)$$

where KE was the kinetic energy of the electrons and the exponent p was 1.0 ± 0.1 . This value of p was determined from data at only three values of KE and is greater than the value of 0.5 suggested by Seah and Dench,²⁶ 0.65 by Cartier et al.,¹³ 0.66 ± 0.10 by Wagner et al.,²⁵ 0.75 by Szajman et al.,²⁷ and 0.78 by Ashley et al.²⁸ We have combined our earlier data for monolayers on gold with the new data described here for copper and silver and redetermined p based on the expanded range of kinetic energies (KE = ~ 550 –1400 eV): the value of p we now estimate ($p = 0.67 \pm 0.11$) is closer to previous determinations^{13,25–28} than is our prior estimate.

Determinations of λ (Figure 1) have rarely included a description of random or systematic errors. As a consequence, it is difficult to assess the relative accuracies of the different values of λ . The random errors in our previous work on gold¹¹ were small. We were able to estimate the magnitude and direction of systematic errors for a single system. Here, by studying monolayers adsorbed on two other substrates, silver and copper, we hoped to decrease the importance of systematic errors in our measurements.

Results

Method. The requisite equations have been discussed previously.¹¹ In brief, modification of eq 1 to accommodate the re-

(24) We do not expect any artefacts due to channelling of photoelectrons along the direction of the hydrocarbon chain; the takeoff angle we use does not match the chain axis of any the SAMs mentioned here.

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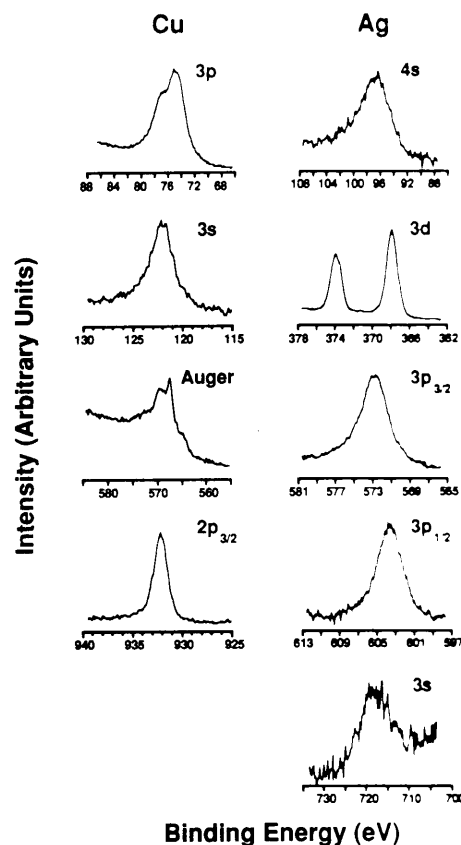


Figure 2. X-ray photoelectron spectra of core-level regions of silver and copper through an *n*-docosanethiolate SAM. Instrumental parameters are provided in the Experimental Section.

lationships between incremental change in the thickness of the film and the change in the number of methylene groups ($\Delta\tau = d \cos \phi \Delta n$) and the effective thickness of the film penetrated by the electrons that are sensed by a detector at an angle θ from the surface parallel ($\tau_{\text{eff}} = \tau / \sin \theta$) leads to eq 3. In eq 3, $I(n)$ is

$$\ln [I(n)] = -\frac{nd \cos \phi}{\lambda \sin \theta} + \text{constant} \quad (3)$$

the intensity of a peak, n is the number of methylene groups in the adsorbate, d is the incremental contribution of a methylene group to the length of an *n*-alkyl chain ($d = 1.27 \text{ \AA}$),²⁹ ϕ is the angle the hydrocarbon chain is canted relative to the surface normal as determined by IR (on copper and silver,^{9,10} $\phi = 12^\circ$; on gold,^{7,9} $\phi \approx 30^\circ$), λ is the attenuation length, and θ —the takeoff angle—is the angle between the surface parallel and the axis of the electron analyzer.³⁰

Intensity of Photoelectron Peaks of Copper and Silver. In any substrate/overlayer experiment, the system must be stable to the experimental conditions—with the most important factors being the extent of X-ray-induced damage to the monolayer, and its stability under UHV conditions—and some description of the signal-to-noise should be provided. SAMs on gold,³¹ silver,³² and copper³³ are chemisorbed to the metal surface via strong metal–thiolate interactions ($\sim 40 \text{ kcal/mol}$) and are stable, at room temperature, to UHV conditions. X-ray-induced damage (due

(29) Abrahamsson, S.; Larsson, G.; von Sydow, E. *Acta Crystallogr.* **1960**, *13*, 770–774.

(30) In our experiment, θ is fixed (35°), ϕ has been determined by IR (for Au = $\sim 30^\circ$; ϕ for Cu and Ag = $\sim 10^\circ$), and $I(n)$ is measured.

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

(32) Harris, A. L.; Rothberg, L.; Dhar, L.; Levinos, N. J.; Dubois, L. H. *Phys. Rev. Lett.* **1990**, *64*, 2086–2089. Harris, A. L.; Rothberg, L.; Dhar, L.; Levinos, N. J.; Dubois, L. H. *J. Chem. Phys.* **1991**, *94*, 2438–2448.

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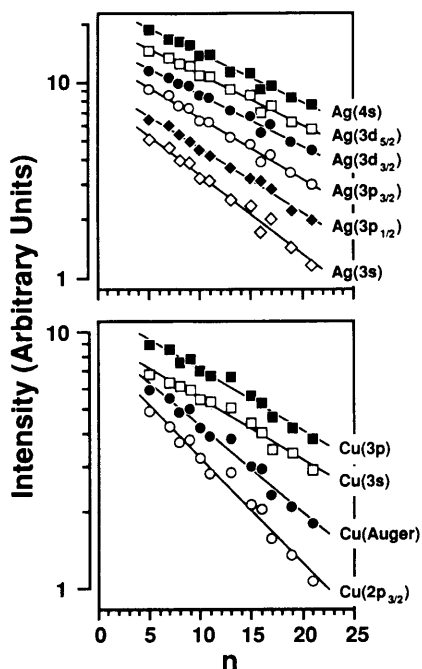


Figure 3. Intensities of X-ray photoelectrons and Auger electrons from silver and copper beneath an *n*-alkanethiolate monolayer as a function of the number of methylenes, *n*, in the adsorbing *n*-alkanethiol, CH₃(CH₂)_{*n*}SH. The points represent single measurements. The data for each core level and Auger transition have been offset vertically to avoid overlap with data from other levels; the slope is the important parameter. The lines represent least-square fits to the data; the slopes are given in Table I.

in part to secondary electrons) occurs at a sufficiently slow rate that it is a negligible factor under our conditions.^{34,35}

In our experimental procedure, we measured each of the defined core-level regions using a common set of acquisition parameters for each sample. We varied the number of scans employed to accommodate differences in intensity and characterized the samples in random order. Figure 2 displays spectra of the photoelectrons emitted by copper and silver beneath docosanethiolate (*n* = 21) monolayers, the thickest layer (~30 Å) we used in this study. These spectra represent those of lowest signal-to-noise; the intensities of these peaks were higher with shorter chain length adsorbates. Total exposure to the X-ray source (monochromatized Al K α radiation) was less than 90 min. The dead time of the detector was always less than 10%.

Monolayers on Silver and Copper. Figure 3 summarizes the intensities of the various photoelectron peaks due to underlying silver and copper as the length of the adsorbate is increased. Included in Figure 3 are data obtained for the L₃M_{4,5}M_{4,5} Auger transition (KE = 918 eV) of copper. Both the photoelectron and Auger electron data are well described by eq 3, but the fits were poorer for data obtained on copper. Minor differences in oxygen content between copper samples may be responsible for the increased scatter. The slopes and calculated values of λ are given in Table I.

Relation between λ and Kinetic Energy. The “universal curve”²⁶ indicates that for KE > ~100 eV, λ increases with increasing

TABLE I: Attenuation Lengths Calculated from Intensities of Photoelectrons or Auger Electrons from Underlying Copper, Silver, and Gold Substrates Functionalized with *n*-Alkanethiolate Monolayers^a

photoelectron or Auger electron	KE, eV	slope	λ , ^b Å
Cu(3p)	1410	-0.054 ± 0.005	40 ± 4
Cu(3s)	1364	-0.054 ± 0.005	40 ± 4
Cu L ₃ M _{4,5} M _{4,5}	918	-0.077 ± 0.008	28 ± 3
Cu(2p _{3/2})	554	-0.094 ± 0.009	23 ± 2
		-0.101 ± 0.008	21 ± 2
Ag(4s)	1390	-0.058 ± 0.003	37 ± 2
Ag(3d _{5/2})	1119	-0.060 ± 0.003	36 ± 2
Ag(3d _{3/2})	1113	-0.061 ± 0.003	35 ± 2
Ag(3p _{3/2})	914	-0.072 ± 0.004	30 ± 2
Ag(3p _{1/2})	883	-0.075 ± 0.004	29 ± 1
Ag(3s)	768	-0.092 ± 0.009	24 ± 2
Au(4f _{7/2})	1402	-0.046 ± 0.001	42 ± 1
Au(4d _{5/2})	1151	-0.056 ± 0.002	34 ± 1
Au(4p _{3/2})	940	-0.068 ± 0.002	28 ± 1

^aThe values presented for monolayers on gold were taken from ref 11. In ref 9, we measured the attenuation of Au(4f_{7/2}) and Au(4d_{5/2}) photoelectrons using *n*-alkanethiolate SAMs. The data can be fit by eq 3 and provide attenuation lengths of 43 and 33 Å, respectively. ^bErrors represent 95% confidence limits. ^cThis value was obtained from a second set of *n*-alkanethiolate SAMs on copper.

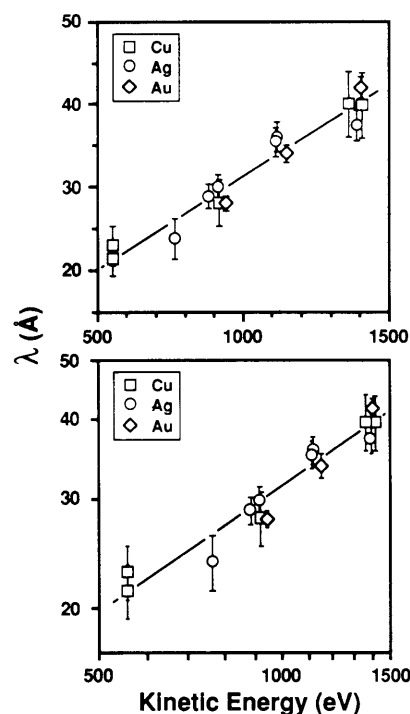


Figure 4. Attenuation lengths, λ , derived from *n*-alkanethiolate monolayers on copper, silver, and gold as a function of the KE of the electrons. Over this energy range, a linear function can be used to relate λ (in angstroms) and KE (in eV): $\lambda = 9.0 + 0.022KE$ (upper panel). The log-log plot (lower panel) demonstrates that the data are also fit by eq 2; the line is a least-squares fit to the data as presented and has a slope $p = 0.67$. We estimate the 95% confidence limit in the slope to be ± 0.11 and the value of $k = 0.31$. Comparison with Figure 1 demonstrates the high degree of reproducibility afforded by this method for three different substrates. The data presented for Cu(2p_{3/2}) (KE = 554 eV) represent two independent experiments.

(34) The XPS spectra of the C(1s) and Ag(3d_{5/2}) regions were obtained on an *n*-octadecanethiolate monolayer on silver before and after 90-min exposure to our X-ray source (Al K α). After exposure, the C(1s) intensity decrease by ~3% and the Ag(3d_{5/2}) intensity increase by ~5%. With use of the values given in Table I, the change in the intensity of Ag(3d_{5/2}) corresponds to a 1-Å decrease in the thickness of the hydrocarbon layer over the interval of our measurements. Total exposure to the X-ray source was less on copper than on silver (30 vs 90 min), and we therefore expect the damage to be less on copper than on silver.

(35) The amount of X-ray-induced damage that we observe³⁴ to the monolayers is much less than others³¹ have reported. The different rates of damage to the monolayers are due to the anodes employed: Nuzzo et al.³¹ used a nonmonochromatized source; we employ monochromatic Al K α X-rays. Monochromatic sources are much less damaging to organic materials and are highly preferred in characterizing organic monolayers.

KE due to decreasing capture efficiencies of materials. Figure 4 displays the values of λ determined from *n*-alkanethiolate monolayers on copper, silver, and gold as a function of the KE of the electrons. Over the energy range 500–1500 eV—the range of energies typically encountered in XPS spectroscopy employing Al K α radiation—we find that λ is proportional to the KE of the photoelectrons. Over this narrow energy range, the expression $\lambda(\text{Å}) = 9.0 + 0.022KE(\text{eV})$ provides a rapid and simple estimate of λ in hydrocarbon films. If the data are plotted as $\ln \lambda = p \ln$

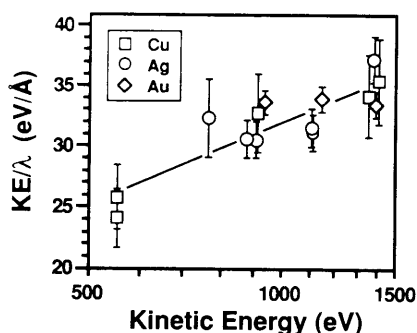


Figure 5. Test of the validity of the Bethe equation³⁸ for attenuation lengths (λ) through hydrocarbon films determined by using SAMs: $KE/\lambda = \beta E_p^2 \ln KE + \gamma E_p^2 \ln \gamma$ (from eq 4); $E_p \approx 16.7$ eV for a polymethylene fragment.³⁹ The solid line represents a least-squares fit to the data where $\beta = 0.034 \pm 0.012$ eV⁻¹ Å⁻¹ and $\gamma = 0.027$ eV⁻¹; γ is related exponentially to the slope and the intercept, and we calculate the value of γ to range from 0.011 to 0.14 eV⁻¹.

KE + k (Figure 4, lower panel), a best fit gives a y -intercept $k = 0.31$ and a slope $p = 0.67 \pm 0.11$ that is in accord with previous studies.^{13,25,27,28} The goodness of the fits to these two empirical relations is statistically the same.

Using a more physical approach, Penn et al.^{36,37} have suggested that the dependence of inelastic mean free paths (IMFPs) on KE be represented by a reformulation (eq 4) of the Bethe equation³⁸

$$\text{IMFP} = \frac{KE}{E_p^2 \beta \ln(\gamma KE)} \cong \lambda \quad (4)$$

for electron scattering in matter where β and γ are empirical parameters and E_p is the free-electron plasmon energy (≈ 16.7 eV for a polymethylene fragment³⁹). IMFPs and λ are, however, not identical except when elastic scattering is negligible. Powell has reported that eq 4, over the energy range 100–1500 eV, describes the energy dependence of λ better than does eq 2.⁴⁰

Figure 5 tests the validity of the Bethe equation as a description of attenuation lengths. The best fit to the data in Figure 5 provides $\beta = 0.034 \pm 0.012$ eV⁻¹ Å⁻¹ and $\gamma = 0.027$ eV⁻¹; γ is, however, related exponentially to both the slope and the intercept, and we calculate that the 95% confidence interval for γ is 0.011–0.14 eV⁻¹. Tanuma et al.³⁶ have suggested that γ (derived from IMFPs) is related to the density ρ (in g/cm³) of a material by eq 5. The

$$\gamma = 0.151 \rho^{-0.49} \quad (5)$$

value of γ we determine from Figure 5 is lower than the value of 0.17 eV⁻¹ calculated from eq 5 for a polymethylene chain ($\rho \approx 0.78$ g/cm³). The density of the hydrocarbon in SAMs and the errors associated with eq 5 have not yet been determined, and the difference in the values of γ is therefore probably not statistically significant.

Discussion

Error Analysis. The scatter present in Table I and Figure 3 illustrates the random errors of the measurement technique and may also reflect differences among samples. In accord with the

(36) Penn, D. R. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 29–40. Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Sci.* **1987**, *192*, L849–L857; *Surf. Interface Anal.* **1988**, *11*, 577–589.

(37) Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Interface Anal.* **1988**, *11*, 577–589.

(38) The Bethe equation is $\text{IMFP} = KE/[a(\ln KE + b)]$. Bethe, H. *Ann. Phys.* **1930**, *5*, 325–400.

(39) We estimated the free-electron plasmon energy E_p for a polymethylene fragment from

$$E_p(\text{eV}) = 28.8(N_{vp}/A)^{1/2} \quad (6)$$

where N_v is the total number of valence electrons per fragment = 6, ρ is the density = 0.78 g/cm³, and A is the molecular weight = 14.0.³⁷

(40) Powell, C. J. *Surf. Interface Anal.* **1985**, *7*, 256–262.

differences noted in the ease of preparing monolayers on the three metals,⁹ the random errors were greatest on copper and smallest on gold.

There are several sources of systematic errors in our determination of λ that we mention briefly; a more complete discussion was presented in our previous work.¹¹ First, the uncertainty in the cant angle of the hydrocarbon chain, ϕ , as determined by IR results in an uncertainty of $\pm \sim 5\%$ in the value of λ . Second, the finite acceptance angle (30°) of our analyzer lens results in a small overestimation of λ . Third, the roughness of our substrates—smooth compared to surfaces used in other investigations—probably also results in a small overestimation of λ .⁴¹ We believe these two factors affect λ on the order of $\sim 5\%$. Fourth, the monolayers formed from shorter ($n \leq 7$) and longer ($n \geq 15$) n -alkanethiols probably differ in packing densities. Monolayers on gold derived from shorter n -alkanethiols are less crystalline than those formed from longer ones.⁷ As n increases, the effective change in thickness is probably slightly greater than that described by $\Delta\tau = d \cos \phi \Delta n$; the values of λ may be, therefore, greater. The magnitude of this systematic error is difficult to estimate; no transition is, however, observed in the data presented in Figure 3 between shorter and longer adsorbates. This observation suggests that the magnitude of any change in packing density is small over the range $n = 5$ –21.

We estimate the net result from these systematic factors is that our values of λ may be overestimated by $<10\%$ and contain an uncertainty of $\pm 10\%$ (not included in the values presented in Table I). Our present evidence⁴² suggests that bare patches do not exist in any of these SAMs, although further work is required to prove this point.

Value of p . The data summarized in Figure 4, over the energy range 500–1500 eV, are fit well by the relation $\lambda \propto KE^p$: $p = 0.67 \pm 0.11$. This fit suggests that although the SAMs formed on the three substrates are structurally different, eq 3 accommodates these differences. Using SAMs on gold, we estimated previously that $p = 1.0 \pm 0.1$;¹¹ this value was, however, determined at only three values of KE and does not fit the data we have obtained on silver and copper.⁴³ We note that the data obtained on gold are adequately described by our revised value of p (Figure 4). On the basis of this and other^{13,25,27,28} studies, we recommend a value of $p = 0.67$ for work with organic films and photoelectrons having energies in the range studied here. We note that the equation $\lambda(\text{Å}) = 9.0 + 0.022KE(\text{eV})$ provides an equally reliable and more convenient estimation of λ over the energy range 500–1500 eV and may prove to be a more useful relation than eq 2.

Importance of Elastic Scattering. The attenuation lengths we have obtained fit eq 4 (Figure 5) less well than the relations examined in Figure 4. In contrast to Powell,⁴⁰ we find that, over the energy range 500–1500 eV, eq 2 describes the energy dependence of λ dependence of λ better than does eq 4. The fit to eq 4 is nonetheless surprising given that attenuation lengths and IMFPs are not identical—the difference between them being elastic scattering processes—and can differ by as much as $\sim 30\%$.³ Figure 5 suggests that elastic scattering events at energies of 500–1500 eV through thin hydrocarbon films (≤ 30 Å) are probably only minor components of λ . The value of γ we obtained, however, is lower than IMFP estimates and suggests that elastic scattering in hydrocarbons may be important over at least some of the kinetic energies we have explored.

Conclusions

Self-assembled monolayers provide a convenient method to generate thin, homogeneous organic films that, once characterized

(41) For discussions of the influence of roughness on the determination of λ , see: Fadley, C. S. *J. Electron Spectrosc.* **1974**, *5*, 725–754.

(42) The hydrocarbon layer passivates underlying copper or silver substrates against oxidation to an extent that is consistent with the absence of bare patches (≥ 100 Å) lacking functionalization. Laibinis, P. E.; Whitesides, G. M. Unpublished results.

(43) A line of slope of $p = 1.0$ in Figure 4 (lower panel) connects the lower left and upper right corners of this plot.

structurally, can be used to calibrate measurements of λ .⁴⁴ For organic films, SAMs are more reproducible as scattering layers than organic films prepared by evaporation or by the Langmuir-Blodgett method. The expression $\lambda(\text{\AA}) = 9.0 + 0.022\text{KE}(\text{eV})$ provides a convenient empirical estimate of λ in hydrocarbon films over the energy range (500–1500 eV) typically encountered in XPS spectroscopy employing Al K α radiation.

Experimental Section

Materials. *n*-Alkanethiols were available from previous studies.^{8,11} Isooctane (Aldrich) was percolated twice through neutral alumina prior to use. Copper and silver were obtained from Aldrich and were of >99.99% purity. Silicon wafers were obtained from Silicon Sense.

Preparation of Monolayers. Substrates of silver and copper were prepared by evaporation onto Cr-primed (200 Å) precut slides of Si(100) as previously described.⁹ The slides were transferred under a flow of prepurified Ar to 1 mM deoxygenated solutions of the alkanethiols in isooctane. After ~1 h of immersion, the slides were removed from solution, washed with ethanol, and blown dry with N₂. The resulting surfaces were hydrophobic ($\theta_a(\text{H}_2\text{O}) \approx 110\text{--}120^\circ$) and were not wet by hexadecane ($\theta_a(\text{HD}) \approx 40\text{--}50^\circ$). SAMs formed on silver exhibited no signals due to oxygen; however, those formed on copper contained an interphase of copper oxide. The quality and charac-

teristics of the monolayers used in this study were no different from those we characterized previously by wetting, XPS, and IR.⁹ Previous SEM and TEM studies indicate that the morphologies of these surfaces consist of rolling hills (100–300 Å across) and that the metals are heavily (111) textured.^{8,9}

X-ray Photoelectron Spectroscopy (XPS). The characteristics of the Surface Science X-100 XPS spectrometer using a monochromatized Al K α source have been detailed in depth in our previous exploration of attenuation lengths.¹¹ All samples on a particular metal were prepared at the same time. The samples were placed in the spectrometer and, in random order, characterized by using a common set of instrumental parameters: pass energy = 100 eV, spot size = 1000 μm , takeoff angle⁴⁵ = 35° from the surface plane. Survey spectra of the samples showed no elements other than the metal, carbon, sulfur, and, on copper, oxygen.⁹ The following sequence of scans were conducted: (a) Ag(4s) (20-eV window, 15 scans (~2 min/scan)); Ag(3d) (25 eV, 2 scans); Ag(3p_{3/2}) (15 eV, 3 scans); Ag(3p_{1/2}) (15 eV, 4 scans); Ag(3s) (30 eV, 20 scans); (2) Cu(3p) (20 eV, 4 scans); Cu(3s) (15 eV, 4 scans); Cu(L₃M_{4,5}M_{4,5}) (30 eV, 4 scans); Cu(2p_{3/2}) (15 eV, 2 scans). An independent experiment was conducted on copper: Cu(2p) (45 eV, 3 scans). The dead time of the detector was always less than 10%. The intensities of the peaks were determined by using a Shirley⁴⁶ background and a 75% Gaussian peak. Spectra presented in Figure 2 are unsmoothed.

(44) The three systems we have explored—*n*-alkanethiolates on copper, silver, and gold—may find further use in determining λ . By using other anode sources, one can vary the kinetic energies of the photoelectrons generated by the substrates. The values of λ could be measured over a wider range of kinetic energies, and a better estimate of the relation between KE and λ could be obtained.

(45) It has recently been suggested that λ may also be a function of film thickness and takeoff angle (Gries, W. H.; Werner, W. *Surf. Interface Anal.* **1990**, *16*, 149–153). The takeoff angle we used—55° from the surface normal—is outside the range—60–90° from the surface normal—suggested to affect λ .

(46) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709–4714.