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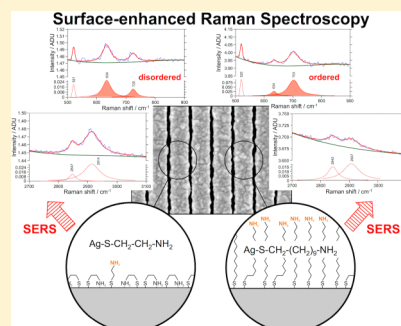
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S Supporting Information

ABSTRACT: We apply well-characterized silver nanowire grating (Ag-NWG) plasmonic surfaces as a Raman surface spectroscopy tool, which is based on surface-enhanced Raman scattering (SERS), to study the surface conformation characteristics of amine terminated alkanethiol self-assembled monolayers (SAMs). The surface conformation has implications for amine group availability, which is important when SAMs are used as linking layers for the binding of secondary molecules. Two different alkanethiols with different alkane chain lengths, namely 2-aminoethanethiol (cysteamine, CEA) and 11-aminoundecanethiol (AUT), are investigated. It is shown that both alkanethiols bind to Ag surfaces forming corresponding Ag-thiolates, however surface conformations, which are related to the ordering of the SAM, are different for these two SAM systems. The degree of SAM ordering is assessed by quantifying the integrated intensity ratio of the trans to gauche $\nu(\text{C}-\text{S})$ vibrational bands from single spectra measurements and from spatially averaged spectra. These vibrational modes occur at different vibrational frequencies depending on the conformation (trans versus gauche) of the neighboring carbon atom. We demonstrate that the CEA SAMs are less ordered than AUT SAMs; thus, the amine terminal group availability differs between both systems.



INTRODUCTION

The most widely used coatings on noble metal electrode surfaces are self-assembled monolayers (SAMs) of ω -functionalized alkanethiols and disulfides.^{1,2} SAMs formed by the chemisorption of the thiol headgroup ($-\text{SH}$) to gold and silver surfaces are commonplace for a variety of applications ranging from electron transport barriers to biocompatible layers for bioassays.² The functional moieties, or terminal-groups, of ω -functionalized alkanethiol SAMs, such as aldehyde ($-\text{COH}$), carboxyl ($-\text{COOH}$), and primary amine ($-\text{NH}_2$), are commonly used for the immobilization of reactive biomolecules.^{2–5} As applications of biofunctional alkanethiol SAMs continue to grow, it is becoming increasingly important to spatially characterize their areal orientation and uniformity, such that the bioreactive terminal-groups are accessible for further conjugation, or direct bioassay applications.

Many different surface sensitive analysis techniques are available for the characterization of SAMs, such as Auger spectroscopy, electron energy loss spectroscopy, low electron energy diffraction, X-ray photoelectron spectroscopy, infrared spectroscopy, and electrochemical analysis.^{6–8} Each technique has advantages and disadvantages, e.g., surface elemental composition and atomic oxidation states can be determined with X-ray photoelectron spectroscopy, however, the sample must be measured in ultrahigh vacuum. On the other hand, electrochemical analysis provides information about electrochemical activity of the surface and surface density in aqueous samples at ambient conditions but does not provide information about molecular composition or structure.⁹

Surface-enhanced Raman spectroscopy is a highly sensitive surface analysis technique that can be used for determining compositional and structural information on molecules near a surface that provides surface-enhanced Raman scattering (SERS). SERS is facilitated by large enhanced electric near-fields at the surface of nanostructured materials, which are induced by the coupling of light of a particular wavelength into surface plasmon resonance modes. The enhanced electric near-field results in an increase in the molecular scattering cross-section of vibration modes that obey the surface selection rules and thus an enhancement of the Raman scattered signal. As long as an appropriate excitation wavelength is used and free charge carriers are present in the nanostructured surface, SERS can be observed in different types of materials. For excitation wavelengths in the visible spectrum, the coinage metals, silver, gold, and copper, meet these requirements and are often used. In terms of SERS enhancement. Silver provides the largest enhancements for excitation wavelengths in the range of 400–600 nm; however, in practice silver has limited chemical stability, and therefore gold is more commonly used in combination with excitation wavelengths greater than 600 nm.

Surface-enhanced Raman spectroscopy offers several advantages compared to other surface sensitive analysis techniques: (1) measurements can be performed on aqueous samples, (2) minimal sample preparation is required, (3) low power

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excitation lasers in the visible spectrum can be used, (4) the technique is comparatively simple and performed at ambient conditions, thus enabling in situ measurements, and (5) it can be combined with other analytical techniques, e.g., electrochemistry for combined spectroelectrochemical analysis. A key point is that the SERS-active substrate requires spatially uniform and reproducible enhancement factor. Different types of SERS substrates have been developed over the last several years and have been summarized in a recent review article.¹⁰ However, there are very few reports of using state-of-the-art SERS-active substrates as spectroscopy tools for real world analytical applications. In the majority of application specific studies, simple surfaces, such as mechanically or electrochemically roughened surfaces are used,^{11–13} which are rarely characterized with respect to the magnitude and spatial uniformity of the Raman scattering enhancement, resonance behavior, and spatial density of the enhancement regions. Additionally, experimental conditions, such as laser power and measurement integration times, are often not reported, thus making quantitative comparison between different research groups problematic. Our group recently developed a new type of SERS-active surface based on large area metal nanowire gratings (m-NWG).¹⁴ The large area m-NWG surfaces contain sub-20 nm separation nanogaps in high length density ($\sim 1 \text{ km cm}^{-2}$) that can be spectrally tuned, by varying the nanogap dimensions, such that the surface plasmon resonance wavelength is induced close to the wavelength of the excitation laser. The m-NWG are different than conventional subwavelength gratings because each nanowire is physically and electrically isolated from adjacent nanowires.¹⁴ Additionally, the nanogaps can be precisely aligned with the laser polarization. All of these properties lead to an optimized electromagnetic field enhancement; Au-NWG SERS-active surfaces with large spatially averaged electromagnetic enhancements $\sim 10^7$ and less than 20% variation over large surface areas have been reported by our group.¹⁴

Surface-enhanced Raman spectroscopy has been used extensively with SAMs on gold and silver surfaces that have large scattering cross sections, such as benzenethiol;^{15,16} however, very few studies of ω -functionalized alkanethiols have been reported. As already described, the SAM functional terminal-groups are commonly used for the immobilization of different biofunctional moieties to a surface. We are particularly interested in studying amine-functionalized alkanethiol SAMs, since amine group functionalization is important for a variety of applications ranging from bioassays to capture agents for the removal of carbon dioxide from flue gases.^{2,5,17,18} Surface-enhanced Raman spectroscopy studies of amine-functionalized alkanethiol SAMs on metals are essentially limited to 2-aminoethanethiol (cysteamine, CEA), which is the shortest stable amine alkanethiol. Figure 1 shows conformations of carbon C2 of the CEA SAM, suggested by Kudelski and co-workers, in a series of SERS studies on roughened silver electrodes.¹⁹ The surface selection rules of molecules on silver surfaces have been described as having larger enhancements in the direction perpendicular to the surface, in this case the z -direction (Figure 1), for molecules with a vibration symmetry along the z -direction and for excitation wavelengths red-shifted from the surface plasmon resonance.^{11,20} Based on these surface selection rules, the characteristics of the C–C and CH₂ stretching vibration intensities, excited with a near-infrared laser, were used to deduce the CEA conformations.

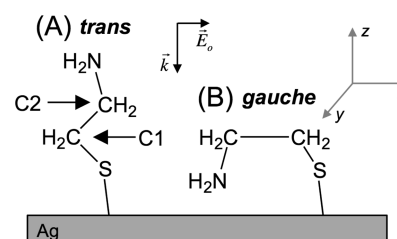


Figure 1. Suggested CEA SAM ($\text{Ag-S-CH}_2\text{-CH}_2\text{-NH}_2$) conformations of carbon C2.¹⁹ (A) trans and (B) gauche. The excitation laser polarization is shown with respect to the Ag surface.

Based on the position of the C–S stretching vibration in the SERS spectrum, the conformation of the C–C–S chain can be determined. A ratio of trans conformation intensity to gauche conformation intensity $\kappa_{T/G}$ is used as a quantitative metric to assess the degree of order in the SAM. The formation and structure of CEA SAMs on silver was compared with the SAM formation on gold,^{21,22} and studies that solely focused on the self-assembly of CEA on other metals, such as gold or copper, have been reported.^{23–27} It was reported that $\kappa_{T/G} \approx 1$, for CEA SAMs on gold surfaces, and $\kappa_{T/G} \geq 2$ on silver surfaces, and the difference was attributed to a greater affinity between the amine terminal-group and the gold surface.²¹ The self-assembly conditions, such as the CEA concentration, incubation time, and the amount of surface adsorbed ions, were varied and found to influence the surface conformation of the Ag-thiolates.^{19,28} The conformation of the surface thiolates can also be influenced by the exposure of the SAM to different ambient surroundings and conditions, such as storage in water, treatment with different electrolytes, as well as pH and applied potential.^{19,28,29} The formation of mixed SAMs of CEA and 3-mercaptopropionic acid, and 2-mercaptoethanesulfonate, were investigated under varying conditions.^{30,31} Kudelski et al. additionally investigated the coverage integrity of CEA SAMs on silver after exposure to different peptides through the observation of SERS spectral changes.^{32,33}

Amine alkanethiols with longer spacer length, such as 11-aminoundecanethiol (AUT), are commonly used as linking layers for the binding of species to surface plasmon resonance (SPR) biosensors,³⁴ SERS-active structures,^{35–37} and as separation layers.^{38,39} The longer chain SAMs are important for applications that require increased separation between the surface and functional moiety. However, no SERS spectra of pure 11-aminoundecanethiol SAMs have been reported. Yonzon et al. reported spectra of a mixed AUT SAM, but did not explain the spectral details.³⁵ In this article, we use Ag-NWG substrates as a spectroscopy tool for studying CEA and AUT SAMs. We use a similar approach as Kudelski et al.¹⁹ and probe the conformation of carbon C2 (Figures 1 and 2). However, with the Ag-NWG surfaces the enhancement of the perpendicular component of the vibration symmetry is larger than the parallel components in the nanogap regions between adjacent nanowires, which is the source of the majority of the Raman scattered signal.²⁰ We confirm formation of the SAM under different assembly conditions and compare the surface conformation and amine terminal-group availability of both CEA and AUT SAMs. Raman images, which consist of a collection of spectra measured from a two-dimensional area of the SERS-active surface, are used to compare the CEA and AUT SAMs using both spatially resolved data consisting of hundreds of individual spectra and from spatially averaged data.

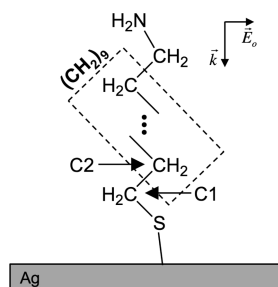


Figure 2. AUT SAM ($\text{Ag-S-CH}_2(\text{CH}_2)_9\text{CH}_2\text{-NH}_2$).

The defect structure in these films is evaluated using the integrated intensity ratio $\kappa_{\text{T/G}}$ of bands due to trans and gauche conformations in $\nu(\text{C-S})$ spectral region.

EXPERIMENTAL METHODS

Materials and Chemicals. The polycrystalline Ag layers were deposited using conventional electron beam evaporation (Balzers, BAK 600) at a pressure of 10^{-6} mbar and 0.2 nm s^{-1} deposition rate. Immediately before the evaporation, an in situ oxygen plasma cleaning step was performed (typically: 200 mA glow discharge current, 180 s). Benzenethiol (BT, Aldrich), 2-aminoethanethiol hydrochloride (CEA, Aldrich), and 11-aminoundecanethiol hydrochloride (AUT, Dojindo) were used as received. Water purified ($18 \text{ M}\Omega \text{ cm}$) with an ultrapure water system (Milli-Q, Millipore) and ethanol (99.8%, Assink Chemie) were used as solvents. The Ag layers were removed using a commercial etchant (Chrome Etch 1, Technic France). Surfaces were cleaned using a combination of 3:1 Piranha solution ($\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) and UV ozone treatment (UV/Ozone ProCleaner Plus, Bioforce Nanosciences).

SERS Substrate Fabrication. The SERS substrate fabrication procedure has been previously reported.¹⁴ Briefly, a silicon nitride (SiN) layer is first deposited on (100) silicon (Si) wafers and subsequently patterned with electron-beam lithography and etched using reactive ion etching. The nanopatterned SiN layer is used as a mask for plane-dependent etching the underlying Si layer, which forms triangular-shaped undercut regions. This structure is used as a template for the deposition of the Ag layer using electron-beam evaporation with thicknesses in the range of 60–70 nm. The nanopatterned SiN templates can be reprocessed multiple times after the selective removal of the Ag layer (2 min.). Following the removal of the Ag layer, the surfaces are cleaned using a combination of immersion in Piranha solution (15 min.) and subsequent rinsing with ultrapure water and blow-drying with N_2 , and a UV ozone treatment (20 min.). After the cleaning step, a new Ag was deposited as previously described.

Scanning Electron Microscopy Imaging. High resolution scanning electron microscopy (SEM) imaging (Zeiss MERLIN) was performed to visualize the surface structure and determine the nanogap dimensions between adjacent nanowires.

Atomic Force Microscopy Imaging. A Digital Instruments Dimension 3100 was used in tapping mode with ultra sharp (average tip diameter $\sim 2 \text{ nm}$) single crystal silicon tips (SSH-NCH-10, NanoandMore, GmbH) for all recorded AFM images.

Reflectance Measurements. Reflectance spectra of the Ag-NWG substrates were measured in a normal incidence configuration with a p-polarized (LPVISB100, Applied Laser

Technology) white light source (100W W-halogen lamp, HLX 6462S, Osram). The Ag-NWG substrate was aligned with the source polarization such that the length of the nanogaps and the polarization plane are perpendicular; this results in the maximum surface plasmon resonance. The light was focused onto the Ag-NWG substrate with a microscope objective ($10 \times /0.3 \text{ NA}$, Leica) and the reflected light was collected through the same objective and coupled to a spectrometer (HR4000, Ocean Optics) with a multimode fiber (QP450-1-XSR, Ocean Optics). Reference measurements were recorded from an unpatterned as-deposited Ag layer.

Raman Instrumentation. A confocal Raman microscope (alpha300R, WiTec GmbH) was used for all Raman measurements. The system consists of a frequency doubled Nd:YAG laser ($\lambda_0 = 532 \text{ nm}$), $f/4$ 300 mm focal length spectrometer with 600 lines mm^{-1} grating that is imaged onto a cooled CCD camera (DU970P-BV, Andor Technology). The laser is focused onto the sample surface with a microscope objective ($100 \times /0.9 \text{ NA}$ or $20 \times /0.4 \text{ NA}$) in a backscatter configuration. Elastically scattered laser light is removed with an edge filter and the laser polarization is aligned perpendicular to the length of the nanogaps by manual rotation of a $\lambda/2$ rotator phase plate. The spectrometer is calibrated with the first order Raman scattering band of silicon (520 cm^{-1}) sample prior to each experiment. The laser power is measured at the entrance of the microscope objective.

Monolayer preparation. All SAMs were formed on the SERS substrates with freshly deposited Ag layers. Reflectance spectra of SERS substrates were measured before and after the chemisorption of a SAM in order to confirm the position of the surface plasmon resonance wavelength. BT SAMs were formed on the Ag-NWG substrates by immersion into 4 mM BT-ethanol solutions for 3 h, and subsequently rinsed with ethanol and dried in air. The alkanethiol SAMs were formed on Ag-NWG substrates by immersion in 4 mM ethanolic (or aqueous) solutions of either CEA or AUT overnight (or for 2 h), and subsequently rinsed with ethanol (or water) and left to dry in air.

Raman Measurements. Reference Raman spectra were measured for all three molecules using conventional Raman scattering measurements. Raman spectra were measured from neat BT sealed in a glass vial. Raman spectra of CEA were measured from a 1 M aqueous solution and the spectra of AUT were measured from a solid sample. A laser power of 20 mW, integration time of 5 s, and $100 \times /0.9 \text{ NA}$ microscope objective were used for all conventional Raman reference measurements. Prior to the SERS measurements, the surface plasmon resonance wavelength of the SERS substrate was spectrally tuned to within a few percent of the excitation wavelength of the laser source (532 nm) by controlling the thickness of the Ag layer, which ensures maximum optical coupling and electromagnetic field enhancement in the nanogap regions. A reflectance spectrum of each SERS substrate was also measured after the chemisorption of the SAM. Raman imaging of the chemisorbed BT was performed with a laser power of 0.8 mW and 0.1 s integration time for each measurement over a surface area of $400 \mu\text{m}^2$ (3600 spectra, $100 \times /0.9 \text{ NA}$ microscope objective). Raman imaging of CEA SAMs was performed with a laser power of 0.5 mW and a 0.1 s integration time per measurement over a surface area of $400 \mu\text{m}^2$ (1600 spectra, $100 \times /0.9 \text{ NA}$ microscope objective). Raman imaging of AUT SAMs was performed with a laser power of 2 mW and a 0.1 s integration time per measurement

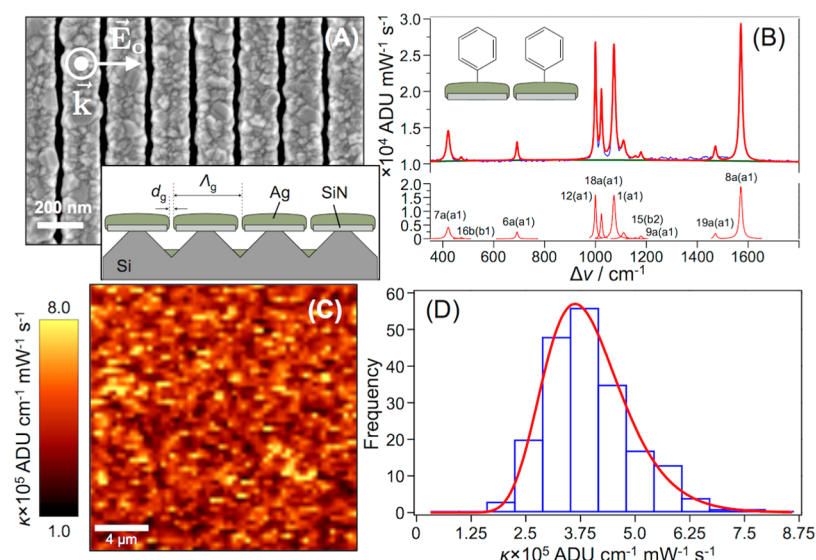


Figure 3. Ag-NWG substrates. (A) SEM image of typical surface. Inset: cartoon of the surface cross-section (inset: excitation laser polarization). (B) Typical BT-Ag SERS spectrum (the blue trace is the experimental data, the red trace is the modeled data, and the green trace corresponds to the modeled background). The bottom part shows the bands obtained from the modeling procedure. Inset: Schematic BT SAM. (C) Raman image of the integrated intensities κ_i of the $8a(a_1)$, $\nu(C-C)$ vibration over the imaged region. (D) Histogram of the distribution of κ_i ($n = 200$) of the $8a(a_1)$, $\nu(C-C)$ vibration mode over the imaged region.

over a surface area of $3600 \mu\text{m}^2$ (900 spectra, $20 \times /0.4$ NA microscope objective), and with a laser power of 0.1 mW and 0.5 s integration time per measurement over a surface area of $400 \mu\text{m}^2$ (1600 spectra, $100 \times /0.9$ NA microscope objective) for layers deposited from ethanolic and aqueous solutions, respectively.

Data Processing. A two-dimensional Raman image consists of N spectra measured over an area of the SERS surface where each measurement contains a Raman spectrum from a particular location (x_i, y_i) , $i = 1, 2, \dots, N$. Each measurement contains a single average Raman spectrum from all molecules in the optical collection volume. Raman image data was analyzed by spectral modeling. Vibration bands of the SAMs and silicon substrate were modeled with Lorentzian and Gaussian band shapes, respectively, after subtraction of the background using a cubic polynomial function. The modeled data includes the center locations of the Raman shift $\Delta\nu_i$, and the integrated intensity κ_i of each band. The integrated intensity is normalized with the laser power and integration time and is presented in units of $\text{ADU cm}^{-1} \text{mW}^{-1} \text{s}^{-1}$, where ADU is analogue digital units of the CCD camera. The labels γ , β , and ν indicate out-of-plane bending, in-plane bending, and stretching modes, respectively. For the BT SERS measurements, the modeling procedure was used over the entire spectral range of the instrument ($0\text{--}3700 \text{ cm}^{-1}$). For the CEA and AUT SAMs, modeling was performed in a stepwise manner in order to optimize the fitting procedure and the frequency ranges of $500\text{--}900 \text{ cm}^{-1}$, $800\text{--}1800 \text{ cm}^{-1}$, and $2700\text{--}3100 \text{ cm}^{-1}$ were modeled independently in each spectrum. CEA and AUT SAM Raman image data was analyzed by modeling a spatially averaged spectrum of all measurements across each imaged area, and by modeling single measurements from a subset of 180 spectra from the total number of N measurements distributed across the imaged region. Modeled results from the spatially averaged and single spectral analyses are compared. The data were processed using WiTec Project (WiTec, GmbH), IGOR Pro (WaveMetrics) and some in-house data reduction programs.

Enhancement Factor. The mean and variance of the spatially averaged SERS enhancement factor are estimated from measurements of BT SAMs on Ag-NWG surfaces ($\Lambda_g = 200 \text{ nm}$) and liquid neat BT. Since SERS is used for surface-enhanced Raman spectroscopy, the analytical enhancement factor for a specific vibrational mode at each measurement location (x_i, y_i) is estimated with $\Gamma_i \approx (\kappa_i/N_{\text{SERS}})(\kappa_{\text{CR}}/N_{\text{CR}})^{-1}$, where κ_i and κ_{CR} are the integrated intensities from the SERS and conventional Raman measurements, respectively. N_{SERS} and N_{CR} are the number of molecules in the collection volume of each measurement, respectively. It should be noted that N_{SERS} is estimated from a monolayer on the SERS substrate surface. 200 SERS spectra from a Raman image were modeled using Lorentzian peak shapes and a cubic polynomial function for background subtraction. The κ_i of the $8a(a_1)$, $\nu(C-C)$ band (1571 cm^{-1}) was estimated for each of the i measurements using modeled bands. The number of molecules within the collection volumes for each measurement is $N_{\text{SERS}} \approx 3 \times 10^6$ molecules and $N_{\text{CR}} \approx 9 \times 10^9$ molecules, as previously described.^{6,14}

RESULTS AND DISCUSSION

SERS Substrates. SERS enables Raman surface spectroscopy of molecules that are attached or adsorbed in close proximity to the SERS substrate surface. Raman surface spectroscopy relies on the capability of the nanostructured metal surface to couple the excitation light of a particular frequency into surface plasmon modes, which generates large electromagnetic field enhancements and the resulting enhanced Raman scattering. For the evaluation of the SERS substrates it is convenient to use a SAM that has a uniform surface coverage with surface density $\sim 10^{14} \text{ molecules cm}^{-2}$ and a terminal group with a large scattering cross-section. The quality of a SERS substrate can be evaluated based on the spatial average $\bar{\Gamma}$ and variance s_{Γ}^2 of the analytical enhancement factor of a particular vibration mode, which are estimated from the modeled spectra of the Raman measurement over two-dimensional regions of the surface. The spatially averaged

enhancement factor $\bar{\Gamma}$ is an indication of the magnitude of the electromagnetic enhancement in the nanogap and the nanogap surface density. The magnitude of the electromagnetic field enhancement g is also related to the proximity of the surface plasmon resonance wavelength to the laser excitation and molecular scattering wavelengths, as well as the alignment of the excitation polarization to the nanogap structure.

The spatial variance s_r^{-2} is an indication of the uniformity of electromagnetic field enhancement across the imaged region, which is related to the reproducibility of the manufacturing method. Figure 3A shows a SEM image of the top view of an Ag-NWG surface with pitch $\Lambda_g = 200$ and 62 nm thick Ag layer, with inset showing the excitation laser polarization with respect to the nanogap orientation. The nanogap spacing between adjacent nanowires (black regions in Figure 3A) is $d_g \leq 20$ nm.

The Ag-NWG surfaces are evaluated by measuring Raman images of the BT chemisorbed on the Ag surface. Figure 3B shows an example of a BT SERS Raman spectrum measured with a 0.8 mW laser power and 0.1 s integration time. The BT spectra were modeled with a cubic polynomial for the background and Lorentzian shape functions for the spectral bands. The blue trace is the experimental data, the red trace is the modeled data, and the green trace corresponds to the modeled background. The Raman vibration bands are observed at $7a_1$, $\nu(C-S) + \beta(C-C-C)$ (421 cm^{-1}); $16b(b_1)$, $\gamma(C-C-C)$ (473 cm^{-1}); $6a(a_1)$, $\beta(C-C-C) + \nu(C-S)$ (692 cm^{-1}); $12(a_1)$, $\beta(C-C-C)$ (1000 cm^{-1}); $18a(a_1)$, $\beta(C-H)$ (1023 cm^{-1}); $1(a_1)$, $\beta(C-C-C) + \nu(C-S)$ (1073 cm^{-1}); $15(b_2)$, $\beta(C-H)$ (1157 cm^{-1}); $9a(a_1)$, $\beta(C-H)$ (1178 cm^{-1}); $19a(a_1)$, $\nu(C-C)$ (1471 cm^{-1}); $8a(a_1)$, $\nu(C-C)$ (1571 cm^{-1}); and $2(a_1)$ $\nu(C-H)$ (3048 cm^{-1} ; not shown), which are in agreement with previous assignments.^{15,40,41} Figure 3C shows a Raman image of the spatial dependence of the integrated intensities κ_i of the $8a(a_1)$, $\nu(C-C)$ mode over a two-dimensional imaged region. Since the Raman images are difficult to interpret quantitatively, 200 spectra, sampled from the Raman image areal data, distributed across the entire surface were modeled and used to estimate the spatial distribution of the κ_i of the $8a(a_1)$ band over the imaged region and is shown in the histogram of Figure 3D. The integrated intensity of the $8a(a_1)$ band follows a log-normal distribution over the imaged region with an average value of $\bar{\kappa} \approx 3.9 \times 10^5\text{ ADU cm}^{-1}\text{ mW}^{-1}\text{ s}^{-1}$ and a standard deviation of about $s_\kappa \approx 1.2 \times 10^5\text{ ADU cm}^{-1}\text{ mW}^{-1}\text{ s}^{-1}$. Comparing this value with the integrated intensity obtained from a conventional Raman spectrum of a neat BT solution results in a spatially averaged Raman enhancement $\bar{\Gamma} \approx 1.2 \times 10^7$, which is extremely large considering that the estimation includes all BT molecules immobilized on the entire surface within the spot size of the microscope objective, while it is known that only molecules in the nanogap regions provide the majority of the measured signal. In this case, the nanowire and pitch dimensions are chosen such that the surface plasmon resonance is spectrally tuned to match the laser excitation wavelength, i.e., 532 nm (Figure S1, Supporting Information). The m-NWG surfaces also provide a convenient means for controlling the alignment of the excitation polarization state to the nanogap structure, thus providing optimal electromagnetic field enhancement. The as-deposited Ag surfaces have a measured RMS surface roughness of 5.2 nm (Figure S2, Supporting Information). The as-deposited Ag layers do not generate any electromagnetic enhancement; this is demonstrated using Raman scattering measurements from BT SAM chemisorbed

on an unpatterned as-deposited Ag layer in which no detectable vibration bands are present in the spectrum (Figure S3, Supporting Information). The SERS enhancement is generated in the nanogap regions between adjacent nanowires, and only when the excitation laser polarization is aligned perpendicular to the length of the nanogap (Figure 3A), as reported in our previous work with Au-NWG surfaces.¹⁴

An important consequence of using SERS surfaces with a large enhancement factor is that the excitation laser power and integration time must be carefully balanced due to the extremely large electromagnetic fields that are generated in the nanogap regions. For example, a laser power of 1 mW focused to a spot size with 1 μm radius and an intensity enhancement of $M \approx 10^4$ results in a local field intensity of about 320 MW cm^{-2} . Therefore, destruction of the sample must be avoided while simultaneously generating a reasonable signal-to-noise ratio, which can be particularly challenging for analytes with a small Raman scattering cross-section.⁴²

Surface Selection Rules. SERS results from molecules positioned in the enhanced electric near-field at the interface between the metal nanostructure and the surrounding dielectric medium. The surface selection rules of a vibration system, composed of an adsorbed molecule on a metal surface, define the vibrations that have zero composite transition dipoles parallel to the surface and the transition dipoles of vibrations perpendicular to the surface that are supported in the molecule-metal system.²⁰ Assuming that a single nanowire has an ideal cylindrical cross-section with radius a and length $L \gg a$, which is uniformly polarized in the x -direction using the electrostatic approximation where $\lambda_0 \gg a$ (Figure 4A),⁴³ the electric near-

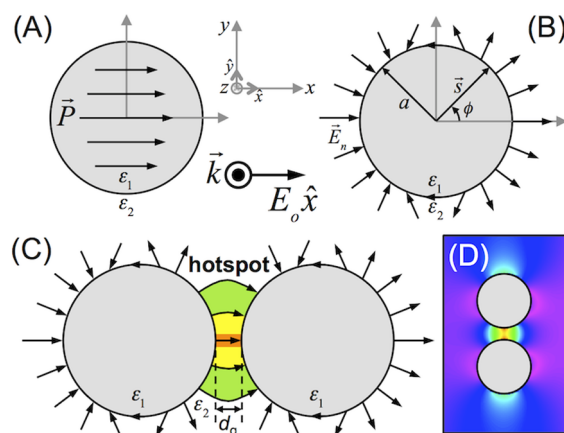


Figure 4. Polarization and electric field characteristics of cylindrical nanowire using the electrostatic approximation. (A) Uniform polarization of a single nanowire in the electrostatic approximation. (B) Electric near-field profile of a single nanowire generated by polarization. (C) Electric near-field profile and hotspot region of a nanowire dimer. (D) Simulated electric near-field profile of a nanowire dimer with $d_g = 10$ nm.

field due to the polarization at the surface, i.e., $r = a$, is $\vec{E}_n(\hat{s}, \omega) = (2\epsilon_2\epsilon_0)^{-1}[(\vec{P} \cdot \hat{s})\hat{s} - \vec{P}]$, where ϵ_2 is the permittivity of the surrounding dielectric medium, ϵ_0 is the vacuum permittivity, \vec{P} is the polarization of the nanowire, and \hat{s} is the radial unit vector of the cylindrical coordinates. The polarization is $\vec{P} = 2\epsilon_2\epsilon_0 g(\omega) \vec{E}_0$, where $g(\omega) = (\epsilon_1(\omega) - \epsilon_2)(\epsilon_1(\omega) + \epsilon_2)^{-1}$ is the electromagnetic enhancement factor, $\epsilon_1(\omega)$ is the frequency dependent dielectric function of the metal, and \vec{E}_0 is the excitation electric field. Therefore, the electric near-field

generated by the polarized nanowire is $\vec{E}_n = -g(\omega)E_0\hat{x} + 2g(\omega)E_0\cos\phi\hat{s}$, where \hat{x} is the x -direction unit vector (Figure 4). The total electric field outside the nanowire and at the surface ($r=a$) is $\vec{E}_2 = \vec{E}_0 + \vec{E}_n = (1 - g(\omega))E_0\hat{x} + 2g(\omega)E_0\cos\phi\hat{s}$, which is shown graphically in Figure 4B with the \vec{E}_n electric field lines at the nanowire surface. The intensity enhancement factor is defined as $M(\phi, \omega) = |\vec{E}_2(\vec{s}, \omega)|^2/|\vec{E}_0|^2$. The enhancement factor can be expressed as $M(\phi, \omega) = M^\perp + M^\parallel$, where $M^\perp = (1 + g(\omega))^2\cos^2\phi$ and $M^\parallel = (1 - g(\omega))^2\sin^2\phi$ are perpendicular and parallel to the nanowire surface, respectively. The perpendicular and parallel components of the enhancement factor are important for assessing the surface selection rules and spectral analyses. The total enhancement is $M(\phi, \omega) = (1 + g(\omega))^2\cos^2\phi + (1 - g(\omega))^2\sin^2\phi$, which indicates that the maximum enhancement perpendicular to the surface occurs is $M(\phi = 0, \omega) = (1 + g(\omega))^2$, where the parallel component of the electric field is zero, and the maximum enhancement parallel to the surface occurs is $M(\phi = \pi/2, \omega) = (1 - g(\omega))^2$, where the perpendicular component of the electric field is ideally zero. The orientation of molecules adsorbed uniformly over the surface leads to an average enhancement of the nanowire surface where the perpendicular and parallel components provide approximately the same contribution, in contrast to a spherical nanoparticle. The corresponding Raman scattering enhancement is $G = [M(\omega_o)][M(\omega_s)]$, where ω_o and ω_s are the frequencies of the incident and scattered radiation, respectively. The maximum Raman enhancement of a single nanowire is $G_{\max} \propto (1 + g(\omega_o))^2(1 + g(\omega_s))^2$, which occurs at $x = a$ and $y = 0$ along the z -axis of the nanowire (Figure 4B) and is about 16 \times smaller than the maximum enhancement produced by a spherical nanoparticle.¹¹

When two metal nanowires are positioned in close proximity to each other, the electric near-field generated by one nanowire interacts with the electric near-field of the other nanowire. Therefore, the total excitation electric field on a nanowire is a combination of the incident electric field and the electric near-field of the adjacent nanowire; the nanowire dimer excitation is $\vec{E}_0 + \vec{E}_n$. This near-field interaction results in a red-shifted coupled plasmon resonance and an increased electric near-field magnitude in the nanogap region between the adjacent nanowires, compared to a single nanowire. The electric near-field is drastically modified when the nanogap dimensions are reduced to the nanometer scale. Nanogaps with $d_g \leq 20$ nm are called hotspots due the large electric near-field enhancement generation induced by the coupled plasmon resonance, as shown in the illustration of a nanowire-dimer pair in Figure 4C. Figure 4D shows an example of a simulated electric near-field profile showing the hotspot region located in the junction between parallel nanowires, where the red region of the hotspot can generate $M \sim 10^4$.⁴⁴

The coupled plasmon resonances have important consequences for surface enhanced Raman scattering of molecules adsorbed on the m-NWG surfaces. Since the electromagnetic field enhancement in the hotspot region is orders of magnitude larger than an enhancement generated by an isolated nanostructure, the measured signal is comprised largely from the scattering of molecules located in the hotspot region (Figure 4C), where the electric field perpendicular to the surface is highly amplified. For molecules located in the nanogap region, a vibration with symmetry perpendicular to the surface will be enhanced to a greater extent compared to a vibration with symmetry parallel to the surface. The validity of this assertion can be assessed using a BT SAM on the Ag-NWG

surface, since the BT-Ag SAM surface density and orientation are well established.^{6,12} BT belongs to the C_{2v} point group and is composed of a_1 , a_2 , b_1 , and b_2 vibration mode symmetries that are distributed as $11a_1 + 10b_2 + 3a_2 + 6b_1$.⁴⁰ The a_1 modes are composed of a linear combination of α_{xx} and α_{yy} , oriented parallel to the surface, and α_{zz} , which is oriented perpendicular to the surface, where α_{ij} are components of the polarizability tensor $\vec{\alpha}$ with excitation polarization state i and induced molecular polarization state j . Note that in this case x and y represent orientations parallel to the surface and z represents an orientation perpendicular to the surface (Figure 4).

From the Raman spectra measured from BT SAMs chemisorbed on the Ag-NWG surfaces (Figure 3B), 12 vibration modes are resolved compared to 14 vibration modes observed from the conventional Raman scattering measurements from a neat BT sample. Table 1 summarizes the

Table 1. Summary of SERS BT Measurements^a

mode assignments	neat BT $\Delta\nu$ / cm ⁻¹	neat BT NII	SERS BT/ Ag $\Delta\nu$ / cm ⁻¹	SERS BT/Ag NII
7a(a_1), $\nu(C-S)+\beta(C-C-C)$	414	0.37	421	0.49
16b(b_1), $\gamma(C-C-C)$	484	0.12	473	0.04
6b(b_2), $\beta(C-C-C)+\nu(C-S)$	619	0.11		
6a(a_1), $\beta(C-C-C)+\nu(C-S)$	701	0.21	691	0.22
$\beta(S-H)$	917	0.26		
12(a_1), $\beta(C-C-C)$	1003	1.0	1000	1.00
18a(a_1), $\beta(C-H)$	1027	0.26	1023	0.59
1(a_1), $\beta(C-C-C)+\nu(C-S)$	1095	0.27	1073	1.59
6a(a_1)+7a(a_1), ($\beta(C-C-C)+\nu(C-S)+\beta(C-C-C)$)	1120	0.13	1111	0.28
15(b_2), $\beta(C-H)$	1159	0.10	1157	0.04
9a(a_1), $\beta(C-H)$	1184	0.05	1178	0.09
19a(a_1), $\nu(C-C)$			1471	0.15
8a(a_1), $\nu(C-C)$	1586	0.44	1571	1.82
$\nu(S-H)$	2568	0.89		
2(a_1), $\nu(C-H)$	3058	0.98	3047	0.36

^aMode assignments are from Varsanyi.⁴⁰ NII is the integrated intensity normalized to the integrated intensity of the 12(a_1) vibration. Each vibration mode is listed according to the Wilson numbering scheme and the symmetry is indicated in parentheses. Labels γ , β and ν indicate out-of-plane bending, in-plane bending and stretching modes, respectively.

BT measurements where the integrated intensities of each band have been normalized with the 12(a_1) mode intensity, which is not influenced by the $\nu(C-S)$ vibration.¹²

Nine of the resolved modes have a_1 symmetry, which results from the large enhancement perpendicular to the surface in the hotspot region. The a_2 symmetry modes are weak in benzene and its derivatives,⁴⁰ and are not observed in either the conventional Raman or the SERS measurements. Additionally, the a_2 symmetry vibrations are least enhanced for BT oriented perpendicular to the surface.¹¹ The b_1 modes are composed of the α_{xz} component and b_2 modes contain the α_{yz} component. Very weak 16b(b_1) and 15(b_2) modes have been resolved in the SERS measurements. Since the b_1 and b_2 modes result from vibrations parallel to the surface that are excited with a perpendicular field their integrated intensities are very weak and at least an order of magnitude smaller than any of the resolved a_1 vibration modes (Table 1). The fact that the integrated intensities of the 16b(b_1) and 15(b_2) modes are similar in

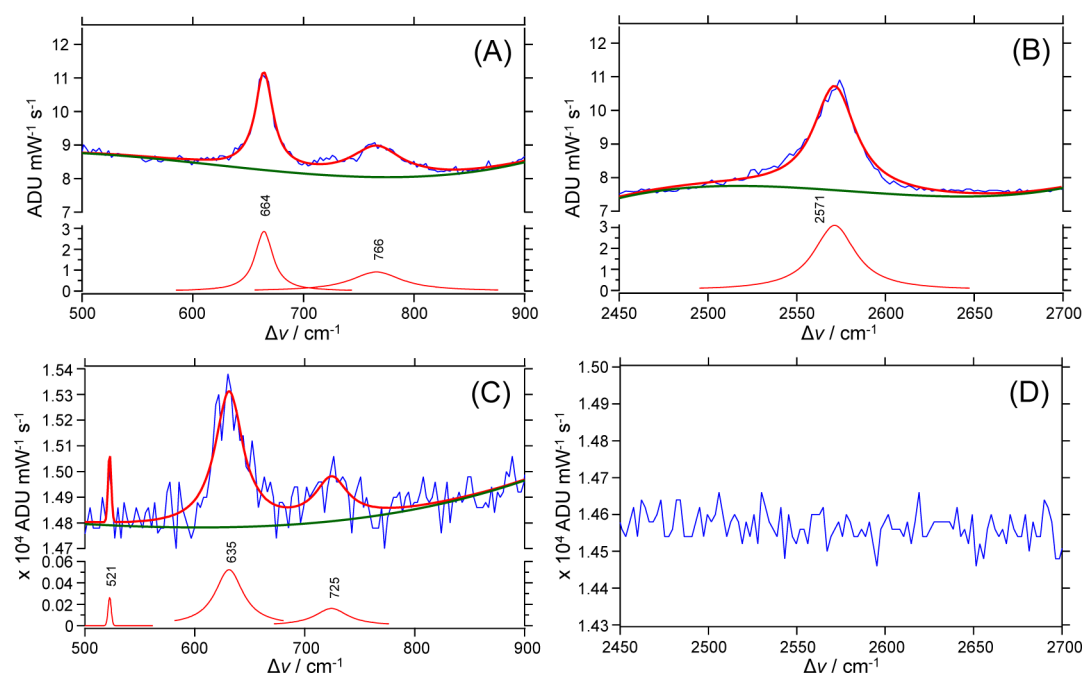


Figure 5. CEA and Ag-thiolate formation. (A, B) Raman spectra of a 1 M CEA solution and (C, D) SERS spectra of a CEA SAM formed on an Ag-NWG surface (overnight immersion in ethanol solution). Blue traces represent the raw measured spectra from a single measurement location, the red traces the modeled bands, and the green traces correspond to the modeled background. The bottom parts of the plots in (A–C) show the modeled bands.

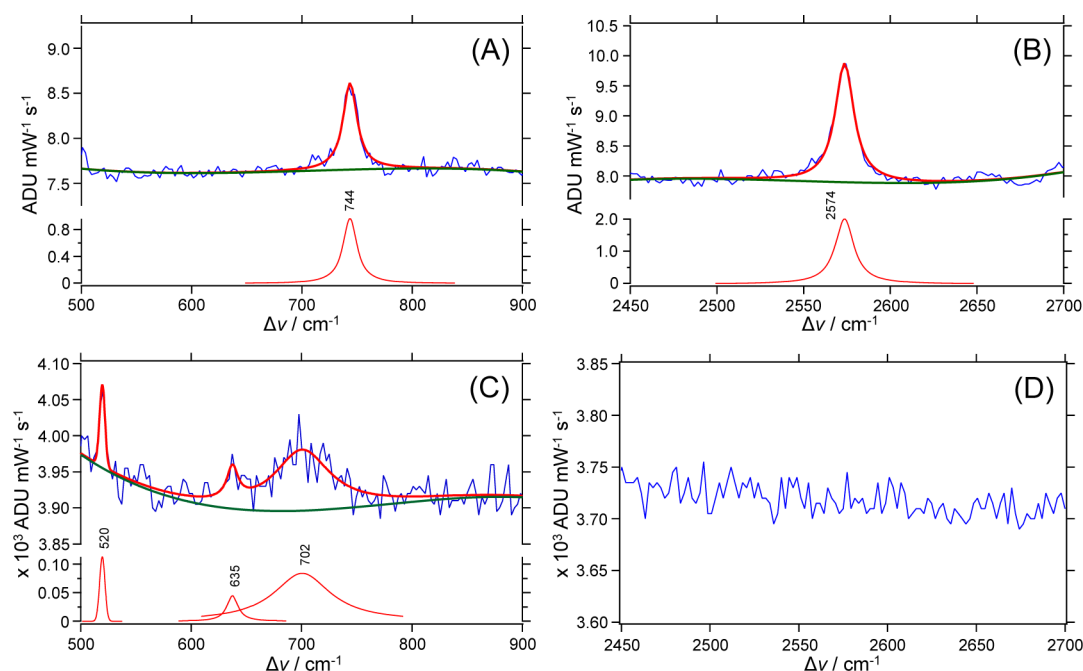


Figure 6. AUT and Ag-thiolate formation. (A, B) Raman spectra of solid AUT and (C, D) SERS spectra of an AUT SAM formed on an Ag-NWG surface (overnight immersion in ethanol). Blue traces represent the raw measured spectra from a single measurement location, the red traces are the modeled bands, and the green traces correspond to the modeled background. The bottom parts of the plots in panels A–C show the modeled bands.

magnitude indicates that the BT SAM is oriented perpendicular to the surface.^{11,15} Although the current results indicate that the BT SAM is oriented perpendicular to the Ag surface, the model to justify the surface selection rules is overly simplistic and for definitive assignment a more careful study is required that takes into account charge transfer effects, ambient surface conditions, and the surface roughness of the Ag layer. Another outstanding feature of this analysis is that modes $1(a_1)$ and $8a(a_1)$ from the

SERS measurements have much larger normalized ratios compared to the conventional Raman measurements. We attribute the increase of the $1(a_1)$ mode to the coupling of the $\nu(C-S)$ stretch with the $\beta(C-C-C)$ ring stretch, which is in close proximity to the surface. However, the integrated intensity of the $8a(a_1)$ mode is the largest of all the observed bands, which is in contrast to the conventional Raman measurements and from BT-Au SERS measurements.¹⁴

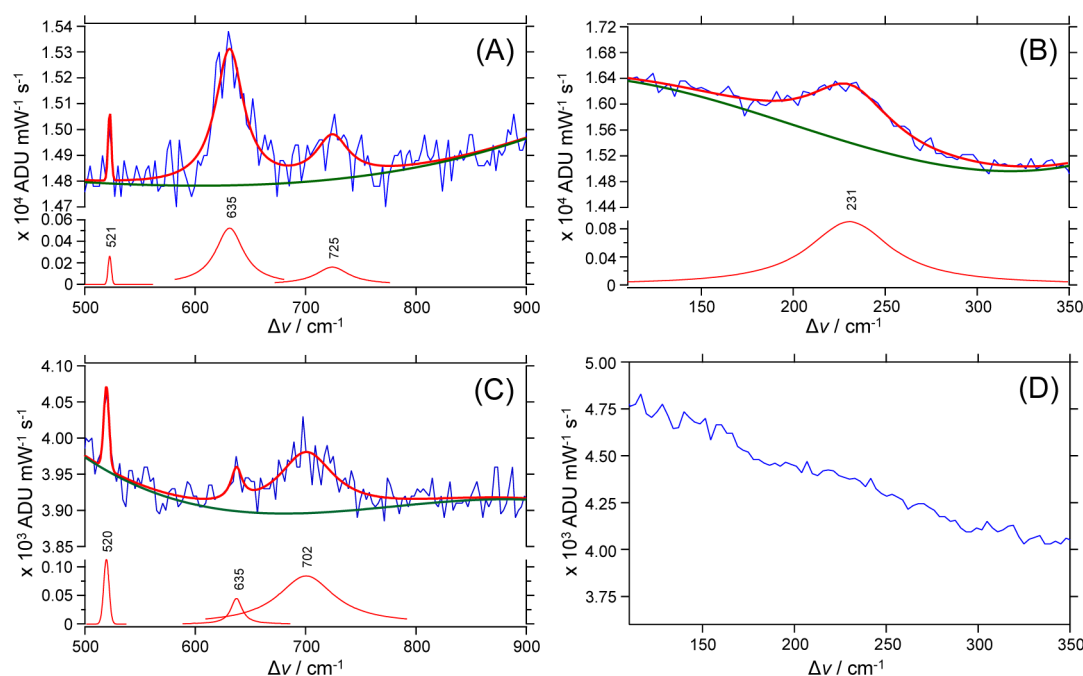


Figure 7. SERS spectra from SAMs on Ag-NWG surfaces. (A, B) CEA SAM and (C, D) AUT SAM (overnight immersion in ethanol solution of the corresponding thiol). Blue traces represent the raw measured spectra from a single measurement location, the red traces are the modeled bands, and the green traces correspond to the modeled background. The bottom parts of the plots in panels A–C show the modeled bands.

Linear chain molecules with the length of the chain oriented perpendicular to the surface, such as alkanethiols, have a low degree of symmetry and in most cases all vibrational modes of adsorbed molecules have vibration mode components perpendicular to the surface.^{13,45} $\nu(\text{C-H})$ stretching vibrations have been reported to have a large component along the axis of vibration,⁴⁶ which was used as a basis to monitor the $\nu(\text{C-S})$ and $\nu(\text{C-C})$ stretching vibrations in order to assess the molecular orientation in either the *trans* and *gauche* conformations of carbon C2 (Figures 1 and 2) of the CEA and AUT SAMs.

CEA and AUT SAMs on Ag SERS Surfaces. Figure 5 shows two spectral regions of interest for the Raman spectra of a 1 M CEA solution (A, B) and CEA SAM formed on an Ag-NWG surface (C, D). For reference, the corresponding spectra with the full spectral range are included in the Supporting Information (Figure S4). The raw data is shown in the blue traces, the red traces correspond to the modeled vibration bands, and the green traces correspond to the modeled background. An immediately apparent difference between the Raman (Figure 5B) and SERS (Figure 5D) spectra is the absence of the strong band near 2571 cm^{-1} in the latter spectra, which has been previously assigned to the $\nu(\text{S-H})$ stretching vibration. The absence of this vibration band indicates the formation of an Ag-thiolate. Additionally, it is observed that the $\nu(\text{C-S})$ *gauche* and *trans* vibrational bands shift from 664 and 766 cm^{-1} (Figure 5A) to approximately 635 and 725 cm^{-1} (Figure 5C) for the SAM chemisorbed on the Ag. This energy increase has been attributed to a depletion of electron density from the C-S bond due to the binding of sulfur to the Ag surface.⁴⁵

Comparing the conventional Raman and SERS spectra of AUT shows a similar pattern with the disappearance of the $\nu(\text{S-H})$ stretching vibration at 2574 cm^{-1} (Figure 6B) upon formation of the Ag-thiolate (Figure 6D), as well as shifting of the $\nu(\text{C-S})$ vibration from 744 cm^{-1} (Figure 6A) to 702 cm^{-1}

(Figure 6C). Thus, it can be concluded that AUT binds well to the Ag surface. Measured Raman and SERS spectra of AUT over the full spectral range are shown in Figure S5 (Supporting Information). The vibration band at 520 cm^{-1} originates from first order Raman scattering of the silicon supporting substrate.⁴⁷

Surface Conformation. The surface confirmations of the CEA and AUT SAMs are first analyzed and compared using single measured spectra, which can be directly compared to previous reports, and then we complement the study by analyzing spectra imaged over a two-dimensional area. The frequency position of the $\nu(\text{C-S})$ stretching band is indicative of the position of carbon C2 (Figures 1 and 2) in the alkane chain with respect to the C-S bond. As such, it can be used to provide information about the ordering of the SAM. The degree of order in the vicinity of the C-S bond of the SAM can be quantified by calculation of the ratio of the integrated intensity of the *trans* (T) band to the *gauche* (G) band, $\kappa_{\text{T/G}} \equiv \kappa_{\text{T}}/\kappa_{\text{G}}$.⁴⁵ In the case of the CEA SAM, two bands can be observed in the spectral region of interest: a band at 635 cm^{-1} , which is due to a *gauche* conformation of the $-\text{C}-\text{C}-\text{S}-$ portion of the alkane chain, and a band at 725 cm^{-1} , which can be attributed to the *trans* conformation (Figure 7A). Clearly, $\kappa_{\text{T/G}} < 1$ for the $\nu(\text{C-S})$ band centered at 725 cm^{-1} , which indicates that the SAM is disordered and the alkane chains are largely oriented parallel to the surface. The SERS spectrum of the AUT SAM (Figure 7C) also shows two $\nu(\text{C-S})$ vibrational modes at 635 and 702 cm^{-1} , which correspond to *gauche* and *trans* conformations of carbon C2 neighboring the C-S bond, respectively. In this case, $\kappa_{\text{T/G}} > 1$, which indicates that there is an increased amount of ordering in the vicinity of the C-S bond when compared to the CEA SAM,⁴⁵ thus indicating that the terminal group is oriented more toward a perpendicular position with respect to the Ag surface.

However, it also has to be considered that AUT is a longer alkane chain than CEA. Using the $\nu(\text{C-S})$ mode as a

conformation probe only provides information about carbon C2 in the vicinity of the C–S bond. In the case of the CEA SAM, the alkane spacer chain consists of two CH₂ groups, and therefore, the C–S vibrational mode probes the conformation of the entire alkyl chain. In the AUT SAM, the position of the $\nu(\text{C–S})$ vibration may only give information about the conformation, or degree of order, within the lower portion of the alkane chain. Bryant and Pemberton studied 1-alkanethiols SAMs of different lengths, including 1-dodecanethiol, which is a CH₃-terminated equivalent of AUT.⁴⁵ They describe the order within the upper part of the alkane chain by investigating intensities of the $\nu(\text{C–C})$ trans and gauche vibrational bands that occur in the 1000–1300 cm^{−1} range. The measured spectra in our analysis do not reveal consistent spectroscopic signatures within the same frequency range due to a low signal-to-noise ratio. This may be an indication that the alkane chain is oriented perpendicular to the Ag surface where the C–C bonds in the upper part of the SAM are less enhanced due to their separation from the Ag surface.

It is known that amine terminal-groups can interact with metal surfaces.⁴⁸ For the CEA SAM, Kudelski and co-workers provided spectroscopic evidence of the Ag–N interaction by studying CEA SAMs on roughened Ag electrodes, where the measured vibrational band at 245 cm^{−1} was attributed to the Ag–N interaction and tentatively assigned to $\nu(\text{Ag–N})$.²⁹ This assignment also corresponds to other reported Ag–N band assignments, such as the $\nu(\text{Ag–N})$ mode at 230 cm^{−1} for pyridine.^{49,50} Interestingly, we also observe a vibrational band at 231 cm^{−1} in the SERS spectra of the CEA SAM formed on Ag (Figure 7B), whereas no spectral features can be observed in the spectra from the AUT SAM formed on Ag (Figure 7D), which provides further support that the AUT SAM is oriented perpendicular to the Ag surface. Spectra from hundreds of different measurement locations were modeled and an average value of the integrated intensity ratio was calculated. For the CEA SAM, $\kappa_{\text{T/G}} \approx 0.3$, which is smaller than a previously reported ratio of 0.6 for a CEA SAM on Ag.¹⁹ For the AUT SAM, the ratio of $\kappa_{\text{T/G}} \approx 6$ has a higher degree of order compared to the CEA SAM. Currently, there are no comparable studies of AUT SAMs in literature. Based on the observation of the Ag–N interaction, and the ordering of the alkane chains, we conclude that the amine terminal-groups are freely available in the case of AUT SAMs, whereas in the case of CEA SAMs they are not. This is an important consequence for applications requiring access to the terminal amine groups for further conjugation to biological moieties using conventional schemes, e.g., the activation of the amine group with a sulfo-succinimide-maleimide cyclohexane carboxylate cross-linker, or for applications requiring direct binding to target analytes, e.g., carbon dioxide. From these analyses, it is recommended that longer alkane chain SAMs are used when free access to the terminal functional group is required.

All SERS measurements of both monolayers chemisorbed on Ag-NWG surfaces have been recorded using a Raman imaging configuration. Since the electromagnetic enhancement of the Ag-NWG surfaces has a high degree of spatial uniformity, spatially averaged data is used to improve the signal-to-noise ratio of the measured spectra and for further analysis of the SAM conformation. The size of the imaged region and the chosen step size determine the total number of recorded spectra. Representative two-dimensional Raman images of the CEA SAM, in the gauche $\nu(\text{C–S})_{\text{G}}$ band region (580–680 cm^{−1}) and the AUT SAM in the trans $\nu(\text{C–S})_{\text{T}}$ band region

(660–760 cm^{−1}), formed on Ag-NWG surfaces are shown in Figure S6 (Supporting Information). In addition to the gauche and trans $\nu(\text{C–S})$ vibrations, symmetric and asymmetric CH₂ stretching vibrations are also observed in the spectra, and single measurement spectra are shown in the Supporting Information (Figures S7 and S8). Figure 8 shows spectra of vibrational

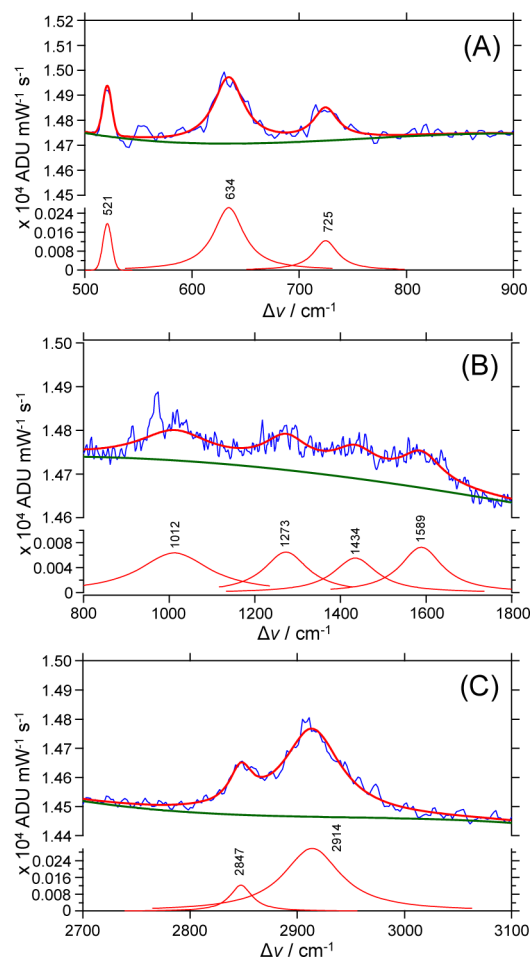


Figure 8. SERS spectra of a CEA SAM formed on an Ag-NWG surface (overnight self-assembly in ethanol solution). (A) 500–900 cm^{−1} spectral range, (B) 800–1800 cm^{−1} spectral range, and (C) 2700–3100 cm^{−1} spectral range. Blue traces represent the spatially averaged measured spectra, red traces the modeled bands, and the green traces correspond to the modeled background. The bottom parts of the plots show the modeled bands.

bands for a spatially averaged spectrum of CEA on an Ag-NWG surface. Spectral bands found in the 500–900 cm^{−1} (Figure 8A) and 2700–3100 cm^{−1} (Figure 8C) spectral regions occur at similar frequencies as bands found in the individual spectra analysis. All band frequencies determined through the fitting of averaged spectra lie within the standard deviation of the individual spectra analysis. Similarly, the average peak areas calculated from both measurements are comparable. Spatially averaged spectra provide a higher signal-to-noise ratio in the intermediate spectral range of 800–1800 cm^{−1} (Figure 8B) however did not have a consistent spectral signature in our measurements. The vibration frequencies, integrated intensities, and assignments obtained from the measured spectra of the CEA SAM on the Ag-NWG surface is summarized in Table S1 (Supporting Information). Figure 9 shows select spectral ranges

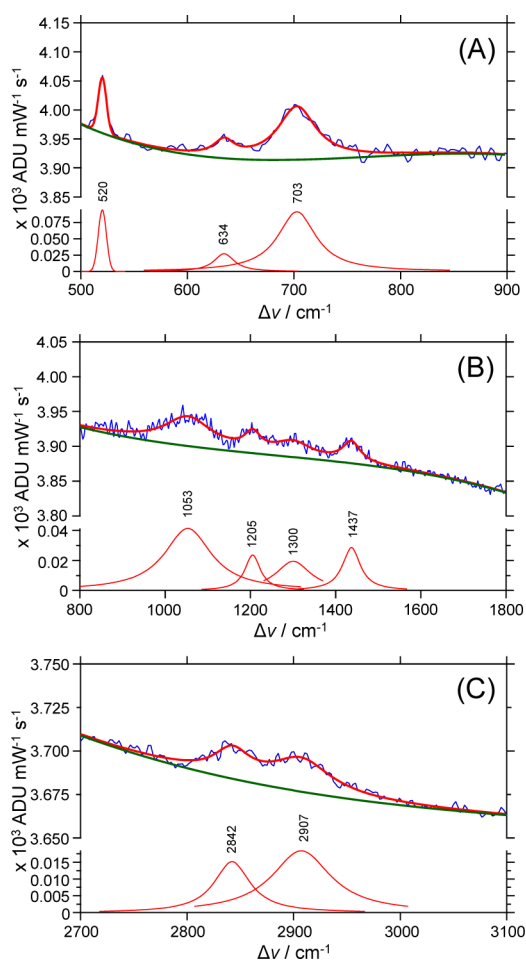


Figure 9. SERS spectra of an AUT SAM formed on an Ag-NWG surface (overnight immersion from ethanol solution). (A) 500–900 cm^{-1} spectral range, (B) 800–1800 cm^{-1} spectral range, and (C) 2700–3100 cm^{-1} spectral range. Blue traces represent the spatially averaged measured spectra, red traces the modeled bands, and green traces correspond to the modeled background. The bottom parts of the plots show the modeled bands.

of spatially averaged spectra obtained from the AUT SAM formed on the Ag-NWG surface. Spatially averaged spectra provide a reasonable signal-to-noise ratio; thus, bands in the intermediate spectral range (800–1800 cm^{-1}) can be resolved. Bands at 1053 and 1205 cm^{-1} are likely due to $\nu(\text{C}-\text{C})$ vibrations, whereas bands at 1300 and 1437 cm^{-1} can be assigned to CH_2 wagging and CH_2 deformation vibrations.^{45,51} The presence of these bands indicates that the AUT SAMs, in addition to being considerably more ordered in the lower part of the SAM compared to the CEA SAM, also have a high degree of order in the upper part of the SAM. This further supports the argument that the amine terminal-group is accessible in case of the AUT SAM, and illustrates a clear difference of alkane chain conformations between the two investigated SAMs.

The vibration frequencies, integrated intensities, and assignments obtained from the measured spectra of the AUT SAM on the Ag-NWG surface is summarized in Table S2 (Supporting Information). Similarly to the CEA SAM, spectral fitting was performed and match well between the analysis of individual and spatially averaged spectra.

Although the spatially averaged spectra provide a higher signal-to-noise ratio in the intermediate spectral range of 800–1800 cm^{-1} (Tables S2 and S3), the bands are very broad with relatively small peak intensity (Figures 8 and 9), thus definitive band assignments are not possible. For both SAMs, the results obtained from the analysis of individual spectra compare well with the spatially averaged spectra. This indicates that sampling a subset of individual spectra from a large data set provides representative data of the entire Raman image, which provides quantitative information on the enhancement distribution. Spatially averaged spectra enable faster data analysis over a larger area, however, can only be used if the SERS substrates have spatially uniform scattering enhancement.

CONCLUSIONS

The Ag-NWG SERS-active substrates have been used as a surface spectroscopy tool to probe the conformation of CEA and AUT SAMs on silver surfaces. Conformations of CEA and AUT SAMs on the surface are different, which has implications for the availability of the amine terminal-group. The SAM conformation is assessed by analyzing the amount of disorder that is revealed by the ratio of the integrated intensity of the trans to gauche position of the C–S bands. The amine terminal-group is more accessible in the case of the AUT SAM, which enables subsequent chemical modification of this group, thus linking of other species to the metal surfaces. Our results of CEA SAMs are consistent with previously reported SERS studies; however, we provide a more complete statistical analysis. The SERS analysis of the AUT SAM on Ag is new, and we find that longer alkane chain spacer layer, compared to the ECA SAM, resulted in perpendicular orientation of the alkane chain, thus resulting in an accessible amine terminal group. Our analyses also show that across the surface the layers are uniform as is evident in the provided statistical modeling data.

ASSOCIATED CONTENT

Supporting Information

Reflectance spectrum obtained from an Ag-NWG substrate. Full spectral ranges for representative Raman spectra of a 1 M aqueous CEA solution and a CEA SAM, Raman spectra of solid AUT and an AUT SAM, 2D Raman image of ADU sum of $\nu(\text{C}-\text{S})_{\text{G}}$ band of CEA SAM, 2D Raman image of ADU sum of $\nu(\text{C}-\text{S})_{\text{T}}$ band of AUT SAM, experimentally recorded and modeled CH_2 vibrational range of a CEA SAM, experimentally recorded and modeled CH_2 vibrational range of an AUT SAM, and summary of vibration frequencies, integrated intensities, and vibration assignment for CEA and AUT SAMs formed from 2h immersion of Ag-NWG substrates in aqueous CEA and AUT thiol solutions. Measured SERS spectra from CEA and AUT SAMs formed with variation of the self-assembly conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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