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**Nanoscale Vibrational Spectroscopy of Gold-Cyanide Self-Assemblies:
From Monolayers to Crystallites**

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Philosophy in Chemistry

by

Kristopher Kent Barr

2020

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ABSTRACT OF THE DISSERTATION

Nanoscale Vibrational Spectroscopy of Gold-Cyanide Self-Assemblies: From Monolayers to Crystallites

by

Kristopher Kent Barr

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2020

Professor Paul S. Weiss, Chair

My thesis work focuses on the integration of scanning tunneling microscopy with infrared spectroscopy, to provide unprecedented Ångstrom-scale resolution in surface imaging with spatially correlated chemical specificity. Scanning probe techniques generally lack chemical information. Inspired by recent advances coupling optical spectroscopies with scanning probe microscopies, I have developed a nanoscale infrared spectroscopic imaging method applying scanning tunneling microscope probe tips as nanoamplifiers to obtain multiplexed molecular vibrational signals utilizing a Fourier transform interferometer at room temperature and ambient pressure. The sensitivity of the tunneling junction and nanoscale probe area enables the measurement of vibrational spectra orders of magnitude below the diffraction limit. I substantiated the effectiveness of this instrument by designing an air- and temperature-stable model system characterized by infrared absorption that couples to the electronic states of the gold substrate. Specifically, aurous cyanide (AuCN) self-assembled monolayers satisfy these requirements with the added benefit that its IR absorption lies outside of the carbon dioxide and water windows, thereby maintaining high signal-to-noise ratios for these experiments. These atomically pristine hexagonal close-packed AuCN monolayers exhibit a strong absorption at 2140 cm^{-1} . Upon thermal annealing, the surface rearranges into a ribbon structure with a blue-shifted absorption to 2230 cm^{-1} . The unique vibrational contrast in AuCN monolayers resulting from thermally induced structural changes serves as an ideal model system for the new infrared scanning tunneling microscope (IR-STM). Upon

prolonged vapor deposition, the self-assembled cyanide monolayers reconfigure into large-scale AuCN crystals, giving two distinct morphologies and significantly different vibrational modes, compared to the AuCN monolayer structures. Once again, temperature can tune gold-cyanide orientation and long-range ordering. This work provides new insights for controlled surface-mediated crystal growth in AuCN systems. Ultimately, combining with the chemical information gained from the developed IR-STM, surface-mediated growth will enable new methodologies for fabricating next-generation nanoscale semiconductors. Nanoscale semiconductors based on AuCN that are similar to nanoribbon structures have been demonstrated to be useful for nanoelectronics as well as in catalytic applications.

The dissertation of Kristopher Kent Barr is approved.

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Alexander Spokoyny

Paul S. Weiss, Committee Chair

University of California, Los Angeles

2020

*To my father . . .
who has always believed in me—
shown me how science is all around us,
and inspired me to keep moving forward.*

TABLE OF CONTENTS

1	Introduction	1
1.1	Nanotechnology and Context	2
1.2	Focus and Scope	4
1.3	Relevance and Importance	5
1.4	Objectives and Measurables	8
1.5	Overview and Structure	9
1.6	References	9
2	Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}	15
2.1	Abstract	16
2.2	Introduction	16
2.3	Experimental Methods	18
2.4	Results	23
2.4.1	Scanning Tunneling Microscopy – Molecular Resolution of Surface Structure	23
2.4.2	Vibrational Spectroscopy – Connectivity	29
2.4.3	Near-Edge X-Ray Absorption Fine Structure Spectroscopy – Molecular Orientation	31
2.4.4	Resonant Auger Electron Spectroscopy – Molecule-Substrate Charge- Transfer Efficiency	33
2.4.5	Discussion of Results – Bonding Scheme and Substrate-Molecule Cou- pling	38
2.5	Conclusions and Prospects	40

2.6	References	41
3	Hexagons to Ribbons: Flipping Cyanide on Au{111}	51
3.1	Abstract	52
3.2	Introduction	52
3.3	Results and Discussion	54
3.3.1	Surface Structure Characterization of Thermally Annealed CN/Au{111}	54
3.4	Conclusions and Prospects	62
3.5	Experimental Methods	63
3.5.1	Monolayer Preparation	63
3.5.2	Scanning Tunneling Microscopy	64
3.5.3	Infrared Spectroscopy	64
3.5.4	Raman Spectroscopy	65
3.5.5	Image Analysis	66
3.6	References	66
4	Surface-Mediated Crystal Growth of Aurous Cyanide from Molecular Self-Assembled Monolayers	75
4.1	Introduction	76
4.2	Methods	78
4.2.1	Sample preparation	78
4.2.2	Raman and optical microscopy	80
4.2.3	Scanning electron microscopy	80
4.3	Results and Discussion	80
4.4	Conclusions and Prospects	86
4.5	References	89

5	Fourier Transform Infrared Scanning Tunneling Microscopy: Probing Molecular Vibrations at the Nanoscale	92
5.1	Introduction	93
5.2	Experimental Layout	95
5.2.1	Scanning Tunneling Microscopy Background	95
5.2.2	Simulation of Fourier Transform Infrared Scanning Tunneling Microscopy Performance	98
5.3	Experimental Results	102
5.3.1	Concurrent Attenuated Total Reflection Data Collection and Scanning Tunneling Microscope Images	102
5.3.2	Analyzing the Current Spectrum	103
5.4	Conclusions and Prospects	103
5.5	Experimental Methods	105
5.6	References	106
6	Conclusions and Prospects	111
6.1	Summary	112
6.2	New Applications and Experiments for AuCN Crystals	113
6.3	Fourier Transform Infrared-Scanning Tunneling Microscopy: New Systems and Outlook	114
6.3.1	Isocyanide Systems	114
6.3.2	Alkynes	115
6.3.3	Modifications to the Fourier Transform Infrared Scanning Tunneling Microscope	115
6.4	Conclusions	117
6.5	References	118

A	Supplemental Information	119
A.2	Chapter 2 Supplemental Information	120
A.3	Chapter 3 Supplemental Information	122
A.3.1	Supplemental Raman Spectroscopy	126
A.3.2	References	128
A.4	Chapter 4 Supplemental Information	129
A.5	Chapter 5 Supplemental Information	136

LIST OF FIGURES

1.1	Scanning tunneling microscope image of decanethiol self-assembled monolayers on Au{111} substrate. Several defect sites exist including a gold step edge (red), vacancy islands (green), domain boundaries (teal), and disorder regions (purple). Reprinted with permission from reference [39]. Copyright 2008 American Chemical Society.	6
1.2	Scanning tunneling microscope images of self-assembled monolayers of two thiolated positional isomers of carboranethiols, (a) 1,7-dicarba-closo-dodecaborane <i>m</i> -1-carboranethiol (M1) and (b) <i>m</i> -9-carboranethiol (M9) on Au{111}. All images were collected at a sample bias of 1.0 V and a tunneling current of 3.0 pA under ambient conditions. (c) Grazing incidence Fourier transform infrared spectra of M1 (red) and M9 (blue) on Au{111}. Adapted with permission from reference [42]. Copyright 2009 American Chemical Society.	7
2.1	AuCN on top of gold surfaces.	15
2.2	Scanning tunneling microscope images of the surface structure of cyanide monolayers on Au{111} at room temperature. (a) The morphology of the cyanide monolayers with representative surface structures denoted by letters A–F in the image and schematic of cyanide with aligned dipole C → N, positive → negative. (b) Molecular resolution images and corresponding Fourier transform showing the hexagonally close-packed lattice with a nearest neighbor distance of $3.8 \pm 0.5 \text{ \AA}$	22

2.3	Scanning tunneling microscope image of CN on Au{111} as deposited at room temperature and structural schematics. Using the Au close-packed substrate direction with respect to straight step edges ($\langle 0\ 1\ 0 \rangle$), we find molecules bind to bridge and atop positions with a ($3.8\ \text{\AA} \times 3.8\ \text{\AA}$) cyanide unit cell at 20, -40 , and 80° orientations with respect to the unreconstructed underlying gold lattice. The dark, larger circles represent the projection of the cyanide molecules on the smaller circles representing the atoms of the Au{111} lattice. Triangles representing examples of the identified orientations relative to the Au{111} lattice are aligned with cyanide domain boundaries and are identified as high-symmetry directions representative of the hexagonally close-packed arrangement.	24
2.4	Au 4f _{7/2} (a), C 1s (b), and N 1s (c) X-ray photoelectron spectra of NC/Au{111} acquired at photon energies of either 350 or 580 eV as marked in the panels (open circles). The spectra are fit and decomposed into individual contributions (thin solid lines). See text for details.	26
2.5	Attenuated total reflection Fourier transform infrared spectrum of CN/Au{111} using custom sapphire prism substrates and showing the CN stretch at $2146\ \text{cm}^{-1}$ along with two side peaks at 2134 and $2161\ \text{cm}^{-1}$. The inset is an enlargement of the region of the spectrum containing the CN vibration.	28
2.6	(a) Raman spectra of CN monolayers formed on Au{111} using a plasmonic nanohole array and (b) surface-enhanced Raman substrates made of polycrystalline Au nanoparticles evaporated onto glass. (c) The inset shows both the low frequency modes attributed to the substrate–molecule bond, Au–CN bend at $304\ \text{cm}^{-1}$, and Au–CN stretch at $400\ \text{cm}^{-1}$, which were only detected on the Au nanoparticles.	32

2.7	C (a) and N (b) K-edge near-edge X-ray absorption fine structure spectra of NC/Au{111} acquired at an X-ray incident angle of 55° (black solid curves), along with the respective difference between the spectra collected under the normal (90°) and grazing (20°) incidence geometry (gray solid curve in panel b). The characteristic absorption resonances are marked. The horizontal dashed line in panel b corresponds to zero intensity.	34
2.8	[N 1s] π^* resonant Auger electron spectra (RAES, black curves) and nonresonant Auger electron (blue curves) spectra of NC-C ₂ H ₄ S/Au (a) and NC/Au{111} (b). The electron transfer contribution in the resonant Auger electron spectra is shown (red curves). P, SP1, and SP2 denote the participator and two spectator features, respectively. A1 and A2 denote two characteristic features in the nonresonant spectra. The derived τ_{ET} are given. The spectra of NC - C ₂ H ₄ S/Au are reprinted with permission from ref [30]. Copyright 2010 American Chemical Society. . . .	36
2.9	Electron transfer (ET) time (top panel) from the excited NC group to the substrate and its natural logarithm (bottom panel) for NC/Au (red square) and NC - (CH ₂) _n S/Au (n = 2-4; black filled circles) versus the number (n) of methylene (CH ₂) units in the aliphatic chain. The gray solid lines in the top and bottom panels represent the best exponential and linear fits, respectively. The intercept of the $\ln \tau_{\text{ET}}$ plot with the y-axis corresponds to the ET time required for transfer from the NC group to the backbone plus the ET time required for transfer from the backbone to the substrate. The intercept of 0.83 gives a $\tau_{n=0}$ value of 2.3 fs. The values for NC - (CH ₂) _n S/Au are reprinted with permission from ref [30]. Copyright 2010 American Chemical Society.	39
2.10	Electron transfer across the Au-C bond is extremely efficient at ~ 1 fs, indicating strong electronic coupling between substrate and molecule.	40
3.1	AuCN rearranging on top of gold surfaces.	51

3.2	Scanning tunneling microscope images of (A) hexagonally close-packed CN/Au{111} as-deposited under ambient conditions and (B) the thermally induced ribbon structure formed by dry annealing for over 18 h at ~ 100 °C. The order in the annealed structure is long range (on the order of tens of nanometers) with the ribbon domains taking on various rotational orientations relative to one another on the surface. Once annealed, the surface never returns to the original HCP arrangement. (C,D) Molecular-resolution images of the as-adsorbed and thermally annealed lattices, respectively. We note tip-change imaging artifacts in (B) that did not disrupt the topography. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA.	53
3.3	(A) Transition from HCP to ribbon structure imaged after 6 h exposure to ~ 100 °C. (B) Higher resolution image, highlighting a region with both (upper right) hexagonally close-packed and (lower left) ribbon structure regions. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA.	56
3.4	(A) Scanning tunneling microscope image of the annealed CN/Au{111} with six separate ribbon domains and three different relative rotations of the ribbon direction. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA. (B) Associated segmented image partitioned in the Fourier domain highlighting the three different orientations. (C) Regions 1–6 represent ribbon regions, with each color indicating a ribbon region of a different rotational orientation. Region 7 is a ribbon domain boundary, and regions 8 and 9 are step edges. Ribbon orientations are relatively offset by rotations of multiples of 60° following the HCP symmetry of the underlying gold surface.	57
3.5	(A) Scanning tunneling microscope image of the region of thermally annealed CN/Au{111} with a domain boundary separating rotational domains. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA. (B) Segmentation analysis results showing the domain boundary (3) and the rotational domains (1 and 2).	59

3.6	(A,C) Scanning tunneling microscope images of the ribbon structures of annealed CN on Au{111} (false colored to highlight the relative apparent height differences and lateral distances). The close-packed substrate lattice direction is indicated by the straight step edge and ribbon orientation in (A). (B) Surface profile shown as the blue line in (A), showing the apparent height variations of the ribbon structure of annealed CN on Au{111} and a step edge, which is used as an internal reference. (C) Higher resolution image of the area indicated in (A), with the unit cell shown as the green box. (D) Corresponding surface profiles along and across the rows shown in (B). Letters a–f correspond to the measured peak-to-peak distances summarized in Table 3.1. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA.	61
3.7	Attenuated total reflection infrared spectra of CN/Au{111} (A) after 6 h of thermal annealing at 100 °C and (B) after 24 h of thermal annealing at ~ 100 °C. (C) Polarization-modulation infrared absorption spectroscopy for CN/Au/Si after 24 h of thermal annealing at 100 °C.	62
3.8	Raman spectrum showing both the low- and high-frequency modes of CN/Au{111} after thermal annealing for over 24 h at ~ 100 °C. The most important aspects of the spectrum are the new peaks at 141 and 2195 cm^{-1} without loss of the vibrations that are also detected on the as-adsorbed sample.	64
3.9	Proposed bonding scheme for annealed cyanide SAMs on Au{111} composed of a mixture of Au–CN and Au–NC bound molecules. Surface profiles that match the scanning tunneling microscope image shown in Figure 3.6 are aligned with the schematic for comparison.	66

4.1	a,b) Well-ordered monolayers of cyanide on Au{111} using a custom-built scanning tunneling microscope. The tunneling current was 5 pA with a sample bias voltage of 1 V with respect to the tip. Upon thermal annealing, at 100 °C, the surface would rearrange forming the ribbon structure b). c) Scanning electron microscopy image of a crystal prior to thermal annealing taken at a 45° angle with respect to the electron beam (layout shown in supplemental information figure A.10a). d) After thermal annealing treatment of the crystal.	79
4.2	Optical microscope image of a) sparse (2 days) and b) high-crystal density structures (90 days). In b), Circle a corresponds to examples of the elongated crystals. They grow to lengths of 50 μm and widths of 15 μm . Circle b contains examples of the amorphous crystals. They tend to grow to 20 μm in diameter. Circle c highlights examples of sunburts made from smaller particulates that collectively have diameters of 50 μm	81
4.3	a) Scanning electron microscopy image of AuCN crystals made from 2-nm-thick Au substrate. The scale bar on each of the images is 5 μm across. Images below a) correspond to element channels: b) nitrogen, c) gold, d) oxygen, and e) silicon. f), g), and h) Correspond to the X-ray spectrum on the crystal (red) and off the crystal (blue). Counts are offset for clarity. The C and N K_{α} are shown in f) at 277 and 392 eV respectively. The Au K_{α} is shown in g) and is minimized off of the crystal as seen in c). There were no potassium K_{α} signals at 3314 eV visible in h).	82
4.4	Scanning electron microscope images of AuCN crystals made from 2-nm Au substrates. a) Wide view image. The red outline corresponds to the location of figure b). Similarly to 100-nm-thick Au substrates, there are elongated and small crystals.	84

4.5	a) 2D Raman mapping of the surface where the intensity of the color corresponds to the location of the 2160 cm^{-1} peak. The 2D mapping correlates well to b) the optical microscope image. A depth scan was performed on the sample in c) resulting in the stitched imaged d). The blue region in d) relates to the 2160 cm^{-1} peak while the red region corresponds to the 2220 cm^{-1} peaks.	87
5.1	A 40-nm-thick layer of gold atop a sapphire substrate forms the crystalline substrate surface. Self-assembled monolayers are adsorbed on the gold substrate. Using a back-illuminated geometry, the surface is illuminated evanescently without significantly thermally heating the scanning tunneling microscope tip.	95
5.2	Simulated scan of current modulation by a random normal distribution of noise for 400 ms. The standard deviation of the noise per step was 0.01 pA.	97
5.3	Fourier transform infrared attenuated total reflection measurements of hexagonally close-packed AuCN (2142 cm^{-1}) and ribbon AuCN (2134 cm^{-1}) on Au/Si substrates.	98
5.4	a) Normal distribution used to create the simulated absorption spectrum at 2142 cm^{-1} with a σ of 10 cm^{-1} . The inlet is the constructed interferogram from the absorption profile in a). b) The portion of the interferogram used to simulate the mirror motion during the data acquisition phase. This simulation starts with t_0 at the mirror at -0.03 cm compared to the center position.	99
5.5	a) The simulated scan with vibronic components, both real and imaginary, added in at 2% intensity. b) The resulting inverse fast Fourier transform of the current found in a) with respect to the mirror velocity.	101
5.6	Simulated absorption spectrum from 2142 cm^{-1} normal mode. Maximum peak found at 2131 cm^{-1}	102

5.7	Photograph of the experimental system. This design uses a multiplex signal from a broadband infrared source with attenuated total reflection geometry. We evanescently excite the surface molecules on the back of the prism into vibration. The reflected beam then heads to a mercury cadmium telluride (MCT) detector to be analyzed. As we bring the scanning tunneling microscope probe tip within tunneling distance of the surface, we can measure the change in the tunneling current due to the and can use that to measure the change in conductance at the tunneling junction.	104
5.8	Scanning tunneling microscope image of AuCN on a Au/sapphire substrate, while simultaneously being irradiated evanescently by a broadband infrared source. The tunneling current was 10 pA with a sample bias voltage of 1 V with respect to the tip. Image adapted from reference [37].	105
A.1	(A) The polarization-modulated Fourier transform infrared reflection absorption spectrum (PM-IRRAS) of CN as-deposited on polycrystalline Au/Si indicating the CN is still primarily upright on the surface without detection of the C–H stretch associated with HCN. (B) The attenuated total internal reflectance Fourier transform infrared spectrum of as-deposited CN on Au{111} showing the multiplet not detected by PM-IRRAS and a blue shift of 5 cm^{-1}	120
A.2	Detail of the (A) CN region from the polarization-modulated Fourier transform infrared reflection absorption spectrum of CN as-deposited on polycrystalline Au/Si and (B) the attenuated total internal reflectance Fourier transform infrared spectrum of as-deposited CN on Au{111}.	121

A.3	(A) Scanning tunneling microscope image, (B) associated manual curvelet partitioning of the Fourier domain using the empirical wavelet transformation, and (C) the segmentation results for the domains with different orientations. The bottom panels represent the manual 2D fast Fourier transformation filtering of the circled Fourier coefficients and the corresponding image textures for each segmented domain. Relative stripe domain rotation angles are calculated to be multiples of 60° using the dot product of the displacement vectors of the position of the circled coefficients from the origin. Only one of the Fourier coefficients was used for each segmented texture region because of symmetry in the Fourier domain. The Fourier domain plots take into account all information in the image.	122
A.4	Scanning tunneling microscope image segmented using a combination of cartoon and texture decomposition. Artifacts associated with the imaging were separated from the analyzed image and stored separately to avoid loss of information. . . .	123
A.5	Classes associated with texture decomposition of the scanning tunneling microscope image shown in Figure A.4 that highlight the different regions of the image associated with the ribbon orientation and domain boundary.	123
A.6	Fourier domain classes associated with the texture decomposition of the scanning tunneling microscope image shown in Figure A.4. The angles between different orientation domains, as shown in Figure A.3, were calculated using the dot product of the displacement vectors from the farthest and largest Fourier coefficient from the origin. Fourier textures C1 and C2 are examples that represent the two stripe orientation domains, Class 1 and Class 6, highlighted in Figure A.5. Equivalently, the Fourier textures from C4 and C5 could be used to calculate the same angle.	124
A.7	(A) Attenuated total reflection-infrared spectrum of as-adsorbed CN/Au{111} at room temperature. (B) Polarization-modulation infrared absorption spectrum of room temperature as-deposited CN/Au/Si.	125

A.8	Surface-enhanced Raman spectrum of as-adsorbed CN/Au{111} at room temperature showing the peaks attributed to the CN vibrations. On the Au{111} surface we were unable to detect the low-frequency modes, but did detect a splitting of the CN vibration. (b) Surface-enhanced Raman spectrum of as-adsorbed CN on a custom roughened polycrystalline Au substrate on glass with the low-frequency vibrations attributed to the AuCN stretch and bend (shown in the inset, c). (d) Surface-enhanced Raman spectrum of CN on Au after annealing using the same custom polycrystalline nanostructured SERS substrate. (As-deposited Raman spectra shown in (a, b, and c) from chapter 2)	126
A.9	Schematic of the crystal structure and distance measurements for solid AuCN, which is composed of hexagonally bundled, linear AuCN chains with alternating Au–C and Au–N bonds (distances from ref [5]).	127
A.10	a) Scanning electron microscope layout. Sample placed on stage at 45° with respect to the electron beam. b,c,d) scanning electron microscope images of AuCN crystals on Au/Si substrate. Grey rectangle inside of b) corresponds to c), and the rectangle in c) corresponds to d) (figure 4.1c).	129
A.11	Scanning electron microscope image of bare Au/Si (without exposure to AuCN). The bare-gold surface is indistinguishable from the off-crystal surfaces in figure A.10b–d.	130
A.12	Contact profilometry measurements of AuCN on a Au/Si substrate. The fast-scan direction is in the horizontal plane. The dimensions of the image are 300 μm $\times$ 100 μm , and the image was processed using background and horizontal slope subtraction. Line profiles of crystals are labeled 1–4 shown in figure A.13.	130
A.13	Line profiles from the profilometry measurements found in figure A.12. The heights of these crystals ranged from 0.9 to 1.5 μm .	131
A.14	AuCN crystal counts of cyanide-limited system from figure 4.2b categorized by size and shape. 1 , 2 , and 3 refer to small, elongated and sunburst structures respectively. Results are shown in table A.1.	132

A.15 AuCN crystal counts of gold-limited system from figure 4.4a categorized by size and shape. 1, 2, and 4 refer to small, elongated and $<4\ \mu\text{m}$ structures respectively. Due to the low quantity of gold on the surface, many particles were less than $4\ \mu\text{m}$ long. Results are shown in table A.1.	133
A.16 Representative Raman vibrational spectrum of AuCN crystals on Au/Si substrates. The lower energy vibration mode from Au–CN stretch at $315\ \text{cm}^{-1}$. The spectrum was background subtracted with cosmic rays removed. The spectrum was acquired at a single location.	134
A.17 A,B) Representative Raman vibrational spectra of AuCN crystals on Au/Si substrates. B) Spectrum post thermal annealing at $100\ ^\circ\text{C}$. Both spectra are background subtracted with cosmic rays removed. Spectra were averaged over the surface and were demixed true component analysis using the WITec’s Suite Five software.	135
A.18 Digital photograph of 40-nm-thick Au/sapphire substrate.	136

LIST OF TABLES

2.1	Comparison of the Different Vibration Energies for the Cyanide/Nitrile Group as a Ligand at Solution and Air Interfaces	30
3.1	Measured Distances for Annealed CN/Au{111} Corresponding to the Profiles Shown in Figure 3.6	60
A.1	Surface counts from figures A.14 and A.15	132

LIST OF ACRONYMS

1h	one hole
2D	2-dimensional
2h1e	two-hole one-electron
Å	Angström
AFM	atomic force microscopy
asec	attosecond
ATR	attenuated total reflection
Au	gold
AuCN	gold cyanide
[Au(CN) ₂] [−]	dicyanoaurate(I)
C	carbon
CaF ₂	calcium fluoride
CHC	core-hole clock
cm	centimeter
cm ^{−1}	wavenumber
CN	cyanide
CO	carbon monoxide
CO ₂	carbon dioxide
COOH	carboxylic acid
DOS	density of states
E	electric field
E _B	binding energy
ET	electron transfer
eV	electron volt
fs	femtosecond
FTIR	Fourier transform infrared
h	hour

HCN	hydrogen cyanide
HCP	hexagonally close-packed
HeNe	helium neon
HRXPS	high-resoluion X-ray photoelectron spectroscopy
Hz	hertz
I	electrical current
IETS	inelastic electron tunneling spectroscopy
IR	infrared
K	Kelvin
KCN	potassium cyanide
m	meter
M1	<i>m</i> -1-carboranethiol
M9	<i>m</i> -9-carboranethiol
MCT	mercury cadmium telluride
μm	micron
n	index of refraction
N	nitrogen
NEXAFS	near-edge X-ray absorption fine structure
nm	nanometer
NP	nanoparticles
O ₂	oxygen
OH ⁻	hydroxide
P	participator channel
pA	picoamp
PEY	partial electron yield
PM-IRRAS	polarization-modulated Fourier transform infrared reflection absorption spectrum

Pt/Ir	platinum/irridium
θ	incident angle
θ_c	critical angle
RAES	resonant Auger electron spectroscopy
RAES	resonant Auger electron spectroscopy
Ru	ruthenium
s	second
S	sulfur
SAMs	self-assembled monolayers
Se	selenium
SEM	scanning electron microscopy
SERS	surface-enhanced Raman spectroscopy
Si	silcon
SP	spectator channel
STM	scanning tunneling microscopy
τ_{core}	core electron lifetime
τ_{ET}	electron transfer time
V	volts
XPS	X-ray photoelectron spectroscopy

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“If I have seen further it is by standing on the shoulders of Giants”

Sir Isaac Newton

To everyone whose shoulder I have stood upon—this one's for you!

Co-Author Contributions

Chapter 2

Guttentag, A. I.; Wächter, T.; **Barr, K. K.**; Abendroth, J. M.; Song, T.-B.; Sullivan N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}. *Journal of Physical Chemistry C* **2016**, *120*, 26736.

A. I. Guttentag developed the project in collaboration with, M. Zharnikov, D. L. Allara, and P. S. Weiss. Experiments were performed by Kristopher K. Barr, A. I. Guttentag, J. M. Abendroth, N. Sullivan, and T.-B. Song. T. Wachter, M. Zharnikov, D. L. Allara performed the photoelectron spectroscopy and analysis for composition, orientation, and electron transfer efficiency. The manuscript was written by A. I. Guttentag with figure preparation from Kristopher Barr and contributions from all other co-authors.

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Chapter 3

Guttentag, A. I.; **Barr, K. K.**; Song, T.; Bui, K. V.; Fauman, J. N.; Torres, L. F.; Kes, D. D.; Ciomaga, A.; Gilles, J.; Sullivan N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Hexagons to Ribbons: Flipping Cyanide on Au{111}. *Journal of the American Chemical Society* **2016**, *138*, 15580.

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Chapter 4

Barr, K. K.; Chiang, N.; Vinnacombe-Wilson, G.; Cheung, K. M.; Guttentag, A. I.; Weiss, P. S. Surface-Mediated Crystal Growth of Aurous Cyanide from Molecular Self-Assembled Monolayers. *in preparation*, **2020**.

Kristopher Barr initiated the project and developed it with A. I. Guttentag, and N. Chiang in collaboration with all co-authors. Kristopher Barr performed all Raman and optical microscopy measurements and collaborated with G. Vinnecombe-Wilson and N. Chiang for scanning electron microscopy imaging measurements. Atomic force microscopy measurements were performed by K. Cheung. Profilometry measurements were collected with the guidance of Omar Leon. Image analysis of optical measurements had contributions from Kristen Stefanescu. Manuscript prepared by Kristopher Barr with contributions from all co-authors.

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Chapter 5

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Kristopher Barr, A. I. Guttentag and P. S. Weiss initiated and developed the project. Fourier transform infrared scanning tunneling microscopy measurements were performed by Kristopher Barr and A. I. Guttentag. The instrument modifications were performed by Kristopher Barr and A. I. Guttentag. Kristopher Barr created the simulations described in the chapter. Manuscript prepared by Kristopher Barr with contributions from co-authors.

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Surface-Mediated Crystal Growth of Aurous Cyanide from Molecular Self-Assembled Monolayers,
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Photoinduced Carrier Generation and Distribution in Solution-Deposited Titanyl Phthalocyanine Monolayers, S. Wang, N. Chiang, H. Guo, N. Wattanatorn, **K. K. Barr**, A. N. Alexandrova, and P. S. Weiss, *Chemistry of Materials* **31**, 10109 (2019).

Hexagons to Ribbons: Flipping Cyanide on Au{111}, A. I. Guttentag, **K. K. Barr**, T.-B. Song, K. V. Bui, J. N. Fauman, L. F. Torres, D. D. Kes, A. Ciomaga, J. Gilles, N. F. Sullivan, Y. Yang, D. L. Allara, M. Zharnikov, and P. S. Weiss, *Journal of the American Chemical Society* **138**, 15580 (2016).

Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}, A. I. Guttentag, T. Wächter, **K. K. Barr**, J. M. Abendroth, T.-B. Song, N. F. Sullivan, Y. Yang, D. L. Allara, M. Zharnikov, and P. S. Weiss, *Journal of Physical Chemistry C* **120**, 26736 (2016).

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Surface-mediated crystal growth of aurous cyanide from molecular self-assembled monolayers

Biennial Conference on Chemical Education, Accepted March 2020 (Corvallis, OR)
Bridging theory to practice: Influence of teaching videos in TA training on TAs' perceptions of pedagogy in a laboratory setting
Note: Conference cancelled due to COVID-19

American Physical Society March Meeting Poster, March 2019 (Boston, MA)
Scanning tunneling microscopy with infrared spectroscopy: Recent findings.

STEM Undergraduate Career Talk, November 2017
Cal State Dominguez Hills
Surface functionalization and control of cyanide on Au{111}

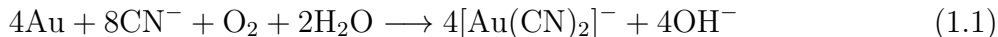
CHAPTER 1

Introduction

1.1 Nanotechnology and Context

The term nanotechnology, coined back in 1974, focuses on applying the various electrical, chemical, and physical interactions of materials that perform differently to bulk materials due to their sizes (*i.e.*, on the scale of 100 nm or less in one or more dimensions).^{1–3} At that time, researchers had focused on new methods of engineering and designing materials that exhibit nanoscale characteristics. The field has grown since then, but fundamental questions and improvements are needed to incorporate these novel nanomaterials into devices and technological advances. Reductions in the cost (*e.g.*, lowering the amount of precious elements needed or increasing the efficiencies of methods) or tunability of material characteristics (*e.g.*, workfunction, surface energy, particle size, surface structure) can enable the creation of new fabrication methods.^{1,4–14} Likewise, probing the mechanisms and the fundamental properties is important to support the flourishing field of nanotechnology.¹² To that end, this dissertation reports the monolayer surface configurations, growth applications, and the use of gold cyanide (AuCN)—a semiconducting compound that has been used as a model in nanofabrication.^{15,16}

The chemistry of cyanide and gold has been studied since the mid-nineteenth century. It was of interest due to cyanide’s capability of creating a species of gold in which oxygen is able to oxidize the gold (equation 1.1).¹⁷ This intriguing property has an obvious downfall, where many rivers, lakes, and streams were harmed due to pioneers and others using this chemistry to dissolve the precious metal from the mined ore. Cyanide has the ability to make strong bonds with metals, but at the cost of high toxicity. Understanding the CN–Au relationship on a fundamental level could aid in the use or replacement of this material, while avoiding the toxicity issues.



Though this poisonous compound should be treated with respect, the chemistry within it is rich due to the strength of the bonds formed between metals and its ability to polymerize.^{18–20} Using the reaction shown above, it is possible to create Au–C bonds under

atmospheric conditions. Our group’s background in surface functionalization has given us the tools to approach chemistry from the surface. These capabilities include using those functionalization tools to create C–Au bonds from alkynes atop gold substrates under ambient conditions.²¹

The second focus of this thesis is understanding the chemical properties of materials at scales far below the diffraction limit. One chemical identifier available to us is vibrational spectroscopy in the form of infrared and Raman spectroscopies. For context, infrared spectroscopy utilizes photons with wavelengths *ca.* 5 μm , so the diffraction-limited resolution is *ca.* 2 μm , which is four orders of magnitude larger than the distances between atoms in a molecule. Generally, the measured absorption is an ensemble-average of the surface vibrations of all the molecules interacting with the source. Due to the scale, this experiment cannot differentiate molecules in varying chemical environments as all are being probed simultaneously, resulting in averaged absorption profiles. However, when engineering systems, it is best to focus on the components that creates the most advantageous effects. For example, various catalytic reactions perform better with one surface arrangement than others. A multitude of techniques have been explored to assess single-molecule-based measurements, including super resolution and surface enhanced techniques.^{22–24} These techniques have been used to elucidate how chemical reactions take place, where molecules reside, and what interactions dominate locally. These properties help us understand the local characteristics and engineer new technologies.

Recently, researchers have shown success incorporating the fields of scanning probe microscopies with spectroscopy by using infrared lasers with atomic force microscopy (AFM) probe tips, combining the chemical precision of the infrared spectroscopy with the spatial resolution of AFM.^{25–27} Others have attempted this in the field of scanning tunneling microscopy (STM), where precise, single molecule interactions can be probed and measured. For example, Raman spectroscopy has been used to elucidate the vibrational modes of molecules within the tunneling junction using STM.^{23,25,28} However, many substrates cannot be studied due to the Raman selection rules or the mode being too weak to identify. Infrared spectroscopy with STM is a complementary research methodology capable of studying these systems that

may not be Raman active on conductive/semiconductive substrates.

1.2 Focus and Scope

Nanoscience is a broad scientific field that includes biology, chemistry, materials science, electrical engineering, and physics.¹⁻³ Due to the multidisciplinary nature of the field, nanoscience is capable of solving problems by incorporating tools from the other subjects. However, to create objectives with measurable outcomes, I will narrow the scope of this research to a few main components. Herein, I will describe the structural properties of AuCN, how this molecule can be used to elucidate properties in nanoelectronics, and the development of an instrument capable of measuring chemical information far below the diffraction limit of infrared photons in order to study these molecules. Although there are already a variety of spectroscopies that can measure the average characteristics of these materials, our group has been able to elucidate more detailed information by focusing on materials properties at the scale of individual molecules.²⁹ The ability to understand and to manipulate the local characteristics of materials at the nanoscale is of importance for engineering new technologies. For example, for heterogeneous catalysts, the surface morphology can change as the reaction progresses. This transformation can change how well the catalyst performs and understanding the mechanisms of the change can prolong their lifetime.¹⁴

As mentioned above, this work will focus on the modifications and properties of AuCN. I will detail how I used this compound as a model system to probe the growth mechanisms and how I tested the limitations of our custom-built Fourier transform infrared (FTIR)-STM. I assessed the growth of AuCN self-assembled monolayers (SAMs) atop gold substrates, monitored the reconfiguration that occurs upon thermal annealing, and probed the vibrational structure of crystals atop the monolayer backbone.

1.3 Relevance and Importance

Probing and elucidating the chemical properties of a surface at the nanoscale is needed to fabricate better-engineered nanotechnologies. Within the literature, there exists a wide variety of surface-sensitive nanoscale techniques, including, but not limited to, scanning probe techniques, surface-enhanced Raman spectroscopies, and fluorescence microscopies.^{22,23,28–30} These techniques enable researchers to design new materials with interfaces based upon the interactions they are trying to magnify. For example, generally, one facet of a heterogeneous catalyst reacts more efficiently than others, so designing materials with reactive interfaces is crucial to creating effective catalysts.

One of the major reasons we wanted to explore the cyanide systems was due to its vibrational energy—these compounds exhibit a C–N stretch *ca.* 2200 cm^{−1}.^{31–36} This energy is in a relatively unoccupied window compared to other vibrational modes and is easily observed with vibrational spectroscopies. The strength of the metal–C bond is related to the energy of the C–N vibrational mode due to the back bonding between the cyanide’s π orbital and the metal’s d orbitals.^{37,38} Therefore, measuring the vibrational energy of the ligand will also encode information about the bond strength of the molecules. However, this information will be averaged over the surface in most techniques. To go beyond this limitation, we have designed a unique scanning tunneling microscope that measures the vibrations of individual molecules.

Scanning tunneling microscopy, which has been applied for decades, has led to surface characterization at resolutions capable of resolving atoms and molecules on a substrate.^{40,41} As shown in figure 1.1, each of the protrusions correlate to an individual molecule on the surface, in this case decanethiolate on Au{111}.³⁹ With the advent of STM, researchers can distinguish well-ordered surfaces and discover the types of defect sites that exist (*i.e.*, step-edges, vacancy islands, domain boundaries, etc.). For well-behaved systems, STM has been immensely successful for characterization; however, when systems contain multiple molecules that are similar, this technique has difficulty distinguishing these molecules on the surface (this is due to the mechanism behind STM and will be discussed further in Chapter 5).

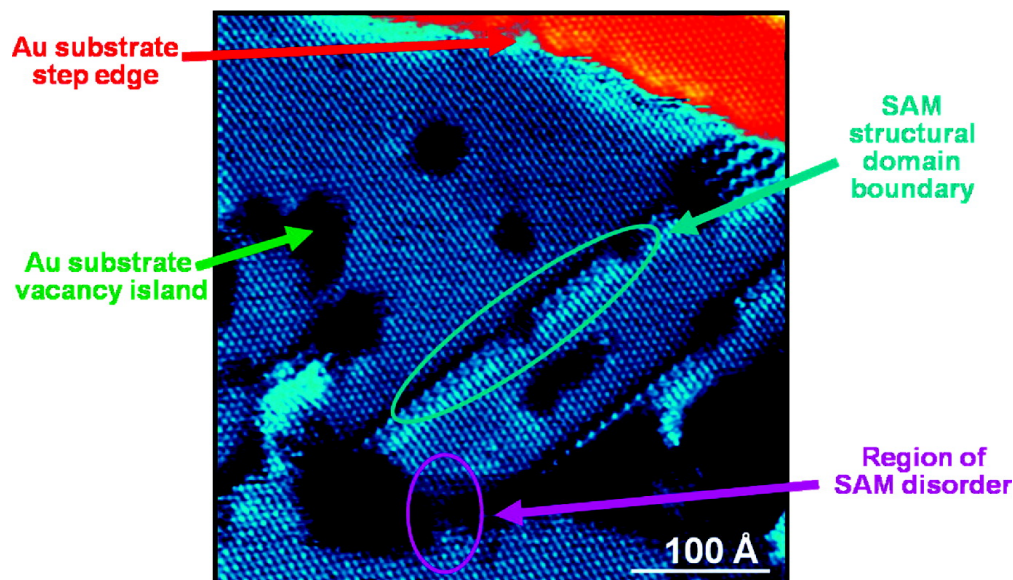


Figure 1.1: Scanning tunneling microscope image of decanethiol self-assembled monolayers on Au{111} substrate. Several defect sites exist including a gold step edge (red), vacancy islands (green), domain boundaries (teal), and disorder regions (purple). Reprinted with permission from reference [39]. Copyright 2008 American Chemical Society.

To increase the efficacy of this technique, distinguishing various molecular moieties on the surface is of the utmost importance. For example, figure 1.2(a,b) are STM images of two different carborane molecules on Au{111} substrates. By simply using STM, the surfaces are indistinguishable from one another. However, using infrared spectroscopy, these surfaces are easily distinguishable and proportions of the monolayer in each form can be calculated (figure 1.2(c)).⁴² Although, through infrared spectroscopy alone, we cannot describe how the molecules are arranged on the surface. In a 1:1 hypothetical mixed monolayer system of M1 and M9 (labeled in figure 1.2), are the domains a proportional mixture of the molecules, are they randomly dispersed, are they segregated by molecule type, or are they intermixed where M1 is next to M9? We will be able to identify surface features chemically and to answer the question above with the instrument designed in Chapter 5.

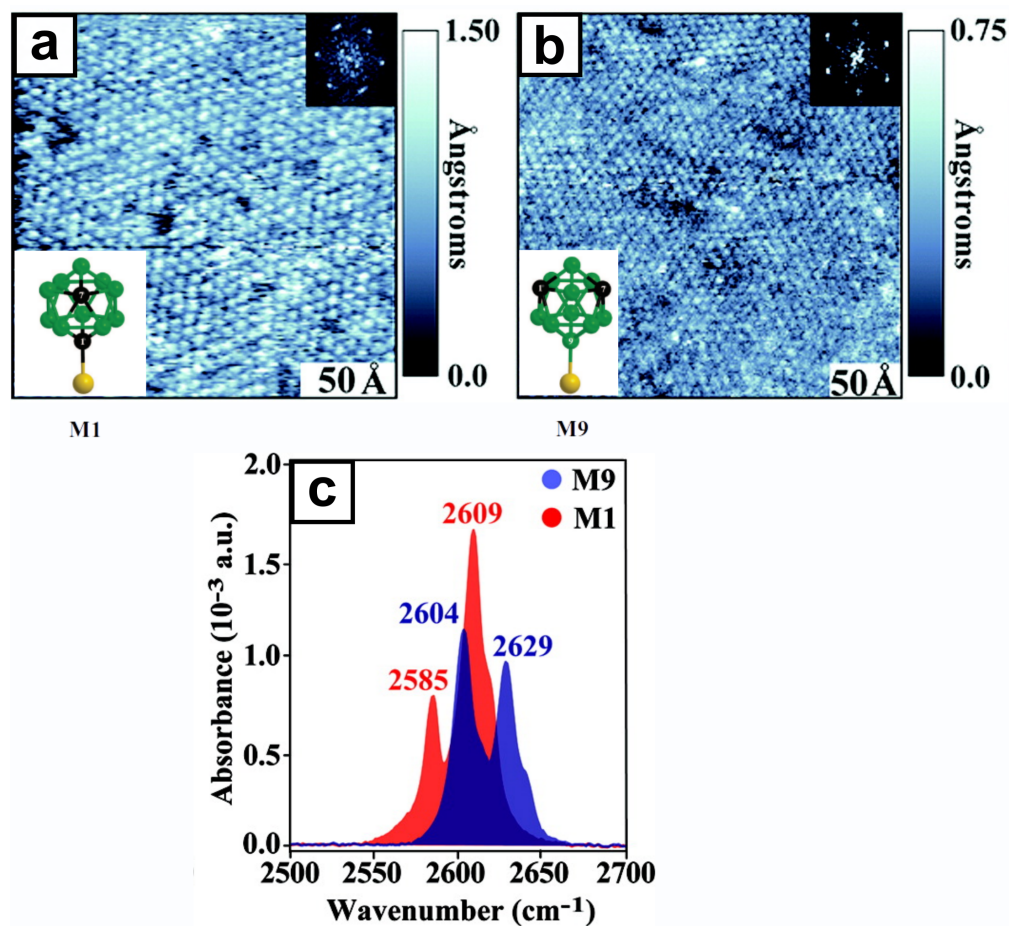


Figure 1.2: Scanning tunneling microscope images of self-assembled monolayers of two thiolated positional isomers of carboranethiols, (a) 1,7-dicarba-closo-dodecaborane *m*-1-carboranethiol (M1) and (b) *m*-9-carboranethiol (M9) on Au{111}. All images were collected at a sample bias of 1.0 V and a tunneling current of 3.0 pA under ambient conditions. (c) Grazing incidence Fourier transform infrared spectra of M1 (red) and M9 (blue) on Au{111}. Adapted with permission from reference [42]. Copyright 2009 American Chemical Society.

1.4 Objectives and Measurables

As mentioned above, one of the main goals of my research was to probe the chemical interactions of AuCN from the nanoscale to micron-sized crystals. We designed the FTIR-STM with this capability in mind, where chemical signatures (*i.e.*, vibrational spectroscopy) can be measured at the nanoscale. Under standard conditions, STM measurements are *not* capable of elucidating chemical features of a system. However, the chemical nature of the surface-substrate interactions can be probed and is of great importance to surface scientists who wish to manipulate the surface interactions.⁴³ To assess this objective, I developed simulations to measure the limitations of the signal needed to measure the effects of the infrared source modulating the tunneling-junction current.

Gold-cyanide was selected as the model system, due to its strong vibrational mode in an otherwise unoccupied spectroscopic region, its ability to form well-ordered SAMs, and its stability under ambient conditions.^{31,34,44} Understanding the chemical environment around this molecule and discerning how that correlates to the structure of the molecule has been a second aim of this project. Using the core-hole clock method described in Chapter 2, the C–Au interactions were compared so that of S–Au. From this, we were able to describe the type of chemical bonding occurring between Au–CN. Using our as-absorbed monolayer system, I assessed the ability to manipulate those surfaces and create metrics to validate those changes. I built the framework to describe the two morphologies that were generated on surfaces utilizing STM and FTIR spectroscopy.

In Chapter 4, I describe my work on the larger growth of the crystals formed atop the monolayers. This work potentially indicated that the majority of the gold surface was covered with the cyanide monolayer. Therefore, growth of the crystal structures could be scaffolded off of the AuCN monolayers and aid in elucidating the chemistry occurring through the growth. Therefore, this work would expand our understanding of the surface-mediated process.

1.5 Overview and Structure

I will discuss how I was able to fabricate SAMs of AuCN on Au/mica substrates via vapor deposition. These samples were imaged with STM and found to form well-ordered monolayer systems. In Chapter 3, I describe how thermal annealing the sample was used to modify the surface. This rearrangement decreased the density of CN adsorbates bound to gold. Not only were these structural changes visible from STM measurements, but I was able to measure the reorganization from the C–N normal vibrational mode via FTIR spectroscopy, as well. This study demonstrated that vibrational spectroscopy can be used to probe the structural changes of the chemical bonding features. In Chapter 4, I discuss the methodology used to create micron size crystals of AuCN through a substrate-mediated growth. Recently, AuCN has been studied for use in nanoelectronics due to its semiconductor properties.¹⁵ Understanding how to grow and to scale these structures could guide researchers and lead to deeper understanding of growth atop repeating substrates. Lastly, I explore a method to probe the AuCN molecules at scales below the diffraction limit. This mechanism will be discussed, as well as the limitations of this methodology. Using an instrument with this design, we and others will be able to probe the chemical properties of a surface at the nanoscale under ambient pressures and temperatures, enabling the understanding and implementation of nanomaterials on surfaces for a wide variety of applications.

1.6 References

- (1) Grimsdale, A. C.; Müllen, K. The Chemistry of Organic Nanomaterials. *Angewandte Chemie International Edition* **2005**, *44*, 5592–5629.
- (2) Nunes, D.; Pimentel, A.; Santos, L.; Barquinha, P.; Pereira, L.; Fortunato, E.; Martins, R., *Metal Oxide Nanostructures: Synthesis, Properties and Applications*; Korotcenkov, G., Ed.; Elsevier: 2019.

- (3) Bayda, S.; Adeel, M.; Tuccinardi, T.; Cordani, M.; Rizzolio, F. The History of Nanoscience and Nanotechnology: From Chemical–Physical Applications to Nanomedicine. *Molecules* **2019**, *25*.
- (4) De Boer, B.; Hadipour, A.; Mandoc, M. M.; van Woudenberg, T.; Blom, P. W. Tuning of Metal Work Functions with Self-Assembled Monolayers. *Advanced Materials* **2005**, *17*, 621–625.
- (5) Chen, C.-Y.; Wu, K.-Y.; Chao, Y.-C.; Zan, H.-W.; Meng, H.-F.; Tao, Y.-T. Concomitant Tuning of Metal Work Function and Wetting Property with Mixed Self-Assembled Monolayers. *Organic Electronics* **2011**, *12*, 148–153.
- (6) Wu, K.-Y.; Yu, S.-Y.; Tao, Y.-T. Continuous Modulation of Electrode Work Function with Mixed Self-Assembled Monolayers and Its Effect in Charge Injection. *Langmuir* **2009**, *25*, 6232–6238.
- (7) Kim, J.; Rim, Y. S.; Liu, Y.; Serino, A. C.; Thomas, J. C.; Chen, H.; Yang, Y.; Weiss, P. S. Interface Control in Organic Electronics Using Mixed Monolayers of Carboranethiol Isomers. *Nano Letters* **2014**, *14*, 2946–2951.
- (8) Serino, A. C.; Anderson, M. E.; Saleh, L. M. A.; Dziedzic, R. M.; Mills, H.; Heidenreich, L. K.; Spokoyny, A. M.; Weiss, P. S. Work Function Control of Germanium through Carborane-Carboxylic Acid Surface Passivation. *ACS Applied Materials & Interfaces* **2017**, *9*, 34592–34596.
- (9) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chemical Reviews* **2005**, *105*, 1103–1170.
- (10) Janssen, D.; De Palma, R.; Verlaak, S.; Heremans, P.; Dehaen, W. Static Solvent Contact Angle Measurements, Surface Free Energy and Wettability Determination of Various Self-Assembled Monolayers on Silicon Dioxide. *Thin Solid Films* **2006**, *515*, 1433–1438.

- (11) Albanese, A.; Tang, P. S.; Chan, W. C. The Effect of Nanoparticle Size, Shape, and Surface Chemistry on Biological Systems. *Annual Review of Biomedical Engineering* **2012**, *14*, 1–16.
- (12) Polshettiwar, V.; S. Varma, R. Green Chemistry by Nano-Catalysis. *Green Chemistry* **2010**, *12*, 743–754.
- (13) Han, X.; Kuang, Q.; Jin, M.; Xie, Z.; Zheng, L. Synthesis of Titania Nanosheets with a High Percentage of Exposed (001) Facets and Related Photocatalytic Properties. *Journal of the American Chemical Society* **2009**, *131*, 3152–3153.
- (14) Zhang, S.; Nguyen, L.; Zhu, Y.; Zhan, S.; Tsung, C.-K. F.; Tao, F. F. In-Situ Studies of Nanocatalysis. *Accounts of Chemical Research* **2013**, *46*, 1731–1739.
- (15) Jang, J.; Lee, Y.; Yoon, J.-Y.; Yoon, H. H.; Koo, J.; Choe, J.; Jeon, S.; Sung, J.; Park, J.; Lee, W. C.; Lee, H.; Jeong, H. Y.; Park, K.; Kim, K. One-Dimensional Assembly on Two-Dimensions: AuCN Nanowire Epitaxy on Graphene for Hybrid Phototransistors. *Nano Letters* **2018**, *18*, 6214–6221.
- (16) Lee, Y.; Koo, J.; Lee, S.; Yoon, J.-Y.; Kim, K.; Jang, M.; Jang, J.; Choe, J.; Li, B.-W.; Le, C. T.; Ullah, F.; Kim, Y. S.; Hwang, J. Y.; Lee, W. C.; Ruoff, R. S.; Cheong, H.; Cheon, J.; Lee, H.; Kim, K. Universal Oriented van der Waals Epitaxy of 1D Cyanide Chains on Hexagonal 2D Crystals. *Advanced Science* **2020**, *7*, 1900757.
- (17) Bhappu, R. B. Hydrometallurgical Processing of Precious Metal Ores. *Mineral Processing and Extractive Metallurgy Review* **1990**, *6*, 67–80.
- (18) Vahrenkamp, H.; Gei, A.; Richardson, G. N. Cyanide-Bridged Oligonuclear Complexes: Features and Attractions. *Journal of the Chemical Society, Dalton Transactions* **1997**, *0*, 3643–3652.
- (19) Matthews, C. N.; Minard, R. D. Hydrogen Cyanide Polymers, Comets and the Origin of Life. *Faraday Discussions* **2006**, *133*, 393–401.
- (20) Corain, B. The Coordination Chemistry of Hydrogen Cyanide, Cyanogen and Cyanogen Halides. *Coordination Chemistry Reviews* **1982**, *47*, 165–200.

- (21) Wang, S.; Goronzy, D. P.; Young, T. D.; Wattanatorn, N.; Stewart, L.; Baše, T.; Weiss, P. S. Formation of Highly Ordered Terminal Alkyne Self-Assembled Monolayers on the Au{111} Surface through Substitution of 1-Decaboranethiolate. *The Journal of Physical Chemistry C* **2019**, *123*, 1348–1353.
- (22) Schermelleh, L.; Ferrand, A.; Huser, T.; Eggeling, C.; Sauer, M.; Biehlmaier, O.; Drummen, G. P. C. Super-Resolution Microscopy Demystified. *Nature Cell Biology* **2019**, *21*, 72–84.
- (23) Zhang, R.; Zhang, Y.; Dong, Z. C.; Jiang, S.; Zhang, C.; Chen, L. G.; Zhang, L.; Liao, Y.; Aizpurua, J.; Luo, Y.; Yang, J. L.; Hou, J. G. Chemical Mapping of a Single Molecule by Plasmon-Enhanced Raman Scattering. *Nature* **2013**, *498*, 82–86.
- (24) Ding, S.-Y.; Yi, J.; Li, J.-F.; Ren, B.; Wu, D.-Y.; Panneerselvam, R.; Tian, Z.-Q. Nanostructure-Based Plasmon-Enhanced Raman Spectroscopy for Surface Analysis of Materials. *Nature Reviews Materials* **2016**, *1*, 1–16.
- (25) Schultz, J. F.; Li, S.; Jiang, S.; Jiang, N. Optical Scanning Tunneling Microscopy Based Chemical Imaging and Spectroscopy. *Journal of Physics: Condensed Matter* **2020**, *32*, 463001.
- (26) Böckmann, H.; Müller, M.; Hammud, A.; Willinger, M.-G.; Pszona, M.; Waluk, J.; Wolf, M.; Kumagai, T. Near-Field Spectral Response of Optically Excited Scanning Tunneling Microscope Junctions Probed by Single-Molecule Action Spectroscopy. *The Journal of Physical Chemistry Letters* **2019**, *10*, 2068–2074.
- (27) Centrone, A. Infrared Imaging and Spectroscopy Beyond the Diffraction Limit. *Annual Review of Analytical Chemistry* **2015**, *8*, 101–126.
- (28) Zrimsek, A. B.; Chiang, N.; Mattei, M.; Zaleski, S.; McAnally, M. O.; Chapman, C. T.; Henry, A.-I.; Schatz, G. C.; Van Duyne, R. P. Single-Molecule Chemistry with Surface- and Tip-Enhanced Raman Spectroscopy. *Chemical Reviews* **2017**, *117*, 7583–7613.
- (29) Claridge, S. A.; Schwartz, J. J.; Weiss, P. S. Electrons, Photons, and Force: Quantitative Single-Molecule Measurements from Physics to Biology. *ACS Nano* **2011**, *5*, 693–729.

- (30) Moerner, W. E.; Fromm, D. P. Methods of Single-Molecule Fluorescence Spectroscopy and Microscopy. *Review of Scientific Instruments* **2003**, *74*, 3597.
- (31) Bowmaker, G. A.; Kennedy, B. J.; Reid, J. C. Crystal Structures of AuCN and AgCN and Vibrational Spectroscopic Studies of AuCN, AgCN, and CuCN. *Inorganic Chemistry* **1998**, *37*, 3968–3974.
- (32) Pettinger, B.; Picardi, G.; Schuster, R.; Ertl, G. Surface-Enhanced and STM Tip-Enhanced Raman Spectroscopy of CN^- Ions at Gold Surfaces. *Journal of Electroanalytical Chemistry* **2003**, *554-555*, 293–299.
- (33) Gao, P.; Weaver, M. J. Metal-Adsorbate Vibrational Frequencies as a Probe of Surface Bonding: Halides and Pseudohalides at Gold Electrodes. *The Journal of Physical Chemistry* **1986**, *90*, 4057–4063.
- (34) Chadwick, B. M.; Frankiss, S. G. Vibrational Spectra and Structures of Some Dicyanoaurate(I) Complexes. *Journal of Molecular Structure* **1976**, *31*, 1–9.
- (35) Zaleski-Ejgierd, P.; Patzschke, M.; Pykkö, P. Structure and Bonding of the MCN Molecules, $\text{M}=\text{Cu,Ag,Au,Rg}$. *The Journal of Chemical Physics* **2008**, *128*, 224303.
- (36) Bozzini, B.; Fanigliulo, A. An in Situ Spectroelectrochemical Raman Investigation of Au Electrodeposition and Electrodissolution in KAu(CN)_2 Solution. *Journal of Applied Electrochemistry* **2002**, *32*, 1043–1048.
- (37) Murgich, J.; Oja, T. Nitrogen-14 Nuclear Quadrupole Resonance Study of Bonding in Transition-Metal Cyanides. *Journal of the Chemical Society, Dalton Transactions* **1987**, 1637–1640.
- (38) Khramov, D. M.; Lynch, V. M.; Bielawski, C. W. *N*-Heterocyclic Carbene Transition Metal Complexes: Spectroscopic and Crystallographic Analyses of π -Back-bonding Interactions. *Organometallics* **2007**, *26*, 6042–6049.
- (39) Weiss, P. S. Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements. *Accounts of Chemical Research* **2008**, *41*, 1772–1781.

- (40) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. Surface Studies by Scanning Tunneling Microscopy. *Physical Review Letters* **1982**, *49*, 57–61.
- (41) Kuk, Y.; Silverman, P. J. Scanning Tunneling Microscope Instrumentation. *Review of Scientific Instruments* **1989**, *60*, 165–180.
- (42) Hohman, J. N.; Zhang, P.; Morin, E. I.; Han, P.; Kim, M.; Kurland, A. R.; McClanahan, P. D.; Balema, V. P.; Weiss, P. S. Self-Assembly of Carboranethiol Isomers on Au{111}: Intermolecular Interactions Determined by Molecular Dipole Orientations. *ACS Nano* **2009**, *3*, 527–536.
- (43) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H.-P. Adsorbate-Substrate Vibrational Modes of Benzene on Ag(110) Resolved with Scanning Tunneling Spectroscopy. *Physical Review Letters* **2001**, *86*, 1050–1053.
- (44) Yamada, T.; Sekine, R.; Sawaguchi, T. Ultrahigh-Vacuum Multitechnique Study of AuCN Monolayers on Au(111) Formed by Electrochemical Deposition. *The Journal of Chemical Physics* **2000**, *113*, 1217–1227.

CHAPTER 2

Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}

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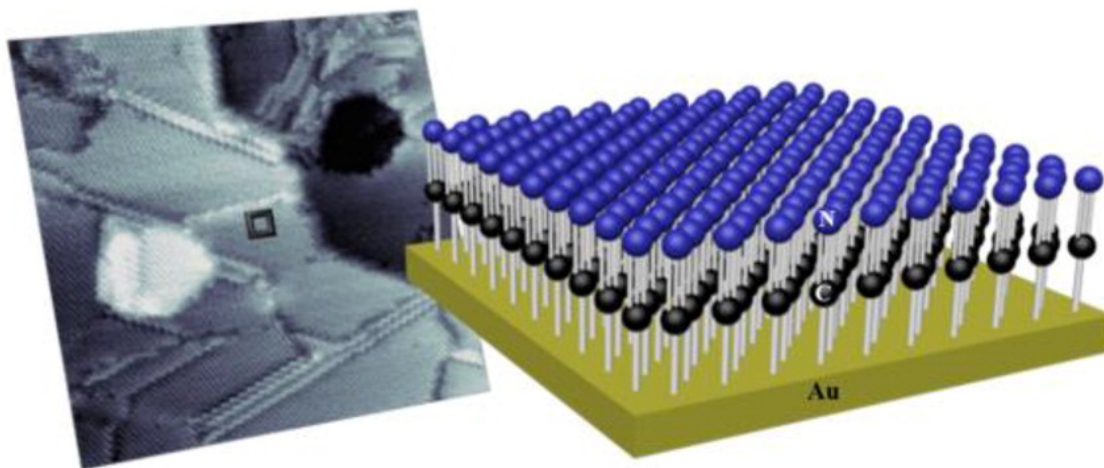


Figure 2.1: AuCN on top of gold surfaces.

2.1 Abstract

A vibronic resonance between Au{111} surface states and adsorbed CN vibrations has been predicted, which we target for study. We have formed stable monolayers of cyanide on Au{111} and observe a hexagonal close-packed lattice with a nearest neighbor distance of 3.8 ± 0.5 Å. Cyanide orients normal to the surface attached via a Au–C bond. We show that the substrate-molecule coupling is particularly strong, leading to ultrafast electron transfer from the cyanide molecules to the Au{111} substrate as measured by resonant Auger spectroscopy using the core-hole clock method. The CN/Au{111} system is a simple example of a strongly interacting adsorbate-substrate system and will be the subject of a number of further studies, as discussed.

2.2 Introduction

A central theme in nanotechnology is to be able to understand and to manipulate materials at the single-molecule level to advance current technologies and to create new technologies. Self-assembled monolayers (SAMs), in which a single layer of molecules are immobilized on a surface, have often served as platforms for probing the effects of the local environment on molecular structure and function as well as for the development of new materials with distinct physical and chemical properties.^{1–8}

Adsorbate-substrate interactions due to immobilization on surfaces strongly influence the function, dynamics, structure, and electronic properties of molecules in SAMs.^{9–12} In some cases, as we have demonstrated in our previous work, we can tune the monolayer matrix defect density to affect the function and/or reactivity of molecules that have been tethered to surfaces.^{13–18} In other cases, the functional group has been decoupled from the surface through molecular ‘spacers’ to avoid substrate quenching effects from efficient electron transfer.^{13,19} Along with affecting electron transport, coupling between the surface electronic structure and molecular vibrations has been observed to enhance the lifetimes and intensities of vibrational modes.^{20,21}

Two primary factors, the strength of the electronic coupling between an adsorbed molecule and substrate and the orientation of the molecular orbitals used during transport directly influence how efficiently an electron is transmitted between molecules to the substrate in SAMs.^{22–27} To this end, electron conductance through nitrile-terminated alkanethiol SAMs has been observed to follow an exponential dependence on molecule length with a characteristic decay rate through the application of the core-hole clock (CHC) method in resonant Auger electron spectroscopy (RAES).^{25,28,29} These results have shown that inclusion of a four-carbon backbone results in approximately 100× lower efficiency for transferring electrons to the Au{111} substrate with average times of ~ 100 fs, when compared with the ~ 2.5 fs transfer time across only the thiolate head group.³⁰ These data are consistent with other measures of contact conductance.^{10,23,24,26,31} The results presented in this work represent the extreme case where the sulfur and carbon backbone are entirely removed and only the nitrile functional group is bound to the Au{111} surface.

Often, the substrate-molecule interface is buried and difficult to probe, requiring special techniques that leverage the well-known chemistry and relatively simple structure of small-molecule probes. One such small molecule is CO, which has been used to elucidate the effect of binding sites on adsorbate vibrational modes.³² Nevertheless, in the case of CO, as with many small molecules that desorb from surfaces well below room temperature, the ambient environment applications are limited. An established coordination chemistry between cyanide and gold³³ has already been leveraged to elucidate the prevalent chemistry, and structure of defects in alkanethiol monolayers,^{34,35} to assemble metal-molecule coordination polymers,^{36,37} and to probe covalent bond formation between gold atoms,³⁸ in addition to a component in the fabrication/or synthesis of conductive carbon nitride nanomaterials.³⁹ The coordination complexes formed between cyanide and gold are stable at room temperature. Our previous attempts to assemble CN on Au{111} failed when cyanogen, C_2N_2 , did not dissociate under the conditions used.⁴⁰ In recent work, we have shown that processing the following as described here, we can also create monolayers and mixed orientations.⁴¹ Isocyanide⁴² and carbene⁴³ systems have already demonstrated the potential for room temperature self-assembly using Au–C as an alternative to the Au–S bond characterizing thiol

systems.

Here, we report the direct observation of the formation of a cyanide SAM on Au{111} under ambient conditions and probe the strength of the Au–CN coupling. Cyanide assembles into a highly ordered, stable, upright monolayer on Au{111} through the formation of a Au–C bond, most likely due to the known gold cyanidation reaction,⁴⁴ with a similar surface structure to that observed in SAMs of alkanethiols.^{4,5,45} Electron-transfer dynamics are measured by RAES using the core-hole clock method and indicate facile transfer from molecule to the Au{111} substrate. We conclude by discussing electronic, vibration, and structural properties as they relate to substrate-molecule coupling strength and future prospects for the CN/Au{111} system as a platform to study the interactions between molecular vibrations and electronic structure.

2.3 Experimental Methods

Several different Au{111} substrates were used in this study, depending on the specific requirements and parameters of individual experimental techniques. Monolayers of cyanide were prepared in the same fashion for all these substrates, viz. by placing 0.1 mg of solid KCN ($\geq 96\%$, Sigma Aldrich, St. Louis, MO), without any further purification or treatment, in a glass vial with the Au{111} substrate for 24 h at room temperature. **Caution: KCN is highly toxic and produces the volatile and flammable HCN(*g*) when it reacts with water and oxygen. It should be used with proper personal protective equipment, in a fume hood, and kept out of extreme temperatures.** Afterwards, the Au{111} substrate was removed from the vial with the KCN and either measured directly or after a short delay or stored under inert gas for delivery to the synchrotrons (see below for details). The monolayers of cyanide were characterized by scanning tunneling microscopy (STM), infrared (IR) spectroscopy, surface-enhanced Raman spectroscopy (SERS), synchrotron-based X-ray photoelectron spectroscopy (XPS), angle-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and resonant Auger electron spectroscopy (RAES). Consequently, after the general description of the sample preparation procedure,

specific substrates will be described before the description of the particular experiments, viz. STM, IR, SERS, and high-resolution XPS/NEXAFS.

For the STM experiments, Au{111}/mica substrates (150 nm of Au{111}, Agilent Technologies, Santa Clara, CA) were used. The substrates were hydrogen flame annealed, as described previously, to clean the surface and to increase the sizes of the atomically flat terraces.^{4,46} After preparation, cyanide monolayers (see above) were allowed to rest in the fume hood for 1 h before being placed in the STM for imaging.

A custom-built, beetle-style STM was used under ambient conditions. All STM images were calibrated against known references: gold step edges for height and a decanethiol on Au{111} SAM matrix for lateral distance measurements. All analyses on STM images were performed using custom software and Matlab.^{47,48}

For collecting IR spectra on Au{111}, we used custom-made Au{111}/sapphire prism substrates. Prism substrates were 0.5 cm radius, 1 cm height c-cut sapphire half-cylinders with a 2-nm-thick Nb adhesion layer deposited at 0.11 Å/s and a 40-nm-thick layer of Au, which is well below the optical penetration depth for metals in the range of the IR frequencies of interest,⁴⁹ deposited at a rate of 0.5 Å/s. A bare Au{111}/sapphire prism sample was used for the background spectrum and an incident angle $\theta = 60^\circ > \theta_c = 34.6^\circ$ as measured from normal to the surface (critical angle calculated using $n = 1.76$ and Snell's Law, $\theta_c = \sin^{-1}(1/n)$).⁴⁹ Infrared spectra were collected using a Thermo-Fisher Nicolet 8700 Interferometer (Thermo-Fisher Scientific, Waltham, MA), and the packaged OMNIC Software (Thermo-Fisher Scientific). The OMNIC software was also used for processing the spectra and identifying peak positions. All samples used for IR measurements were incubated with KCN in the same manner as described for the STM samples. After incubation, both STM and IR samples were directly analyzed without rinsing.

Surface-enhanced Raman spectroscopy (SERS) was performed on a Renishaw confocal Raman microscope (Renishaw, Inc., Hoffman Estates, Illinois) configured with a laser at 514 nm wavelength, using WiRE 3.2 (Renishaw, Inc.) for spectral processing and analysis. Two substrates designed for surface enhancement were used in this work: Au{111}/mica with

nanohole arrays and nanostructured Au on glass. The nanohole arrays (175 nm diameter, 300 nm periodicity) on Au{111}/mica were fabricated using a focused ion beam.⁵⁰ The nanostructured Au on glass substrates were made by evaporating 50-Å-thick Au at 1 Å/s onto a glass slide and annealing at 400 °C for 24 h. All the SERS substrates were annealed and incubated in the same manner as the STM/IR samples.

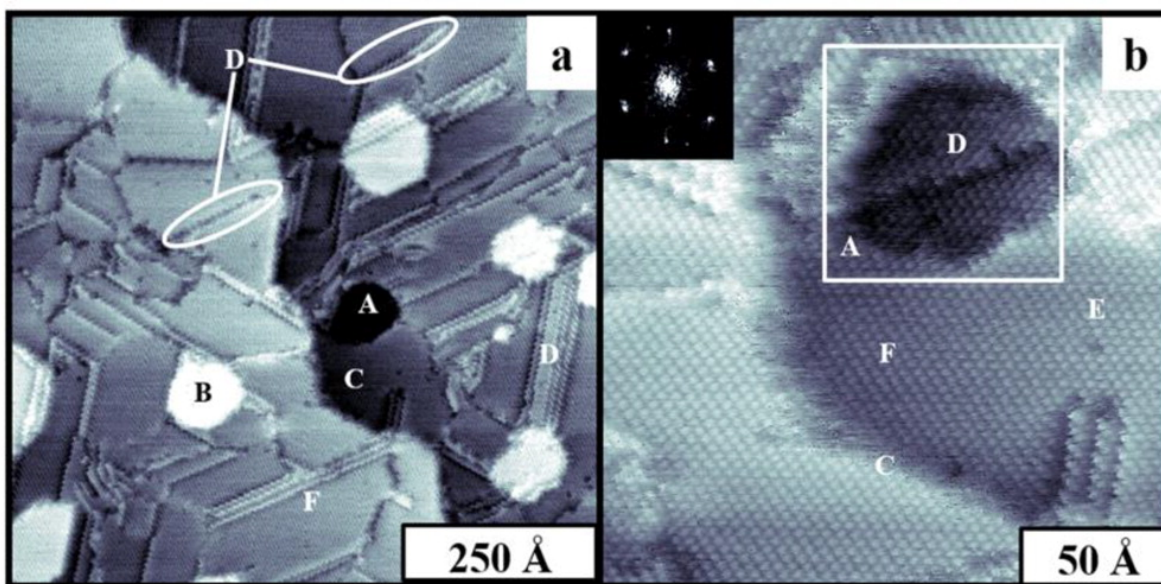
The gold substrates for the XPS, NEXAFS spectroscopy, and RAES experiments were prepared by polished single-crystal silicon (100) wafers (Silicon Sense, Nashua, NH) primed with a 10-nm chromium adhesion layer. The resulting metal films were polycrystalline with grains exhibiting the (111) orientation and sizes of 20–50 nm. After preparation of the cyanide monolayers (see above), the samples were put into glass containers and stored under inert gas atmosphere until characterization at the synchrotron (see below). The measurements were performed at room temperature and under ultrahigh vacuum conditions (base pressure $<1.5 \times 10^{-9}$ mbar). The spectral acquisition time at a particular sample spot was kept sufficiently short to avoid possible damage by the primary X-rays occurring during the measurements.^{51,52}

The experiments were performed at the HE-SGM beamline (bending magnet) of the synchrotron storage ring BESSY II in Berlin, Germany and at the D1011 beamline (bending magnet, plane grating monochromator) of the MAX II storage ring at the MAX-IV laboratory in Lund, Sweden. The experimental stations at both facilities were equipped with a Scienta electron energy analyzer (R3000 at HE-SGM and SES200 at D1011) and a partial electron yield (PEY) detector. All experimental adjustments were exactly the same at both beamlines, except for somewhat better energy resolution at D1011 (~ 70 meV vs. ~ 0.3 eV at HESGM) and a minor difference in the polarization factor of the primary X-ray light, viz. 91% at HESGM and 95% at D1011. The experiments were repeated several times with the same results within experimental error. Independent sets of samples were used.

X-ray photoelectron spectra were recorded with a normal emission geometry at excitation energies of 350 and 580 eV. Synchrotron light was used as the primary X-ray source. The binding energy (E_B) scale of the spectra was referenced to the Au 4f_{7/5} peak at a $E_B = 84.0$ eV.⁵³ The spectra were fit by symmetric Voigt functions and a Shirley-type background.⁴³

The acquisition of the NEXAFS spectra was carried for the carbon and nitrogen regions in the PEY mode with retarding voltages of -150 V and -300 V, respectively. Linearly polarized synchrotron light was used as the primary X-ray source. The incidence angle of X-rays was varied from 90° ($\mathbf{E}$ vector in the surface plane) to 20° ($\mathbf{E}$ vector near the surface normal) in steps of 10 – 20° to monitor the molecular orientation in the SAMs. This approach is based on the dependence of the cross section of the resonant photoexcitation process on the orientation of the electric field vector of the synchrotron light with respect to the molecular orbital of interest (so-called linear dichroism in X-ray absorption).⁵⁴ The energy scale was calibrated by means of the most intense π^* resonance of highly oriented pyrolytic graphite at 285.38 eV⁵⁵ in combination with the well-known $\Delta h\nu \propto (h\nu)^{3/2}$ behavior of plane grating monochromators.⁵⁶

The RAES spectra were acquired using either a Scienta R3000 electron energy analyzer (BESSY II) or a SCIENTA SES200 spectrometer (Max-lab). The X-ray incidence angle was set to 55° to suppress possible orientational effects;⁵⁴ the take-off geometry of the electrons was close to normal emission. Resonant excitation was performed at the nitrogen K-edge, at the position of the $\pi(\text{CN}^*)$ resonance. The excitation energy was determined in the preliminary NEXAFS experiments. In addition, non-resonant Auger electron spectra were recorded at an excitation energy of 5 – 6 eV above the absorption edge. This setting was mimicked from similar experiments on nitrile-substituted SAMs on $\text{Au}\{111\}$, where it was found to be optimal in order to maximize the signal-to-noise ratio and to avoid appearance of interfering gold photoemission in the spectra.²⁵ Finally, for every sample, a reference spectrum for the pre-edge excitation was measured. This spectrum was subtracted from the RAES and non-resonant AES spectra to correct them for a contribution to the photoemission that could not be avoided completely.



$$V_{\text{tip}} = 1.00 \text{ V}, I_{\text{tunnel}} = 5.00 \text{ pA}$$

A – Substrate Vacancy Island	B – Molecular Mesa
C – Step Edge	D – Domain Boundary
E – Single-Molecule Vacancy	F – Highly Ordered Region

Figure 2.2: Scanning tunneling microscope images of the surface structure of cyanide monolayers on Au{111} at room temperature. (a) The morphology of the cyanide monolayers with representative surface structures denoted by letters A–F in the image and schematic of cyanide with aligned dipole C $\rightarrow$ N, positive $\rightarrow$ negative. (b) Molecular resolution images and corresponding Fourier transform showing the hexagonally close-packed lattice with a nearest neighbor distance of $3.8 \pm 0.5 \text{ Å}$.

2.4 Results

2.4.1 Scanning Tunneling Microscopy – Molecular Resolution of Surface Structure

The STM image in Figure 2.2a shows the structural details of monolayers of cyanide formed from exposure of Au{111} to HCN(*g*) at room temperature and humidity, most likely due to the established gold cyanidation redox reaction that involves water and oxygen.^{33,44} In comparison to the relatively featureless AuCN monolayers on Au{111} in solution, which is formed through electrochemical deposition,⁵⁷ cyanide molecules deposited in this manner are arranged into numerous, highly ordered domains, one-atom deep substrate vacancy islands, and one-atom high substrate mesas. At this resolution, the surface morphology closely resembles alkanethiol SAMs, which are also observed to form hexagonally close-packed (HCP) lattices that contain single-substrate-atom deep vacancy islands and domain boundaries^{4,11,45} with the exception of the mesas and the simpler domain boundary structures here. The observed loss of the Au{111} herringbone structure and the appearance of vacancy islands indicate removal of the reconstruction of the underlying gold lattice and the relatively strong molecule-substrate interactions.^{4,11,45,58} This change is not surprising; the thiolate Au–S bond reported at ~ 2 eV^{4,45} is weaker than the Au–C bond reported at > 2.4 eV,^{59,60} and the alkanethiol system also removes the reconstruction of the underlying Au{111} lattice.^{4,11,45} Note that the existence of a strong dipole of the cyanide molecule,⁶¹ (positive $\rightarrow$ negative, C $\rightarrow$ N, see schematic in Figure 2.2) axis is a significant property difference from alkanethiol monolayers on Au{111} that can be leveraged to elucidate dipole-mediated interactions.^{23,62,63}

Higher resolution images (Figure 2.2b) reveal the arrangement of individual molecules that are positioned in a HCP arrangement. In addition to the previously mentioned structures, missing single-molecule vacancies can be observed in the molecular lattice. A Fourier transform of the STM image in Figure 2.2b (inset) shows a hexagonal lattice with the first-order reciprocal lattice spots displayed. The distance from the center in Fourier space to one of the frequency modes corresponds to an average measured nearest neighbor distance of 3.8 ± 0.5 Å and was obtained using measurements from > 50 images of different sample

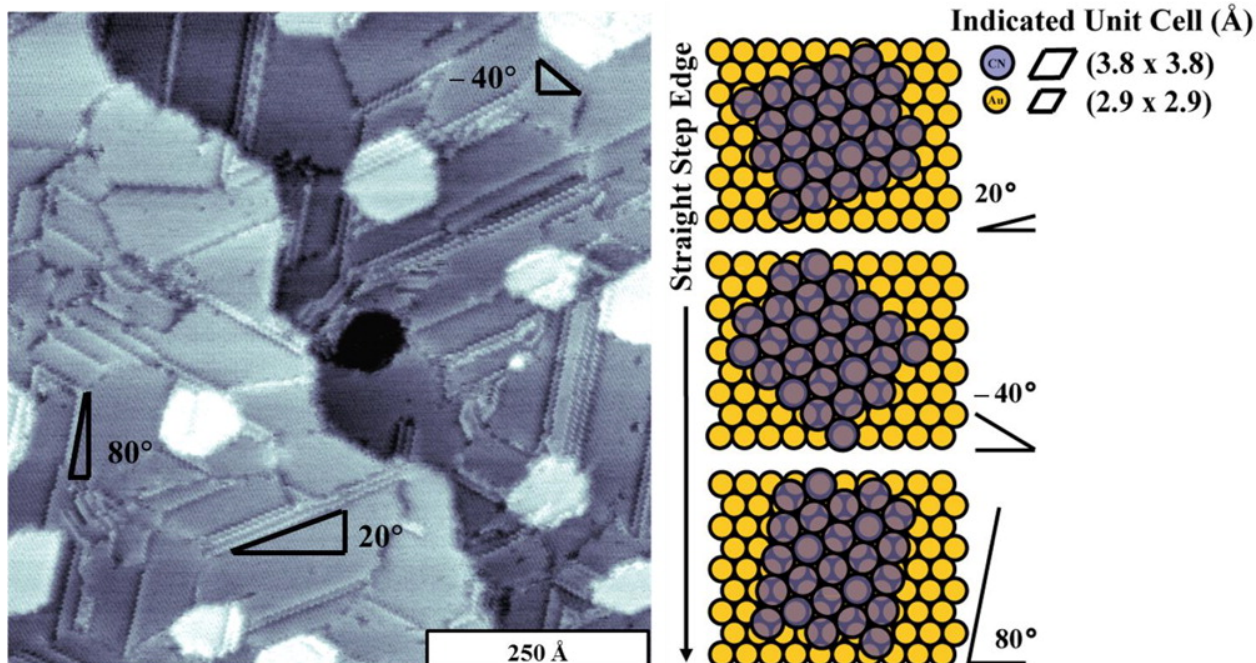


Figure 2.3: Scanning tunneling microscope image of CN on Au{111} as deposited at room temperature and structural schematics. Using the Au close-packed substrate direction with respect to straight step edges ($\langle 0\ 1\ 0 \rangle$), we find molecules bind to bridge and atop positions with a ($3.8\ \text{\AA} \times 3.8\ \text{\AA}$) cyanide unit cell at 20, -40 , and 80° orientations with respect to the unreconstructed underlying gold lattice. The dark, larger circles represent the projection of the cyanide molecules on the smaller circles representing the atoms of the Au{111} lattice. Triangles representing examples of the identified orientations relative to the Au{111} lattice are aligned with cyanide domain boundaries and are identified as high-symmetry directions representative of the hexagonally close-packed arrangement.

regions from >10 different samples. These measurements agree well with reported Au–Au bond spacing in gold-cyanide crystals.^{36,38,64} All images were obtained and calibrated against a known SAM of decanethiol on Au{111} before and directly after imaging cyanide to minimize measurement error. Using the calculated nearest neighbor spacing, the Au lattice spacing of $2.89\ \text{\AA}$, and the HCP arrangement, the surface packing density for cyanide on Au{111} was calculated to be approximately 1 CN molecule per 1.3 Au atoms. This result differs slightly from the bonding configuration in most coordination complexes composed of gold and cyanide where multiple cyanide molecules bind to one gold atom.

The specific rotational orientation of the monolayer with respect to the underlying gold lattice is determined with respect to the close-packed direction of the Au{111} formed along straight step edges.⁶⁵ The schematic in Figure 2.3 uses dark circles to represent the space-filling projection of the cyanide molecules on the surface using the spatial measurements from the STM images. We find that at the 20°, -40°, and 80° in-plane rotations with respect to the underlying gold lattice that bound cyanide molecules primarily occupied the two-fold bridge site with the remaining minority aligned with atop positions. The two-fold bridge location has been calculated to be the one of the most stable surface locations based on DFT calculations for cyanide bonding to Au{100}, Au{110}, and Au{111}.⁶⁶ These in-plane orientational rotations are identified as black triangles in the STM image included in Figure 2.3 when aligning with monolayer domain boundaries and can be seen to be examples of high symmetry points maintaining the characteristic 60° rotations of the HCP arrangement. In comparison, all other angles introduced binding at three-fold hollow sites, reduced the number of two-fold bridges, and were observed less frequently than these other rotations in STM images via domain boundary inspection.

Representative Au 4f_{7/5} (a), C 1s (b), and N 1s (c) XPS spectra of NC/Au{111} are shown in Figure 2.4. The Au 4f_{7/5} spectra in Figure 2.4a exhibit a weak shoulder at the high E_B side of the main emission, at a E_B of 84.95 eV. The appearance of this shoulder is attributed to the effects of adsorbed NC, which is strong and, in its extent, is similar to the oxidation of the gold substrate.⁶⁷ Significantly, only the topmost layer of the Au{111} substrate is affected, as seen from the direct comparison of the spectra acquired at PEs of 350 and 580 eV in Figure 2.4a. Due to the strong dependence of the sampling depth of XPS on the kinetic energy of photoelectrons,⁶⁸ the contribution of the surface as compared to bulk should be much weaker in the latter case and, indeed, the high E_B shoulder decreases significantly in intensity at a PE of 580 eV as compared to 350 eV. Further, the intensity relation between the shoulder and the main emission in the 350 eV spectrum can be compared to the analogous relation in the spectrum of clean Au{111}, where the contributions of the topmost layer and the bulk can be straightforwardly distinguished.⁵² Accordingly, the shoulder is indeed exclusively related to the topmost layer of the Au{111} substrate, corresponding, according to its spectral weight,

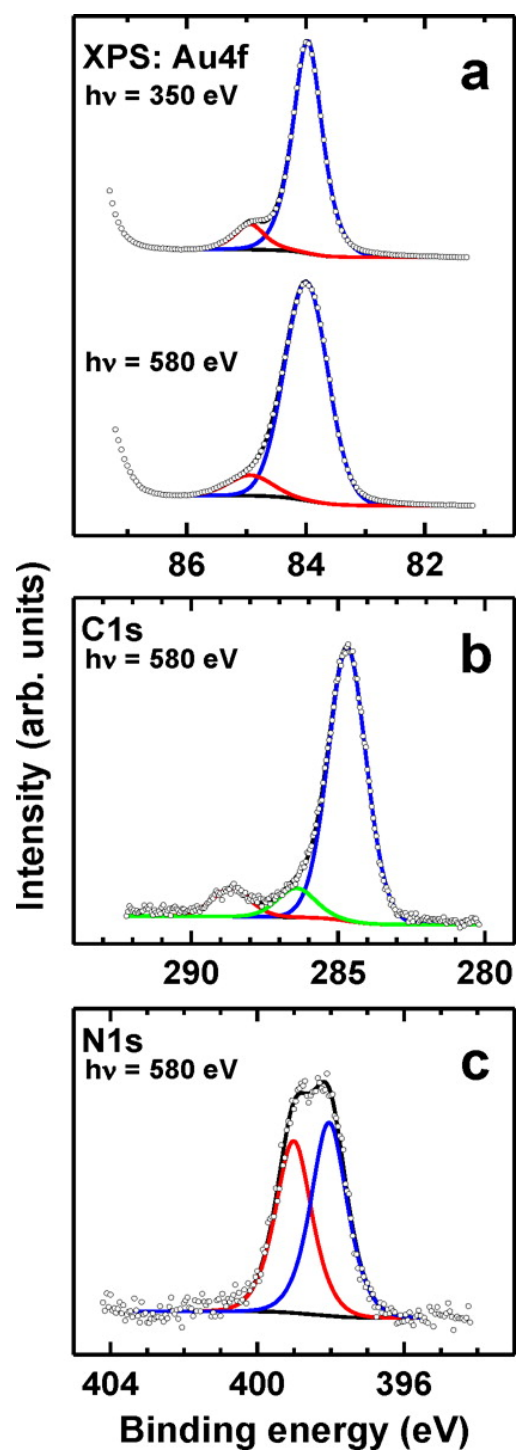


Figure 2.4: Au $4f_{7/2}$ (a), C 1s (b), and N 1s (c) X-ray photoelectron spectra of NC/Au{111} acquired at photon energies of either 350 or 580 eV as marked in the panels (open circles). The spectra are fit and decomposed into individual contributions (thin solid lines). See text for details.

to 25–30% of atoms in this layer.⁶⁹

The C 1s XP spectrum of NC/Au{111} in Figure 2.4b exhibits strong emission at ~ 284.7 eV accompanied by two weak peaks at ~ 286.4 eV and ~ 288.65 eV. The dominant emission can be assigned to the adsorbed NC molecules while the low intensity peaks presumably stem from contamination, most likely CO (~ 286.4 eV) and COOH (~ 288.65 eV).⁷⁰ Such contamination can hardly be avoided considering the ultimate thinness of the NC monolayer and its exposure to ambient in the course of the sample handling. However, the formation of well-ordered monolayers, as indicated by the STM images, suggests that such contamination is inconsequential. As to dominant emission, note for comparison that, as expected, its E_B is much lower than that of the nitrile carbon in SAMs of the nitrile-substituted alkanethiols, NC – (CH₂)_n – SH (NC – C_n) on Au{111}, e.g., 286.2 eV at $n = 3$.³⁰ The lower E_B in the case of NC/Au{111} can be attributed to the direct bonding of NC to the substrate (chemical shift) as well as to more efficient screening of the photoemission hole by the substrate electrons (the screening effect scales according to the Coulomb potential, i.e., is proportional to $1/r$).

The N 1s XP spectrum of NC/Au{111} in Figure 2.4c exhibits a broad peak that can be tentatively decomposed into two individual emissions at ~ 398.1 and ~ 399.0 eV, with the former emission being more intense. This emission can be unequivocally attributed to the CN molecules attached to the substrate over C–Au bond. The E_B of 398.1 eV correlates well with the respective E_B for the NC-alkyl SAMs on Au{111}, viz. 398.84 eV for the NC – C₂H₄S film and 398.98 eV for the NC – C₃H₆S monolayer,³⁰ being noticeably smaller than these values because of the stronger proximity on CN to the substrate in the case of NC/Au{111} (see discussion regarding the C 1s spectrum). The value of ~ 399.0 eV is even higher than the value of 398.84 eV for the NC – C₂H₄S film on Au{111} suggesting that the respective species are bound only weakly to the substrate, probably in a physisorbed fashion, or, most likely, CNH or CN – H₂O species. It is well known that the protonation or association with H₂O shifts the N 1s binding energy to higher values.^{71–73} The C atom attached directly to the metal substrate will not be affected strongly by this process, resulting in only a small binding energy shift and, consequently, in only one joint C 1s emission.

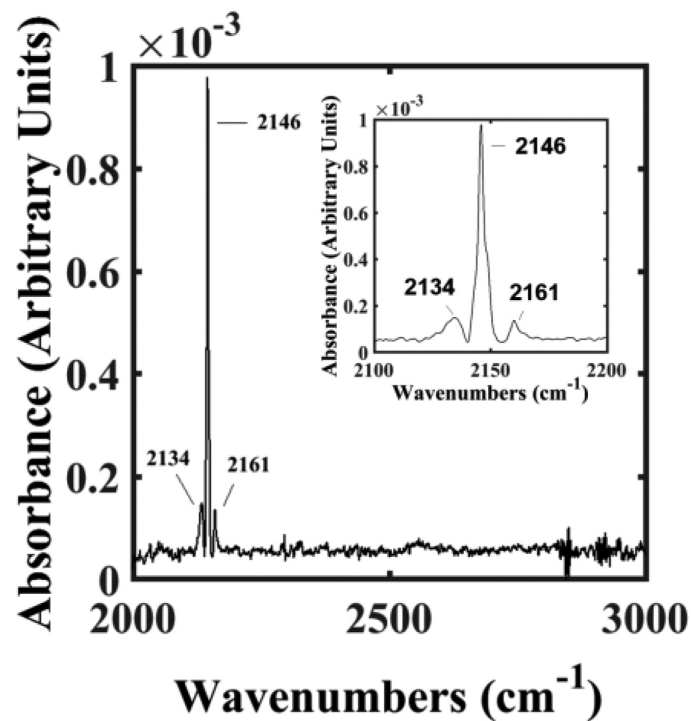


Figure 2.5: Attenuated total reflection Fourier transform infrared spectrum of CN/Au{111} using custom sapphire prism substrates and showing the CN stretch at 2146 cm^{-1} along with two side peaks at 2134 and 2161 cm^{-1} . The inset is an enlargement of the region of the spectrum containing the CN vibration.

2.4.2 Vibrational Spectroscopy – Connectivity

To determine the chemical state and identity of cyanide molecules on Au{111}, we utilized attenuated total internal reflection Fourier transform infrared spectroscopy (ATR-FTIR). The IR absorption spectrum of Au{111} after exposure to HCN(*g*) is shown in Figure 2.5. The primary CN stretching mode, as shown in the inset of Figure 2.5, detected at 2146 cm^{-1} on the Au{111} is in good agreement with spectra for cyanide adsorbed on the surface of gold electrodes in a cyanide solution,⁷³ is red shifted when compared to the $2200\text{--}2300\text{ cm}^{-1}$ range given for the nitrile functional group,⁷⁴ and shows the typical blue shift due to substrate coupling from the approximately 2080 cm^{-1} for the free cyanide ion in solution^{73,75,76} (see Table 2.1 for comparisons). We observed two small side peaks at 2134 and 2161 cm^{-1} on the Au{111} surface using ATR-FTIR, which is more sensitive to thin films, on either side of the larger, distinct CN stretch at 2146 cm^{-1} . These two additional modes are also likely attributed to the CN stretch, supporting the nitrogen XPS results suggesting different surface states exist for cyanide molecules on the surface. The asymmetric side peaks are not detected for CN adsorbed on polycrystalline Au⁷³ most likely because the same amount of order cannot be achieved due to the amorphous nature of the surface (see Supplementary Figure A.1 and Figure A.2 for more detailed comparisons).

No vibrational modes were identified near 3300 cm^{-1} for the CH vibrational mode of the HCN molecule (also shown in Table 2.1).⁷⁷ This observation is consistent with deprotonation during monolayer formation. All spectral measurements were recorded with a bare Au surface as a reference that showed no peaks in the region of interest; peak locations were reproducible over different samples and days.

Raman spectroscopy was used to detect low-frequency, substrate-adsorbate binding modes and the high-frequency internal stretching mode. The Raman spectra for Au{111} and polycrystalline Au nanoparticles (NPs) after exposure to HCN(*g*) are shown in Figures 2.6a and 2.6b, respectively. The low-frequency modes detected around 304 and 400 cm^{-1} (see Figure 2.6c inset, Table 2.1 for comparisons) agree well with values reported for a Au–C stretch and a Au–C–N bend for cyanide ions adsorbed both on Au electrode surfaces in

Table 2.1: Comparison of the Different Vibration Energies for the Cyanide/Nitrile Group as a Ligand at Solution and Air Interfaces

substance	CN triple bond stretch cm^{-1}	CH single bond stretch cm^{-1}	CN triple bond Raman shift cm^{-1}	Au-C-N Raman shift cm^{-1}	Au-C Raman shift cm^{-1}	ref
CN/Au, solution	2105	N/A _a	2135	300	380	[73, 78]
Au(CN) ₂ ⁻ , solution	2146	N/A	2156	294	371	[73, 76]
AuCN, solid/crystal	2236	N/A	2230	358	598	[64]64
HCN, gas	2089	3312	N/A	N/A	N/A	[77]
CN ⁻ , solution	2080	N/A	N/A	N/A	N/A	[73, 75, 76]
CN/Au, air _b	2146	none	2140-2165, 2235	304	400	N/A
CN (nitrile)	220-2300	2900-3000	2248	N/A	N/A	[74, 79]

^aN/A - Not applicable

^bResults presented here

cyanide-ion-containing solution⁷⁸ and cyanide-coated gold nanoparticles.⁷⁶ No modes were detected in the 100-250 cm^{-1} region that is detected in linear chains of AuCN and are attributed to the CN–Au vibrational mode in solid AuCN.⁶⁴ However, we were only able to detect the low-frequency modes on the custom Au NP SERS surface, as the signal-to-noise ratio was much better on the Au NPs. The results are further evidence that the cyanide assemblies here attached through Au–C bonds, and not through nitrogen, maintaining the typical bonding scheme for gold-cyanide coordination complexes.^{33,38}

The high-frequency mode located at 2140 cm^{-1} for the Au NP’s detected by Raman compares well with the detected IR mode for the Au{111} substrate, but is blue shifted by 25 cm^{-1} when compared to the peak at 2165 cm^{-1} detected by Raman for CN/Au{111} and red shifted when compared with the 2248 cm^{-1} reported for the Raman spectra of the nitrile functional group.⁷⁹ The comparison with the nitrile group demonstrates that there is a significant difference in the balance between substrate-molecule and molecule-molecule interactions resulting from direct attachment to the Au surface. An additional peak, which is further evidence of different cyanide states, was located in the CN/Au{111} spectrum at 2235 cm^{-1} , a value that closely matches values reported for CN in solid AuCN crystals.⁶⁴ We note that all the Raman shifts detected on the polycrystalline Au NPs are blue shifted $\sim 20 \text{ cm}^{-1}$ compared to cyanide molecules adsorbed on Au{111}. The results presented here may be more accurate, as they are not complicated by dissolving the gold into the surrounding solution or applied electric fields.

2.4.3 Near-Edge X-Ray Absorption Fine Structure Spectroscopy – Molecular Orientation

C and N K-edge NEXAFS spectra of NC/Au{111} acquired at an X-ray incident angle of 55° are presented in Figure 2.7, along with the respective difference between the N K-edge spectra collected under the normal (90°) and grazing (20°) incidence geometry. Note that the “magic angle”, 55° spectra are free of orientational effects and, subsequently, only representative of the electronic structure of the studied systems.⁵⁴ In contrast, the difference

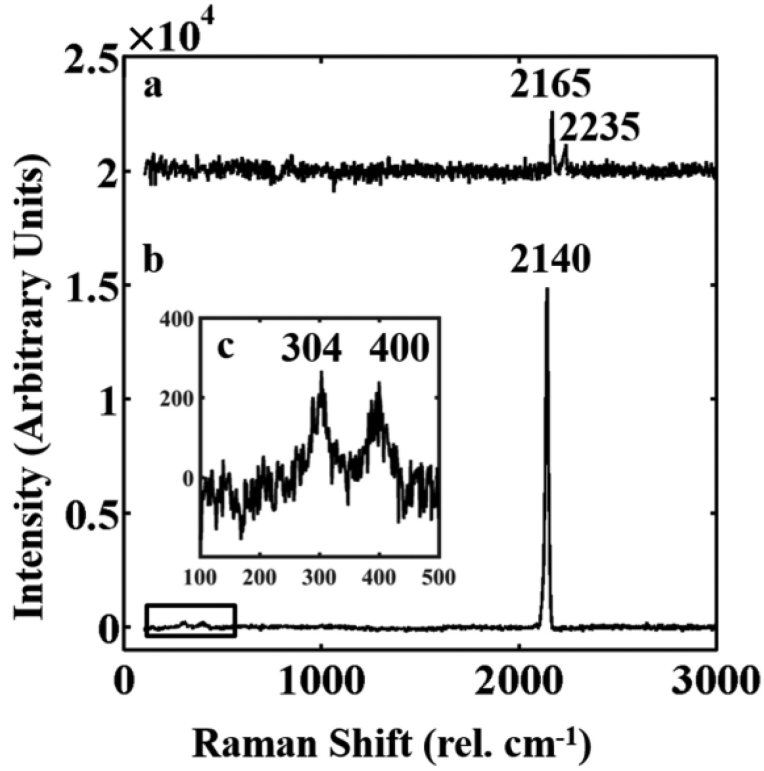


Figure 2.6: (a) Raman spectra of CN monolayers formed on Au{111} using a plasmonic nanohole array and (b) surface-enhanced Raman substrates made of polycrystalline Au nanoparticles evaporated onto glass. (c) The inset shows both the low frequency modes attributed to the substrate–molecule bond, Au–CN bend at 304 cm^{-1} , and Au–CN stretch at 400 cm^{-1} , which were only detected on the Au nanoparticles.

between the spectra acquired at normal and grazing incidence of X-rays are representative of the molecular orientation, averaged over the probed ensemble, relying on the linear dichroism effect in X-ray absorption.⁵⁴

The C K-edge spectrum of NC/Au{111} in Figure 2.7a exhibits several absorption resonances superimposed onto the absorption edge. These features include the $\pi^*(\text{C}=\text{C})$ resonance at 285.1 eV, the $\pi(\text{C}^*\equiv\text{N})$ resonance at 286.2 eV, and the $\pi^*(\text{COOH})$ at 288.5 eV (the assignments were made according to refs [30] and [53]). The $\pi^*(\text{C}=\text{C})$ and $\pi^*(\text{COOH})$ features stem from contamination while the $\pi(\text{C}^*\equiv\text{N})$ resonance is characteristic of the CN groups and is attributed to two (almost) degenerate, mutually orthogonal $\pi(\text{C}^*\equiv\text{N})$ orbitals.^{25,27} Its position depends only weakly on the chemical state of the CN group (unless there is $\pi^*-\pi^*$ hybridization with the adjacent functional group)²⁸ and, in particular, does not vary much across the NC-alkyl/Au{111} series, being 286.8–286.9 eV.

The 55° N K-edge spectrum of NC/Au{111} in Figure 2.7b exhibits a characteristic π^* resonance of the nitrile group at 399.7 eV. Similar to the $\pi(\text{C}^*\equiv\text{N})$ resonance, it is attributed to two (almost) degenerate, mutually orthogonal $\pi(\text{C}\equiv\text{N})$ orbitals.^{25,27} The presence of this feature as well as the $\pi(\text{C}^*\equiv\text{N})$ resonance at the C K-edge (see above) suggests an upright orientation of the NC moieties in NC/Au{111}. Otherwise, both $\pi(\text{C}^*\equiv\text{N})$ and $\pi(\text{C}\equiv\text{N}^*)$ resonances would be quenched through the direct interaction with the substrate and be imperceptible in the spectra. The energy of the $\pi(\text{C}\equiv\text{N}^*)$ resonance for NC/Au{111} is close to the analogous value for the NC-alkyl SAMs on Au{111}, viz. 399.75 eV (independent of chain length).³⁰

2.4.4 Resonant Auger Electron Spectroscopy – Molecule-Substrate Charge-Transfer Efficiency

Nitrile groups have been used before as the starting point for electron transfer (ET) through the molecular framework in SAMs on conductive substrates.^{12,25,27–30} These functional groups were attached to the molecular backbone as a tail moiety at the SAM-ambient interface while the molecules were coupled to the substrate, Au{111}, by the thiolate anchors. The ET was

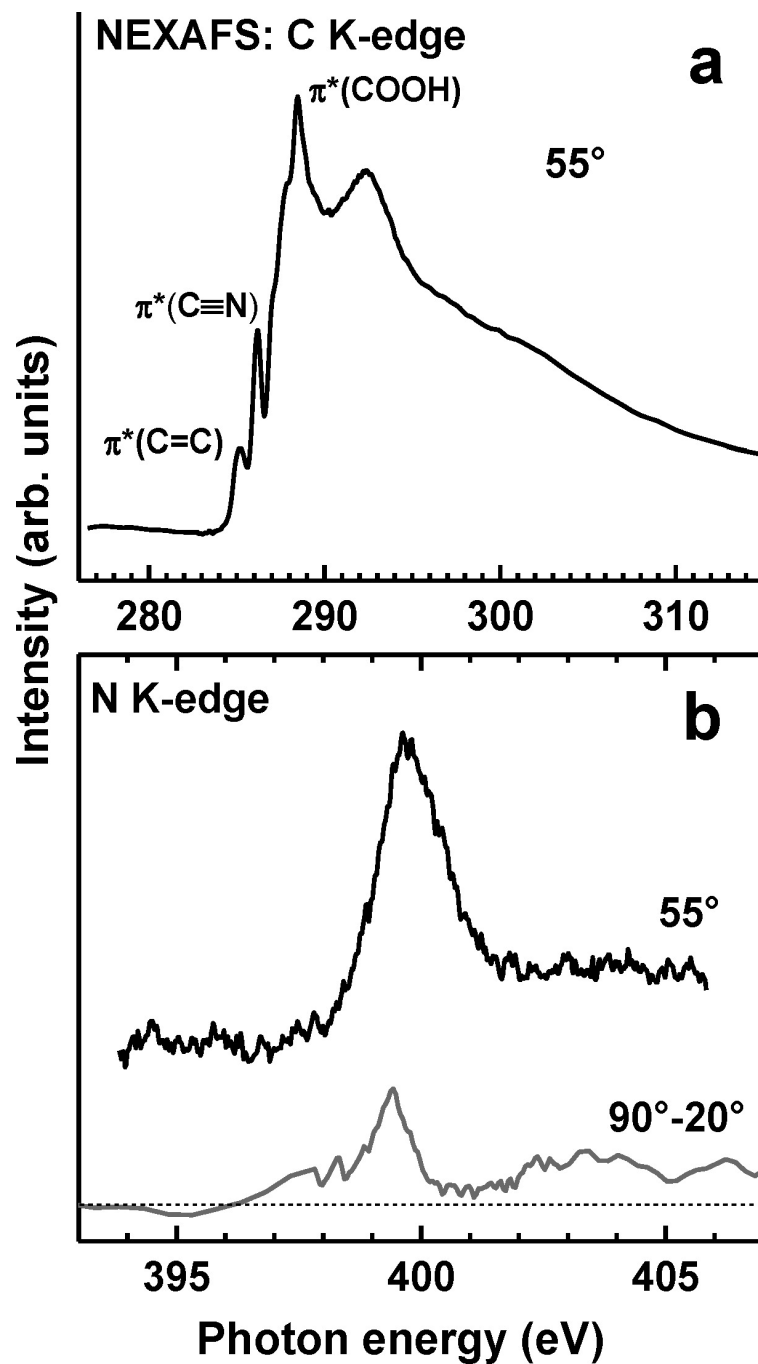


Figure 2.7: C (a) and N (b) K-edge near-edge X-ray absorption fine structure spectra of NC/Au{111} acquired at an X-ray incident angle of 55° (black solid curves), along with the respective difference between the spectra collected under the normal (90°) and grazing (20°) incidence geometry (gray solid curve in panel b). The characteristic absorption resonances are marked. The horizontal dashed line in panel b corresponds to zero intensity.

triggered by the resonant excitation of the N 1s electron into the $\pi(\text{C}\equiv\text{N}^*)$ orbital and monitored by RAES within the CHC approach.^{80–84} Within this approach, different de-excitation channels of the $[\text{N1s}]\pi^*$ state are followed, viz. the emission of the excited electron (participator channel; P), emission of another electron from occupied valence molecular orbital (spectator channel; SP), and ET of the excited electron to the substrate, all accompanied by an interband transition from occupied valence molecular orbital to the N1s hole. The P and SP processes, which are the standard de-excitation routes for RAES, result in one hole (1h) and a two-hole one-electron (2h1e) states, respectively (see ref [29] for details and schematic illustration of the relevant processes). In contrast, the ET scenario results in a 2h state, which is almost identical to the final state of non-resonant Auger electron emission processes.⁸⁵ Due to the different final states, all the above processes have different spectroscopic signatures in the overall RAES spectrum, which can be distinguished and the ET contribution, P_{ET} , precisely extracted. Consequently, characteristic ET time, τ_{ET} can be evaluated using the major formula of the CHC approach, viz. $\tau_{\text{ET}} = \tau_{\text{core}}(1 - P_{\text{ET}})/P_{\text{ET}}$, where τ_{core} is the core-hole lifetime serving as internal clock for the ET process and giving the name to the approach.⁸¹ This lifetime is 6.4 fs for the N1s core hole,⁸⁰ providing access to the femtosecond time domain without use of any complex experimental setup relying on pump-probe techniques.

The length of the molecular backbone in the CHC experiments on nitrile-substituted SAMs was varied, with P_{ET} increasing and τ_{ET} decreasing progressively with decreasing backbone length.^{28–30} In particular, τ_{ET} varied from 100 ± 26 fs for $\text{NC} - \text{C}_4\text{H}_8\text{S}/\text{Au}$ to 35 ± 9 fs for $\text{NC} - \text{C}_3\text{H}_6\text{S}/\text{Au}$ to 14 ± 4 fs for $\text{NC} - \text{C}_2\text{H}_4\text{S}/\text{Au}$.³⁰ Further, in the extrapolated limit of the negligible short backbone, the characteristic time for ET from the NC group directly attached to the thiolate anchor to the substrate was found to be ~ 2.3 fs³⁰ and ~ 2.8 fs²⁸ in the independent experiments on different systems, being ~ 2.5 fs on average. In this context, $\text{NC}/\text{Au}\{111\}$ represents a further, ultimate case, with the exclusion of the “intermediate” thiolate moiety and direct attachment of the nitrile group to $\text{Au}\{111\}$ with C–Au bond. Under these circumstances, ET to the substrate should be especially efficient, representing, most likely, the major de-excitation channel of the $[\text{N1s}]\pi^*$ state.

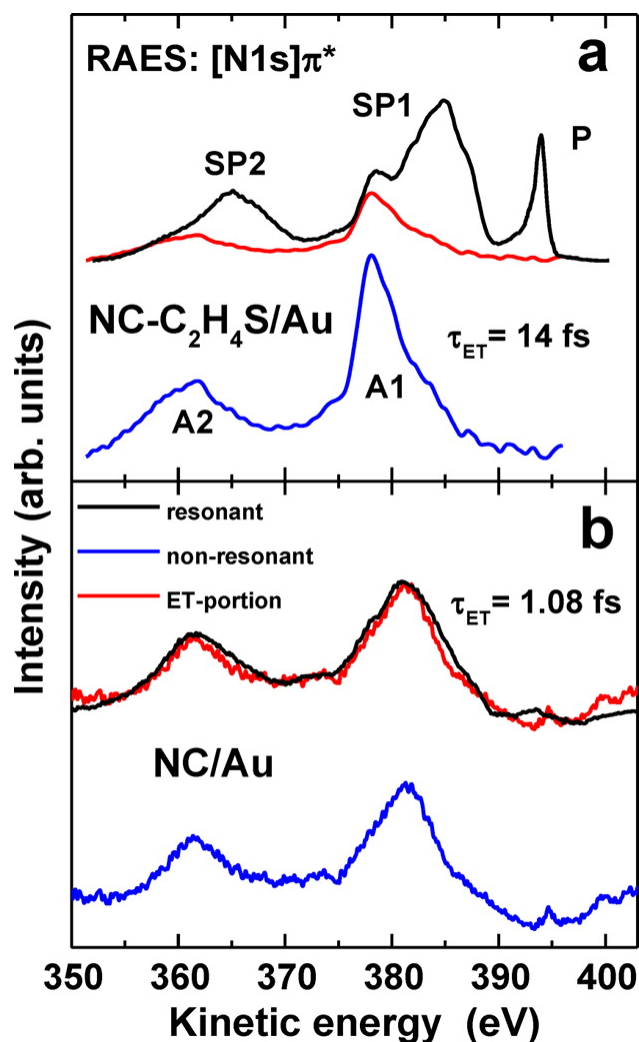


Figure 2.8: $[N\ 1s]\pi^*$ resonant Auger electron spectra (RAES, black curves) and nonresonant Auger electron (blue curves) spectra of NC-C₂H₄S/Au (a) and NC/Au{111} (b). The electron transfer contribution in the resonant Auger electron spectra is shown (red curves). P, SP1, and SP2 denote the participator and two spectator features, respectively. A1 and A2 denote two characteristic features in the nonresonant spectra. The derived τ_{ET} are given. The spectra of NC - C₂H₄S/Au are reprinted with permission from ref [30]. Copyright 2010 American Chemical Society.

This efficient ET to the substrate is indeed the case, as shown in Figure 2.8, where the $[N1s]\pi^*$ resonant Auger electron spectra (RAES) and corresponding Auger electron spectra (AES) for NC/Au{111} are presented, along with the analogous data for NC – C₂H₄S/Au{111},^{25,30} for comparison. The RAES spectra of NC – C₂H₄S/Au{111} are dominated by the SP and P contributions, while the ET part, shown separately, contributes only $\sim 30\%$ of the entire spectral weight. In contrast, the RAES and AES spectra of NC/Au{111} are almost identical suggesting that the former spectra are dominated by the ET contribution, while the SP and P parts are barely perceptible. Taking the RAES spectrum of NC – C₁₆H₃₂S/Au{111} as the reference for the purely resonant (autoionization) spectrum^{25,30} and non-resonant AES spectrum of NC/Au{111} as representative for the ET process (see above), the RAES spectrum of NC/Au{111} can be decomposed into the SP/P and ET contributions and τ_{ET} can be calculated according to the major formula of the CHC approach (see above). Three independent sets of experiments resulted in τ_{ET} values of 0.25, 1.08, and 1.38 fs, giving 0.9 fs on average. The accuracy of this value is ± 0.5 fs from the statistical viewpoint and ± 0.25 fs based on the accuracy of the τ_{core} value.⁸⁰ The comparison of this value with the analogous values for NC – (CH₂)₂S/Au is given in Figure 2.9. The most important feature, however, is the dominance of the ET process over the SP/P contributions in the $[N1s]\pi^*$ decay spectrum of NC/Au{111}, suggesting strong coupling to the substrate. Another important result, is an ultimate proof for the CHC approach in its specific application to SAMs, based on the resonantly addressable NC group.^{12,25,27–30} Indeed, as can be expected, the value of τ_{ET} for the direct attachment of the nitrile group to the Au{111} substrate is noticeably smaller than that for any molecular backbone, e.g., 14.4 fs for NC – C₂H₄S/Au^{25,30} and 9 ± 3 fs for SAMs of NC – C₆H₄ – SH/Au{111}, fitting well to the proposed exponential dependence of τ_{ET} on the length of the alkyl chain derived from the NC – (CH₂)_nS/Au data (Figure 2.9a). The τ_{ET} for NC/Au{111} is somewhat smaller than the characteristic time for n=0, obtained from the intercept of the $\ln \tau_{ET}$ plot with the y-axis, viz. 2.3 fs.³⁰ (2.8 fs in ref [28]). This result is understandable since the latter value, $\tau_{n=0}$, is associated with both ET time required for transfer from NC group to the backbone and the ET time required for transfer from the backbone to the substrate. Assuming that

the former contribution is close to τ_{ET} for NC/Au{111}, the latter time can be coarsely estimated at ~ 1.3 fs. This value is comparable to a characteristic time of ~ 320 asec observed for ET from an adsorbed sulfur atom to the substrate in the $c(4 \times 2)$ -S/Ru(0001) system.⁸⁴ The difference, which is reasonably small, can be explained by band alignment differences, the stronger bonding of the S atoms to the substrate in the latter case, as well as by the different characters of the involved orbitals serving as the starting point for ET in both cases. It is well known that the character of the primary molecular or atomic orbital affects the efficiency of ET.^{27,28}

2.4.5 Discussion of Results – Bonding Scheme and Substrate-Molecule Coupling

Combining our structural and spectroscopic measurements with known Au-cyanide chemistry, we propose a bonding scheme for cyanide monolayers on Au{111}. Assuming that the molecules on the surface organize to maximize intermolecular interactions for monolayer stability, and to offset unfavorable dipole coupling,⁷³ we propose a bonding scheme where the cyanide molecules are bound via an Au–C bond and are oriented normal to the surface. Note that when cyanide is attached to a carbon backbone as a nitrile group it has an inclined orientation measured around 65° ,^{3,30} suggesting that the strength of the substrate-molecule bond is dominant over the intermolecular interactions and overpowers the unfavorable dipole-dipole interactions.

Finally, from the CHC results measuring the ~ 1 fs charge transfer from the cyanide directly to the gold, as shown schematically in Figure 2.10. We can infer that the electronic coupling is particularly strong between the carbon and gold based on the facile electron transfer. This result directly supports the expected dominance of σ bonding suggested by the increase in CN vibrational frequency. The electron transfer efficiency, coupled with the molecule orientation, is an indication that there is a favorable energetic overlap between the molecular transport orbitals and substrate Fermi level²⁴ and follows the trend for electron transfer time as a function of the length of the carbon backbone in nitrile functionalized

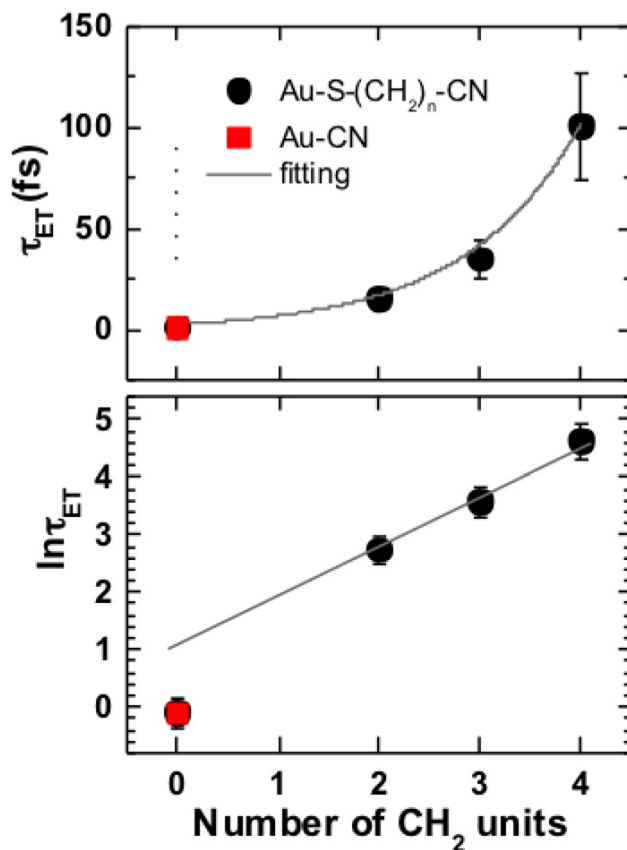


Figure 2.9: Electron transfer (ET) time (top panel) from the excited NC group to the substrate and its natural logarithm (bottom panel) for NC/Au (red square) and NC – (CH₂)_nS/Au (n = 2–4; black filled circles) versus the number (n) of methylene (CH₂) units in the aliphatic chain. The gray solid lines in the top and bottom panels represent the best exponential and linear fits, respectively. The intercept of the $\ln \tau_{\text{ET}}$ plot with the y-axis corresponds to the ET time required for transfer from the NC group to the backbone plus the ET time required for transfer from the backbone to the substrate. The intercept of 0.83 gives a $\tau_{n=0}$ value of 2.3 fs. The values for NC – (CH₂)_nS/Au are reprinted with permission from ref [30]. Copyright 2010 American Chemical Society.

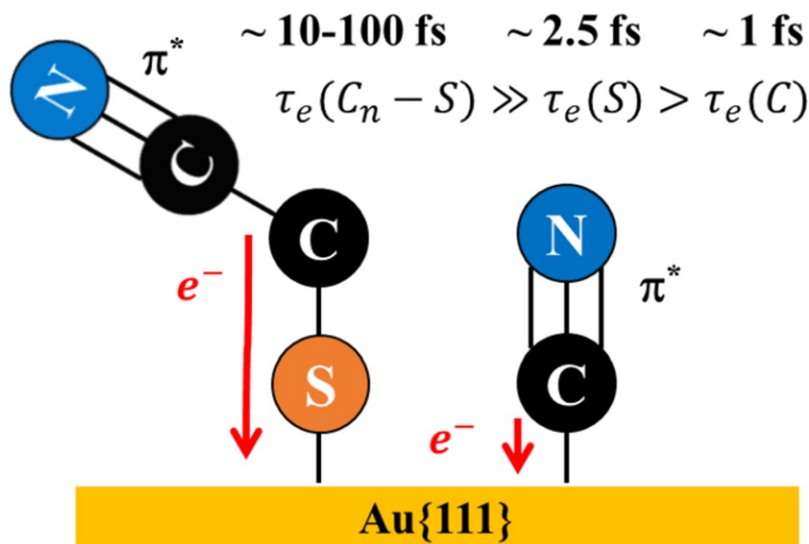


Figure 2.10: Electron transfer across the Au–C bond is extremely efficient at ~ 1 fs, indicating strong electronic coupling between substrate and molecule.

alkanethiol SAMs previously shown in Figure 2.9.³⁰ In fact, complementary to these results, it has been reported that the conduction efficiency is significantly lower for isocyanide or Au–NC bound, molecules.³¹

2.5 Conclusions and Prospects

The vibrational and structural characteristics of stable cyanide monolayers on Au{111} are revealed and we show that coupling to the gold substrate is particularly strong, leading to facile electron transfer. Cyanide molecules form a hexagonal close-packed lattice with a nearest neighbor spacing of $3.8 \pm 0.5 \text{ \AA}$. It was discovered using ATR-FTIR and SERS that the cyanide molecules are attached to the gold through the carbon atom and oriented normal to the surface. The molecular composition and orientation was supported by high-resolution XPS (HRXPS) and NEXAFS and we discuss a bonding scheme that compares favorably with the structure observed in the STM images. The CHC method of RAES measured the charge transfer from the cyanide to the gold to be below 1 fs, comparable to charge transfer across the sulfur bond of thiols and 100 times faster than when an alkyl backbone is present. These results further validate the use of the core-hole clock method for

measuring the ultrafast process of electron transfer between molecule and substrate for self-assembled monolayers. Current research is aimed at exploiting the strong dipole moment of cyanide, molecule orientation, and the strength of the molecule-substrate electronic coupling for probing the interactions between molecular electronic structure and molecular vibrations at room temperature, which is critical to developing more generally applicable single-molecule spectroscopic techniques.

2.6 References

- (1) Netzer, L.; Iscovici, R.; Sagiv, J. Adsorbed Monolayers Versus Langmuir-Blodgett Monolayers—Why and How? II: Characterization of Built-Up Films Constructed by Stepwise Adsorption of Individual Monolayers. *Thin Solid Films* **1983**, *100*, 67–76.
- (2) Stranick, S. J.; Kamna, M. M.; Krom, K. R.; Parikh, A. N.; Allara, D. L.; Weiss, P. S. Scanning Tunneling Microscopy Studies of Self-Assembled Monolayers of Alkanethiols on Gold. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **1994**, *12*, 2004–2007.
- (3) Frey, S.; Shaporenko, A.; Zharnikov, M.; Harder, P.; Allara, D. L. Self-Assembled Monolayers of Nitrile-Functionalized Alkanethiols on Gold and Silver Substrates. *Journal of Physical Chemistry B* **2003**, *107*, 7716–7725.
- (4) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chemical Reviews* **2005**, *105*, 1103–1170.
- (5) Weiss, P. S. Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements. *Accounts of Chemical Research* **2008**, *41*, 1772–1781.
- (6) Liao, W.-S.; Cheunkar, S.; Cao, H. H.; Bednar, H. R.; Weiss, P. S.; Andrews, A. M. Subtractive Patterning via Chemical Lift-Off Lithography. *Science* **2012**, *337*, 1517–1521.

- (7) Kim, J.; Rim, Y. S.; Liu, Y.; Serino, A. C.; Thomas, J. C.; Chen, H.; Yang, Y.; Weiss, P. S. Interface Control in Organic Electronics Using Mixed Monolayers of Carboranethiol Isomers. *Nano Letters* **2014**, *14*, 2946–2951.
- (8) Abendroth, J. M.; Bushuyev, O. S.; Weiss, P. S.; Barrett, C. J. Controlling Motion at the Nanoscale: Rise of the Molecular Machines. *ACS Nano* **2015**, *9*, 7746–7768.
- (9) Sykes, E. C. H.; Han, P.; Kandel, S. A.; Kelly, K. F.; McCarty, G. S.; Weiss, P. S. Substrate-Mediated Interactions and Intermolecular Forces between Molecules Adsorbed on Surfaces. *Accounts of Chemical Research* **2003**, *36*, 945–953.
- (10) Monnell, J. D.; Stapleton, J. J.; Dirk, S. M.; Reinerth, W. A.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Relative Conductances of Alkaneselenolate and Alkanethiolate Monolayers on Au{111}. *Journal of Physical Chemistry B* **2005**, *109*, 20343–20349.
- (11) Häkkinen, H. The Gold-Sulfur Interface at the Nanoscale. *Nature Chemistry* **2012**, *4*, 443–455.
- (12) Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort, A.; Cyganik, P.; Zharnikov, M. Thiolate Versus Selenolate: Structure, Stability, and Charge Transfer Properties. *ACS Nano* **2015**, *9*, 4508–4526.
- (13) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. Insertion, Conductivity, and Structures of Conjugated Organic Oligomers in Self-Assembled Alkanethiol Monolayers on Au{111}. *Journal of the American Chemical Society* **1998**, *120*, 2721–2732.
- (14) Weck, M.; Jackiw, J. J.; Rossi, R. R.; Weiss, P. S.; Grubbs, R. H. Ring-Opening Metathesis Polymerization from Surfaces. *Journal of the American Chemical Society* **1999**, *121*, 4088–4089.
- (15) Saavedra, H. M.; Thompson, C. M.; Hohman, J. N.; Crespi, V. H.; Weiss, P. S. Reversible Lability by In Situ Reaction of Self-Assembled Monolayers. *Journal of the American Chemical Society* **2009**, *131*, 2252–2259.

- (16) Saavedra, H. M.; Mullen, T. J.; Zhang, P.; Dewey, D. C.; Claridge, S. A.; Weiss, P. S. Hybrid Strategies in Nanolithography. *Reports on Progress in Physics* **2010**, *73*, 036501.
- (17) Kim, M.; Hohman, J. N.; Cao, Y.; Houk, K. N.; Ma, H.; Jen, A. K.-Y.; Weiss, P. S. Creating Favorable Geometries for Directing Organic Photoreactions in Alkanethiolate Monolayers. *Science* **2011**, *331*, 1312–1315.
- (18) Cao, H. H.; Nakatsuka, N.; Serino, A. C.; Liao, W.-S.; Cheunkar, S.; Yang, H.; Weiss, P. S.; Andrews, A. M. Controlled DNA Patterning by Chemical Lift-Off Lithography: Matrix Matters. *ACS Nano* **2015**, *9*, 11439–11454.
- (19) Kumar, A. S.; Ye, T.; Takami, T.; Yu, B.-C.; Flatt, A. K.; Tour, J. M.; Weiss, P. S. Reversible Photo-Switching of Single Azobenzene Molecules in Controlled Nanoscale Environments. *Nano Letters* **2008**, *8*, 1644–1648.
- (20) Gao, P.; Weaver, M. J. Metal-Adsorbate Vibrational Frequencies as a Probe of Surface Bonding: Halides and Pseudohalides at Gold Electrodes. *The Journal of Physical Chemistry* **1986**, *90*, 4057–4063.
- (21) Galperin, M.; Ratner, M. A.; Nitzan, A. Molecular Transport Junctions: Vibrational Effects. *Journal of Physics: Condensed Matter* **2007**, *19*, 103201.
- (22) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. Conductance Switching in Single Molecules Through Conformational Changes. *Science* **2001**, *292*, 2303–2307.
- (23) Lewis, P. A.; Inman, C. E.; Maya, F.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. Molecular Engineering of the Polarity and Interactions of Molecular Electronic Switches. *Journal of the American Chemical Society* **2005**, *127*, 17421–17426.
- (24) Zangmeister, C. D.; Robey, S. W.; van Zee, R. D.; Kushmerick, J. G.; Naciri, J.; Yao, Y.; Tour, J. M.; Varughese, B.; Xu, B.; Reutt-Robey, J. E. Fermi Level Alignment in Self-Assembled Molecular Layers: The Effect of Coupling Chemistry. *The Journal of Physical Chemistry B* **2006**, *110*, 17138–17144.

- (25) Neppl, S.; Bauer, U.; Menzel, D.; Feulner, P.; Shaporenko, A.; Zharnikov, M.; Kao, P.; Allara, D. L. Charge Transfer Dynamics in Self-Assembled Monomolecular Films. *Chemical Physics Letters* **2007**, *447*, 227–231.
- (26) Moore, A. M.; Weiss, P. S. Functional and Spectroscopic Measurements with Scanning Tunneling Microscopy. *Annual Review of Analytical Chemistry* **2008**, *1*, 857–882.
- (27) Blobner, F.; Coto, P. B.; Allegretti, F.; Bockstedte, M.; Rubio-Pons, O.; Wang, H.; Allara, D. L.; Zharnikov, M.; Thoss, M.; Feulner, P. Orbital-Symmetry-Dependent Electron Transfer Through Molecules Assembled on Metal Substrates. *The Journal of Physical Chemistry Letters* **2012**, *3*, 436–440.
- (28) Hamoudi, H.; Neppl, S.; Kao, P.; Schüpbach, B.; Feulner, P.; Terfort, A.; Allara, D.; Zharnikov, M. Orbital-Dependent Charge Transfer Dynamics in Conjugated Self-Assembled Monolayers. *Physical Review Letters* **2011**, *107*, 027801.
- (29) Zharnikov, M. Probing Charge Transfer Dynamics in Self-Assembled Monolayers by Core Hole Clock Approach. *Journal of Electron Spectroscopy and Related Phenomena* **2015**, *200*, 160–173.
- (30) Kao, P.; Neppl, S.; Feulner, P.; Allara, D. L.; Zharnikov, M. Charge Transfer Time in Alkanethiolate Self-Assembled Monolayers via Resonant Auger Electron Spectroscopy. *The Journal of Physical Chemistry C* **2010**, *114*, 13766–13773.
- (31) Kiguchi, M.; Miura, S.; Hara, K.; Sawamura, M.; Murakoshi, K. Conductance of a Single Molecule Anchored by An Isocyanide Substituent to Gold Electrodes. *Applied Physics Letters* **2006**, *89*, 213104.
- (32) Lauhon, L. J.; Ho, W. Single-Molecule Vibrational Spectroscopy and Microscopy: CO on Cu(001) and Cu(110). *Physical Review B* **1999**, *60*, R8525–R8528.
- (33) Ahmad, S. The Chemistry of Cyano Complexes of Gold(I) with Emphasis on the Ligand Scrambling Reactions. *Coordination Chemistry Reviews* **2004**, *248*, 231–243.

- (34) McCarley, R. L.; Bard, A. J. Surface Reactions of Gold(111) with Aqueous Cyanide Studied by Scanning Tunneling Microscopy. *The Journal of Physical Chemistry* **1992**, *96*, 7410–7416.
- (35) Sun, L.; Crooks, R. M. Indirect Visualization of Defect Structures Contained Within Self-Assembled Organomercaptan Monolayers: Combined Use of Electrochemistry and Scanning Tunneling Microscopy. *Langmuir* **1993**, *9*, 1951–1954.
- (36) Katz, M. J.; Sakai, K.; Leznoff, D. B. The Use of Auophilic and Other Metal–metal Interactions as Crystal Engineering Design Elements to Increase Structural Dimensionality. *Chemical Society Reviews* **2008**, *37*, 1884–1895.
- (37) Hu, M.; Belik, A. A.; Imura, M.; Yamauchi, Y. Tailored Design of Multiple Nanoarchitectures in Metal-Cyanide Hybrid Coordination Polymers. *Journal of the American Chemical Society* **2013**, *135*, 384–391.
- (38) Kim, K. H.; Kim, J. G.; Nozawa, S.; Sato, T.; Oang, K. Y.; Kim, T. W.; Ki, H.; Jo, J.; Park, S.; Song, C.; Sato, T.; Ogawa, K.; Togashi, T.; Tono, K.; Yabashi, M.; Ishikawa, T.; Kim, J.; Ryoo, R.; Kim, J.; Ihse, H.; Adachi, S.-i. Direct Observation of Bond Formation in Solution with Femtosecond X-Ray Scattering. *Nature* **2015**, *518*, 385–389.
- (39) Chattopadhyay, S.; Ganguly, A.; Chen, K.-H.; Chen, L.-C. One-Dimensional Group III-Nitrides: Growth, Properties, and Applications in Nanosensing and Nano-Optoelectronics. *Critical Reviews in Solid State and Materials Sciences* **2009**, *34*, 224–279.
- (40) Han, P.; Sykes, E. C. H.; Pearl, T. P.; Weiss, P. S. A Comparative Scanning Tunneling Microscopy Study of Physisorbed Linear Quadrupolar Molecules: C₂N₂ and CS₂ on Au{111} at 4 K. *Journal of Physical Chemistry A* **2003**, *107*, 8124–8129.
- (41) Guttentag, A. I.; Barr, K. K.; Song, T.-B.; Bui, K. V.; Fauman, J. N.; Torres, L. F.; Kes, D. D.; Ciomaga, A.; Gilles, J.; Sullivan, N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Hexagons to Ribbons: Flipping Cyanide on Au{111}. *Journal of the American Chemical Society* **2016**, *138*, 15580–15586.

- (42) Swanson, S. A.; McClain, R.; Lovejoy, K. S.; Alamdari, N. B.; Hamilton, J. S.; Scott, J. C. Self-Assembled Diisocyanide Monolayer Films on Gold and Palladium. *Langmuir* **2005**, *21*, 5034–5039.
- (43) Crudden, C. M.; Horton, J. H.; Ebralidze, I. I.; Zenkina, O. V.; McLean, A. B.; Drevniok, B.; She, Z.; Kraatz, H.-B.; Mosey, N. J.; Seki, T.; Keske, E. C.; Leake, J. D.; Rousina-Webb, A.; Wu, G. Ultra Stable Self-Assembled Monolayers of *N*-Heterocyclic Carbenes on Gold. *Nature Chemistry* **2014**, *6*, 409–414.
- (44) Senanayake, G. Kinetics and Reaction Mechanism of Gold Cyanidation: Surface Reaction Model via Au(I)–OH–CN Complexes. *Hydrometallurgy* **2005**, *80*, 1–12.
- (45) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chemical Reviews* **1996**, *96*, 1533–1554.
- (46) Porath, D.; Millo, O.; Gersten, J. I. Scanning Tunneling Microscopy Studies and Computer Simulations of Annealing of Gold Films. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **1996**, *14*, 30–37.
- (47) Bumm, L. A.; Arnold, J. J.; Charles, L. F.; Dunbar, T. D.; Allara, D. L.; Weiss, P. S. Directed Self-Assembly to Create Molecular Terraces with Molecularly Sharp Boundaries in Organic Monolayers. *Journal of the American Chemical Society* **1999**, *121*, 8017–8021.
- (48) Mantooth, B. A. Nanoscopic Analyses: Single Molecule Characterization in Molecular Electronics and Surface Science., Ph.D. Thesis, University Park, PA, USA: The Pennsylvania State University, 2004.
- (49) Wakamatsu, T.; Aizawa, K. Penetration-Depth Characteristics of Evanescent Fields at Metal Attenuated Total Reflection. *Japanese Journal of Applied Physics* **2005**, *44*, 4272.
- (50) Zheng, Y. B.; Payton, J. L.; Chung, C.-H.; Liu, R.; Cheunkar, S.; Pathem, B. K.; Yang, Y.; Jensen, L.; Weiss, P. S. Surface-Enhanced Raman Spectroscopy to Probe

- Reversibly Photoswitchable Azobenzene in Controlled Nanoscale Environments. *Nano Letters* **2011**, *11*, 3447–3452.
- (51) Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A. Characterization of X-Ray Induced Damage in Alkanethiolate Monolayers by High-Resolution Photoelectron Spectroscopy. *Langmuir* **2001**, *17*, 8–11.
- (52) Zharnikov, M. High-Resolution X-Ray Photoelectron Spectroscopy in Studies of Self-Assembled Organic Monolayers. *Journal of Electron Spectroscopy and Related Phenomena* **2010**, *178–179*, 380–393.
- (53) Moulder, J.; Chastain, J., *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*; Physical Electronics Division, Perkin-Elmer Corporation: Eden Prairie, Minnesota, 1992.
- (54) Stöhr, J., *NEXAFS Spectroscopy*; Springer-Verlag: Berlin, Heidelberg, 1992.
- (55) Batson, P. E. Carbon 1s Near-Edge-Absorption Fine Structure in Graphite. *Physical Review B* **1993**, *48*, 2608–2610.
- (56) Domke, M.; Mandel, T.; Puschmann, A.; Xue, C.; Shirley, D. A.; Kaindl, G.; Petersen, H.; Kuske, P. Performance of the High-Resolution SX700/II Monochromator. *Review of Scientific Instruments* **1992**, *63*, 80–89.
- (57) Yamada, T.; Sekine, R.; Sawaguchi, T. Ultrahigh-Vacuum Multitechnique Study of AuCN Monolayers on Au(111) Formed by Electrochemical Deposition. *The Journal of Chemical Physics* **2000**, *113*, 1217–1227.
- (58) Han, P.; Weiss, P. S. Electronic Substrate-Mediated Interactions. *Surface Science Reports* **2012**, *67*, 19–81.
- (59) Wang, X.-B.; Wang, Y.-L.; Yang, J.; Xing, X.-P.; Li, J.; Wang, L.-S. Evidence of Significant Covalent Bonding in $\text{Au}(\text{CN})_2^-$. *Journal of the American Chemical Society* **2009**, *131*, 16368–16370.

- (60) Liu, H.-T.; Xiong, X.-G.; Diem Dau, P.; Wang, Y.-L.; Huang, D.-L.; Li, J.; Wang, L.-S. Probing the Nature of Gold–Carbon Bonding in Goldalkynyl–Complexes. *Nature Communications* **2013**, *4*, 2223.
- (61) Smyth, C. P.; McAlpine, K. B. The Dipole Moments of PHOSGENE, Hydrogen Cyanide and Certain Substituted Methanes. *Journal of the American Chemical Society* **1934**, *56*, 1697–1700.
- (62) Thomas, J. C.; Schwartz, J. J.; Hohman, J. N.; Claridge, S. A.; Auluck, H. S.; Serino, A. C.; Spokoyny, A. M.; Tran, G.; Kelly, K. F.; Mirkin, C. A.; Gilles, J.; Osher, S. J.; Weiss, P. S. Defect-Tolerant Aligned Dipoles within Two-Dimensional Plastic Lattices. *ACS Nano* **2015**, *9*, 4734–4742.
- (63) Schwartz, J. J.; Mendoza, A. M.; Wattanatorn, N.; Zhao, Y.; Nguyen, V. T.; Spokoyny, A. M.; Mirkin, C. A.; Baše, T.; Weiss, P. S. Surface Dipole Control of Liquid Crystal Alignment. *Journal of the American Chemical Society* **2016**, *138*, 5957–5967.
- (64) Bowmaker, G. A.; Kennedy, B. J.; Reid, J. C. Crystal Structures of AuCN and AgCN and Vibrational Spectroscopic Studies of AuCN, AgCN, and CuCN. *Inorganic Chemistry* **1998**, *37*, 3968–3974.
- (65) Dameron, A. A.; Charles, L. F.; Weiss, P. S. Structures and Displacement of 1-Adamantanethiol Self-Assembled Monolayers on Au{111}. *Journal of the American Chemical Society* **2005**, *127*, 8697–8704.
- (66) Beltramo, G. L.; Shubina, T. E.; Mitchell, S. J.; Koper, M. T. M. Cyanide Adsorption on Gold Electrodes: a Combined Surface Enhanced Raman Spectroscopy and Density Functional Theory Study. *Journal of Electroanalytical Chemistry* **2004**, *563*, 111–120.
- (67) Yan, C.; Götzhäuser, A.; Grunze, M.; Wöll, C. Formation of Alkanethiolate Self-Assembled Monolayers on Oxidized Gold Surfaces. *Langmuir* **1999**, *15*, 2414–2419.
- (68) Ratner, B. D.; Castner, D. G.; Surface Analysis – The Principal Techniques. *Electron Spectroscopy for Chemical Analysis*; John Wiley & Sons, Ltd: West Sussex, United Kingdom, 2009, pp 47–112.

- (69) Pireaux, J. J.; Liehr, M.; Thiry, P. A.; Delrue, J. P.; Caudano, R. Electron Spectroscopic Characterization of Oxygen Adsorption on Gold Surfaces: II. Production of Gold Oxide in Oxygen DC Reactive Sputtering. *Surface Science* **1984**, *141*, 221–232.
- (70) Cebula, I.; Lu, H.; Zharnikov, M.; Buck, M. Monolayers of Trimesic and Isophthalic Acid on Cu and Ag: the Influence of Coordination Strength on Adsorption Geometry. *Chemical Science* **2013**, *4*, 4455–4464.
- (71) Zhou; Baunach, T.; Ivanova, V.; Kolb, D. M. Structure and Electrochemistry of 4,4'-Dithiodipyridine Self-Assembled Monolayers in Comparison with 4-Mercaptopyridine Self-Assembled Monolayers on Au(111). *Langmuir* **2004**, *20*, 4590–4595.
- (72) Zubavichus, Y.; Zharnikov, M.; Yang, Y.; Fuchs, O.; Umbach, E.; Heske, C.; Ulman, A.; Grunze, M. X-ray Photoelectron Spectroscopy and Near-Edge X-ray Absorption Fine Structure Study of Water Adsorption on Pyridine-Terminated Thiolate Self-Assembled Monolayers. *Langmuir* **2004**, *20*, 11022–11029.
- (73) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G.; Philpott, M. R. A Study of the Gold/Cyanide Solution Interface by In Situ Polarization-Modulated Fourier Transform Infrared Reflection Absorption Spectroscopy. *Langmuir* **1988**, *4*, 337–341.
- (74) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J. The Infrared Spectra of Nitriles and Related Compounds Frozen in Ar and H₂O. *The Astrophysical Journal* **1997**, *476*, 932.
- (75) Jobe, D. J.; Westaway, K. C. Fourier Transform Infrared Spectroscopy Studies of Cyanide Ion Solutions of Dimethylformamide and Aqueous Dimethylformamide. *Canadian Journal of Chemistry* **1993**, *71*, 1353–1361.
- (76) Senapati, D.; Dasary, S. S. R.; Singh, A. K.; Senapati, T.; Yu, H.; Ray, P. C. A Label-Free Gold-Nanoparticle-Based SERS Assay for Direct Cyanide Detection at the Parts-Per-Trillion Level. *Chemistry – A European Journal* **2011**, *17*, 8445–8451.
- (77) Keedy, C. R. The Rotational-Vibrational Spectra of HCN and DCN: A Physical Chemistry Experiment. *Journal of Chemical Education* **1992**, *69*, A296.

- (78) Pettinger, B.; Picardi, G.; Schuster, R.; Ertl, G. Surface-Enhanced and STM Tip-Enhanced Raman Spectroscopy of CN^- Ions at Gold Surfaces. *Journal of Electroanalytical Chemistry* **2003**, 554-555, 293–299.
- (79) Neelakantan, P. Raman Spectrum of Acetonitrile. *Proceedings of the Indian Academy of Sciences-Section A* **1964**, 60, 422–424.
- (80) Kempgens, B.; Kivimäki, A.; Neeb, M.; Köppe, H. M.; Bradshaw, A. M.; Feldhaus, J. A High-Resolution N 1s Photoionization Study of the Molecule in the Near-Threshold Region. *Journal of Physics B: Atomic, Molecular and Optical Physics* **1996**, 29, 5389–5402.
- (81) Brühwiler, P. A.; Karis, O.; Mårtensson, N. Charge-Transfer Dynamics Studied Using Resonant Core Spectroscopies. *Reviews of Modern Physics* **2002**, 74, 703–740.
- (82) Schnadt, J.; Brühwiler, P. A.; Patthey, L.; O'Shea, J. N.; Södergren, S.; Odelius, M.; Ahuja, R.; Karis, O.; Bässler, M.; Persson, P.; Siegbahn, H.; Lunell, S.; Mårtensson, N. Experimental Evidence for Sub-3-fs Charge Transfer from an Aromatic Adsorbate to a Semiconductor. *Nature* **2002**, 418, 620–623.
- (83) De Jong, M. P.; Friedlein, R.; Sorensen, S. L.; Öhrwall, G.; Osikowicz, W.; Tengsted, C.; Jönsson, S. K. M.; Fahlman, M.; Salaneck, W. R. Orbital-Specific Dynamic Charge Transfer from Fe(II)-Tetraphenylporphyrin Molecules to Molybdenum Disulfide Substrates. *Physical Review B* **2005**, 72, 035448.
- (84) Föhlisch, A.; Feulner, P.; Hennies, F.; Fink, A.; Menzel, D.; Sanchez-Portal, D.; Echenique, P. M.; Wurth, W. Direct Observation of Electron Dynamics in the Attosecond Domain. *Nature* **2005**, 436, 373–376.
- (85) Piancastelli, M. N. Auger Resonant Raman Studies of Atoms and Molecules. *Journal of Electron Spectroscopy and Related Phenomena* **2000**, 107, 1–26.

CHAPTER 3

Hexagons to Ribbons: Flipping Cyanide on Au{111}

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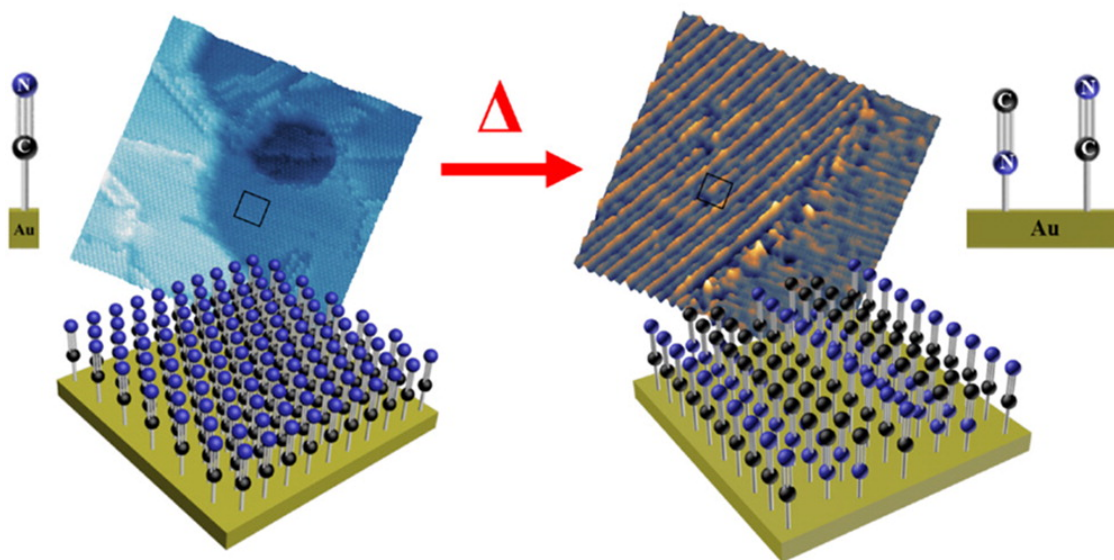


Figure 3.1: AuCN rearranging on top of gold surfaces.

3.1 Abstract

Cyanide monolayers on Au{111} restructure from a hexagonal close-packed lattice to a mixed orientation ‘ribbon’ structure through thermal annealing. The new surface structure loses most of the observed surface features characterizing the initial as-adsorbed system with ‘ribbon’ domain boundaries isolating rotationally offset surface regions where the orientation is guided by the underlying gold lattice. A blue shift to higher frequencies of the CN vibration to 2235 cm^{-1} with respect to the as-adsorbed CN/Au{111} vibration at 2146 cm^{-1} is observed. In addition, a new low frequency mode is observed at 145 cm^{-1} suggesting a chemical environment change similar to gold-cyanide crystallization. We discuss this new structure with respect to a mixed cyanide/isocyanide monolayer and propose a bonding scheme consisting of Au–CN and Au–NC bound molecules that are oriented normal to the Au{111} surface.

3.2 Introduction

Directing the self-organization of molecular systems requires understanding the effects of changing the basic parameters and external stimuli, such as temperature, electrical potential, and illumination on molecular and intermolecular structure and function.^{1–5} Self-assembled monolayers (SAMs) are a common system to test these effects, which can result in both physical and chemical changes.^{6–9} Similar to thiols and selenols, carbon-bound molecules have been shown to form ordered monolayers on gold substrates.^{10–14} The strength of the Au–C bond is similar in strength to the Au–S and Au–Se bonds.^{13,14} There is significant interest in understanding how temperature affects the organization,^{6,15–17} conductivity,¹⁷ adsorption,¹⁸ stability,^{13,19} and molecular reactivity²⁰ of self-assembled monolayers, which are critical in effectively tailoring molecular design for research and applications in nanotechnology.^{4,21,22}

Monolayer structures can be elucidated through vibrational spectroscopy,^{10,23–26} molecular-resolution imaging,^{27–30} and complementary techniques. Even relatively small shifts of vibration peaks can be sources of significant information pertaining to the morphology,^{24,31} structure,^{10,32–35} composition, and defects of self-assembled monolayers.^{24,36,37} To this end, we

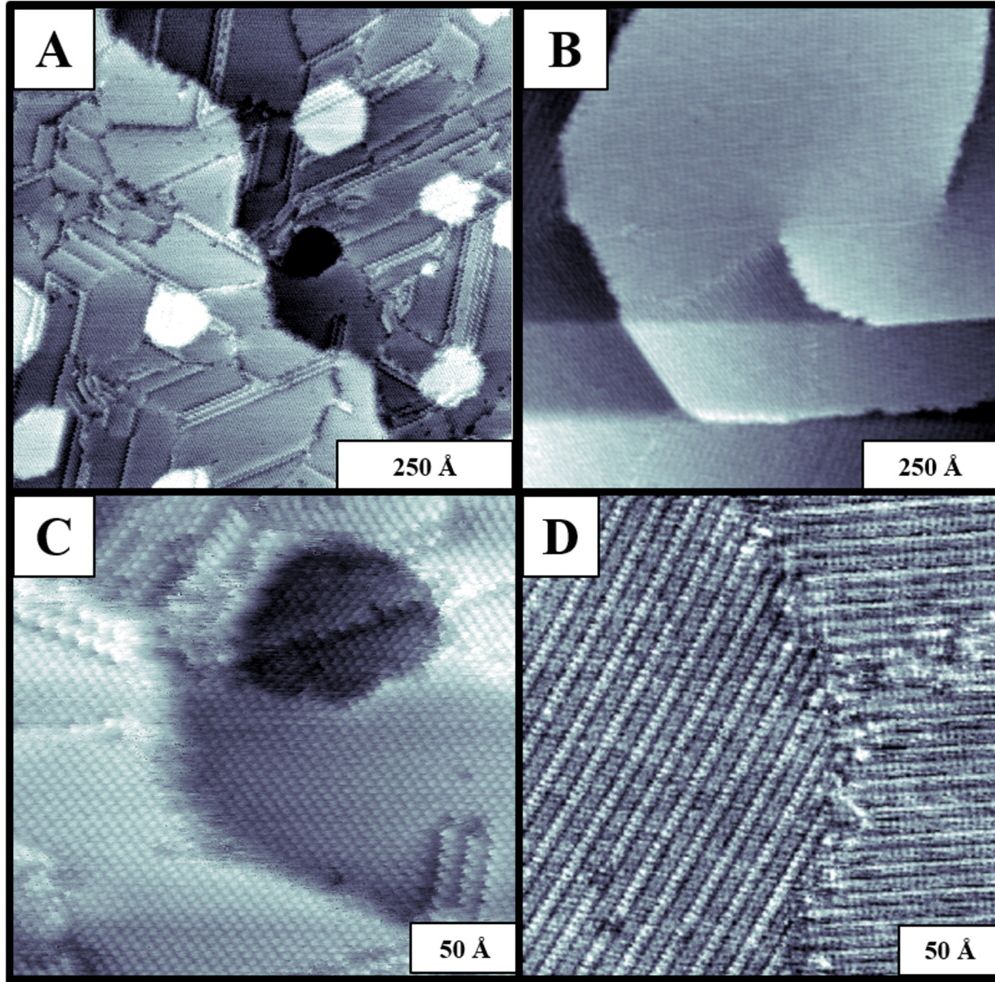


Figure 3.2: Scanning tunneling microscope images of (A) hexagonally close-packed CN/Au{111} as-deposited under ambient conditions and (B) the thermally induced ribbon structure formed by dry annealing for over 18 h at ~ 100 °C. The order in the annealed structure is long range (on the order of tens of nanometers) with the ribbon domains taking on various rotational orientations relative to one another on the surface. Once annealed, the surface never returns to the original HCP arrangement. (C,D) Molecular-resolution images of the as-adsorbed and thermally annealed lattices, respectively. We note tip-change imaging artifacts in (B) that did not disrupt the topography. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA.

have fabricated and probed the vibrational spectra and structures of monolayers of cyanide molecules on Au{111}.^{7,38} In this work, we report the structure and orientation for annealed cyanide monolayers on Au{111}, report changes in the vibrational spectra, and propose mixed bonding schemes to explain the appearance of ‘ribbons’ consisting of rows of cyanide molecules.

Initially, cyanide molecules deposited at room temperature assemble on Au{111} in a hexagonally close-packed lattice attached through the carbon atom, that are oriented primarily normal to the surface.³⁸ Cyanide has a strong dipole moment of 2.8 D that makes it ideal as a small-molecule probe.^{39,40} In our previous work we adsorbed cyanogen (C_2N_2) on Au{111}, but it did not dissociate under the conditions used.⁴¹ Here, we were able to deposit CN on Au{111} and to induce a structural change upon a simple dry thermal annealing process.

3.3 Results and Discussion

3.3.1 Surface Structure Characterization of Thermally Annealed CN/Au{111}

Cyanide molecules deposited on Au{111} from exposure to $\text{HCN}(g)$ under atmospheric conditions order in a hexagonal close-packed lattice (HCP) at room temperature.³⁸ Figure 3.2A shows the structural details of cyanide monolayers, obtained under ambient conditions by scanning tunneling microscopy (STM), which include surface features such as vacancy islands, protruding islands, and multiple highly ordered domains. In this cyanide on Au{111} structure, the measured nearest-neighbor spacing is $3.8 \pm 0.5 \text{ \AA}$.³⁸

After heating as-adsorbed CN/Au{111} samples to 100 °C for over 18 h, the original surface features are completely replaced, as shown in Figure 3.2B, with ribbon-like structural domains that are typically larger, spanning tens to hundreds of nanometers, than those observed prior to thermal annealing, which are on the order of 1–10 nm. Closer inspection of the surface structure reveals the changes at the molecular level from the initial CN/Au{111} HCP lattice, shown in Figure 3.2C, to the new ribbon arrangement, shown in Figure 3.2D.

Two common defects found in the ribbon system are highlighted in Figure 3.2D, molecular-level disruptions of the individual ribbon ‘stripes’ and domain boundaries between regions of different surface orientation. Once converted, the ribbon structure has not been observed to return to the HCP lattice, and has been stable for imaging for several months using standard storage conditions (*i.e.*, in a dark, dry, sealed container).

Annealing up to 60 °C for over 18 h induced no observable change in the as-adsorbed CN/Au{111} HCP lattice, while annealing to 100 ± 5 °C induces ribbon formation, typically to completion. Using this same temperature window, both structures coexisting are observed on the surface after 6 h, as in Figure 3.3A. Single-molecule resolution of this system with STM, in Figure 3.3B, shows both the HCP lattice in the top right corner and the emergence of the ribbon region in the bottom left with isolated molecule features appearing in both regions that are not part of the respective lattices. Importantly, annealing for over 18 h does not affect the ribbon structure; annealing periods of 24 h were typically used to ensure complete conversion. However, annealing at temperatures above 105 °C for 18–24 h generally results in deterioration of the sample. This observation agrees with the established temperature dependence of gold dissolution, which reports the decomposition of cyanide in aqueous solutions with gold at temperatures above 100 °C,^{42–44} however, the thermal decomposition for polymeric AuCN complexes has been reported to occur at temperatures above 350 °C.⁴⁵ Thus, it is possible that restructuring competes with the predicted decomposition mechanism in which the as-adsorbed CN/Au{111} is hydrolyzed by atmospheric water vapor.⁴²

Segmentation analysis,^{46–49} which takes into account all information in the images, was used to highlight the information pertaining to the ribbon orientation of the annealed CN/Au{111} system. Ribbon domains were observed to be rotationally offset from one another separated by topologically distinct boundaries as shown in Figure 3.4A, a STM image of annealed CN/Au{111}. Information based on the analysis of detected Fourier modes (see Supplementary Information) reveals, as shown in Figure 3.4B, the orientations of the different domains, identifies the domain boundaries, and detects Au{111} step edges. The measured angles between the different ribbon domains are all calculated to be multiples of 60° indicating that ribbon direction is significantly influenced by the hexagonal symmetry

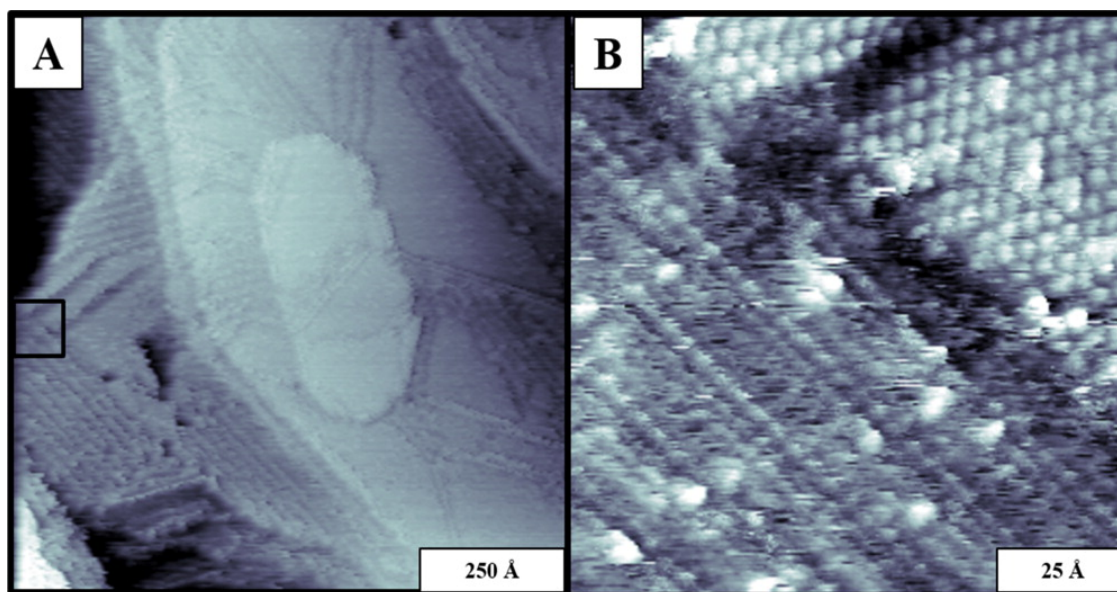


Figure 3.3: (A) Transition from HCP to ribbon structure imaged after 6 h exposure to ~ 100 °C. (B) Higher resolution image, highlighting a region with both (upper right) hexagonally close-packed and (lower left) ribbon structure regions. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA.

of the underlying gold substrate.

Segmentation analysis was further utilized on the molecular-resolution STM image in Figure 3.5A to isolate the three distinct regions shown in Figure 3.5B that compose the ribbons.^{46–49} The regions identified as 1 and 2 in the segmented image are two separate ribbon regions that are offset by 120° . Region 3 is an example of a typical domain boundary between two orientation domains observed to be a topographically distinct molecular region. Within region 1, three distinct rows compose the ribbon features along with disordered portions disrupting the continuity of the ribbons. These disordered molecular regions are similar in structure to the molecules observed in the domain boundary.

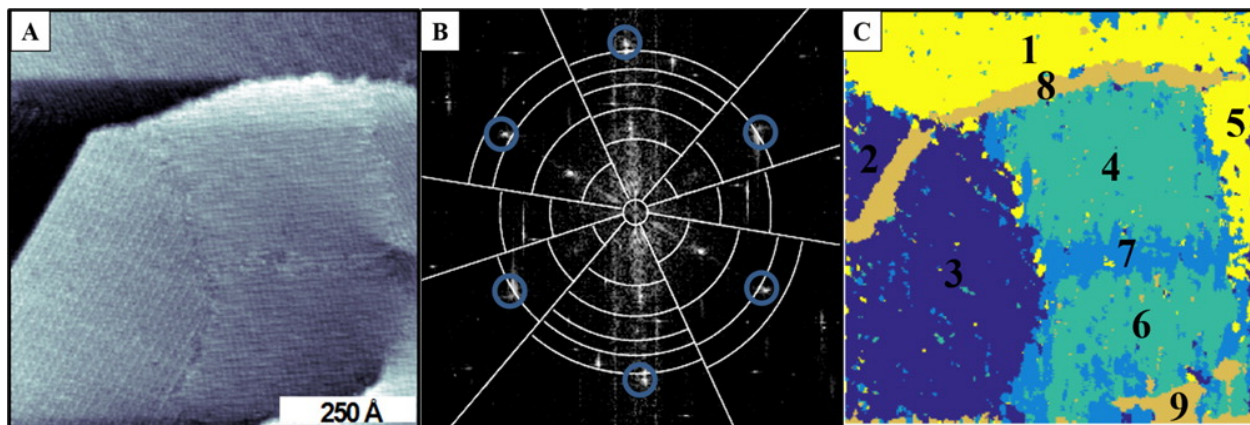


Figure 3.4: (A) Scanning tunneling microscope image of the annealed CN/Au{111} with six separate ribbon domains and three different relative rotations of the ribbon direction. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA. (B) Associated segmented image partitioned in the Fourier domain highlighting the three different orientations. (C) Regions 1–6 represent ribbon regions, with each color indicating a ribbon region of a different rotational orientation. Region 7 is a ribbon domain boundary, and regions 8 and 9 are step edges. Ribbon orientations are relatively offset by rotations of multiples of 60° following the HCP symmetry of the underlying gold surface.

Positions of the molecules within the different ribbon regions were analyzed to develop a structural model. The STM images in Figure 3.6, along with corresponding surface profiles, were used to generate the lattice spacing and apparent height information summarized in Table 3.1. Figures 3.6A and 3.6B show the expected apparent height of a typical step edge on the Au{111} surface. Using this distance as an internal reference, the relative apparent height difference between two adjacent rows of the ribbons under these conditions is 0.33 ± 0.09 Å. This measurement is close to the published experimental and calculated results for the difference between Au–C and Au–N bond lengths in solid, crystalline AuCN, in which the Au–C bond is reported as longer,⁵⁰ although we do not expect STM images to yield physical height differences because they are convolutions of geometric and electronic structure.^{51–54} Lateral distances for the ribbon structure are also summarized in Table 3.1, and correspond to letters a–f from the profiles of Figure 3.6C shown in Figure 3.6D. Note that all of the observed lateral distances are within experimental error of the lattice constant we measured for the initial as-adsorbed CN/Au{111} and take into account at least

10 independent samples using over 50 images, suggesting that the upright orientations of the molecules are maintained. This result is further supported by vibrational spectroscopic results discussed below.

The vibrational spectra were analyzed to help construct a structural model for annealed cyanide SAMs on Au{111}. The process of annealing monolayers of CN on Au{111} results in a blue shift of the frequency of the CN vibration. Cyanide molecules initially adsorbed on Au{111} at room temperature exhibit a peak at 2146 cm^{-1} using attenuated total reflection-infrared spectroscopy (ATR-IR), which is in good agreement with the typical blue shift expected from the free cyanide ion in solution.^{38,40,55} The character of the Au–CN bond is typically considered to be of partially covalent character in gold-cyanide coordination complexes with the bond strength exceeding that of Au–S.^{7,13,56,57} Alkanethiol SAMs exhibit mobility on the surface,^{7,58} and the same can be suggested for cyanide monolayers. After 6 h of heating at $100\text{ }^{\circ}\text{C}$, the spectrum in Figure 3.7A shows a new peak at 2235 cm^{-1} along with original as-adsorbed peak. The new peak is within the expected range for covalently bound CN on Au.^{38,50,59} Additional heating, typically after 18 h, generates a monolayer with the spectrum shown in Figure 3.7B, where the original peak has disappeared. Surprisingly, the IR spectra did not contain a separate measurable peak for the weaker Au–NC bound molecules, and no other peaks were observed in regions indicating new bond formation. Breaking the CN bond and/or desorption of the CN molecules from the surface would result in complete loss of the detected vibrational mode in this region. As described below, surface-enhanced Raman spectroscopy *does* yield additional spectral features (*vide infra*).

The orientation of the cyanide molecules in the annealed system was determined through the use polarization-modulation infrared spectroscopy (PM-IRRAS). The selection rules for PM-IRRAS require that only the interaction with dipoles oriented normal to the surface are detected.⁶⁰ Because of challenges due to rigidity and the thinness of the molecular layer and specular reflection from the flatness of the Au{111}, we used polycrystalline Au/Si (as opposed to Au on mica for STM measurements) for PM-IRRAS measurements (see Supplementary Information). Figure 3.6C shows the PM-IRRAS spectra for annealed CN/Au{111}, along with ATR-IR spectra for the as-adsorbed and annealed cyanide monolayers. Apart from

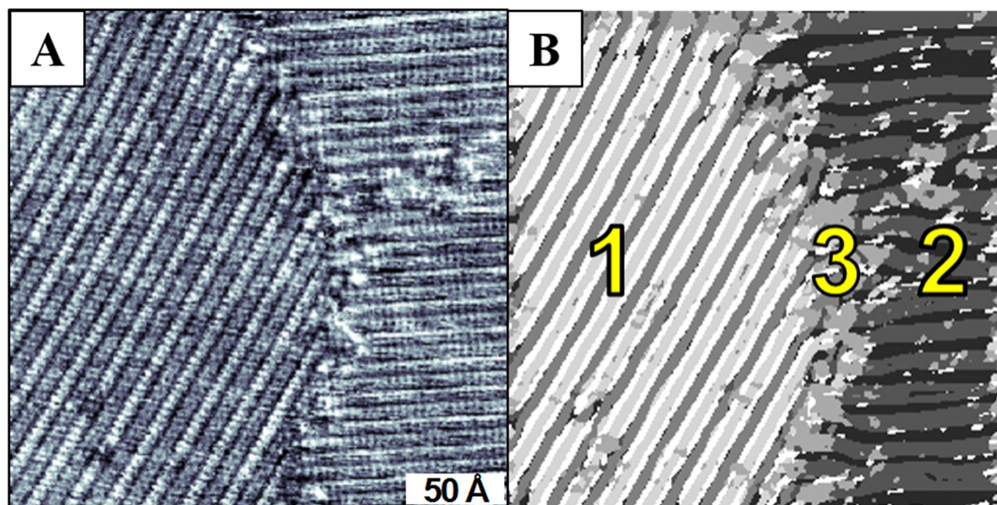


Figure 3.5: (A) Scanning tunneling microscope image of the region of thermally annealed CN/Au{111} with a domain boundary separating rotational domains. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA. (B) Segmentation analysis results showing the domain boundary (3) and the rotational domains (1 and 2).

the small deviation (2 cm^{-1}) between the annealed ATR-IR and PM-IRRAS, the spectra were in good agreement indicating that bonding interpretations based on the spectral analyses should be valid for both systems. The results indicate that after thermal annealing, the molecules are oriented normal to the surface.

Substrate-adsorbate modes for cyanide bound to gold surfaces are found in the low-frequency region, $100\text{--}500 \text{ cm}^{-1}$, of the Raman spectra.^{50,57} The surface-enhanced Raman spectra of cyanide SAMs on Au{111} after annealing for 24 h at 100°C are shown in Figure 3.8 with the typical vibrational modes, also observed in the as-deposited monolayers, which are known to be characteristic of Au–CN bonding. The values of 304 and 396 cm^{-1} , representing the Au–CN stretch and Au–CN bend, are red shifted by 10 cm^{-1} in comparison to the initial as-adsorbed cyanide.^{50,53,61,62} An additional low frequency peak is observed at 141 cm^{-1} , a value that is close to the AuNC vibrational frequency reported for the AuNC containing hexagonally bundled, linear AuCN chains of the solid crystal.⁵⁰ Furthermore, a second, blue-shifted peak is observed in the region of the CN vibrational frequency at 2195 cm^{-1} , which is also close to the reported value for the same crystalline structure (see

Table 3.1: Measured Distances for Annealed CN/Au{111} Corresponding to the Profiles Shown in Figure 3.6

feature	lateral distance (Å)	apparent height (Å)
a	–	2.39 ± 0.09
b	–	0.33 ± 0.09
c	18.1 ± 0.1	–
d	3.5 ± 0.4	–
e	11.5 ± 0.2	–
f	3.8 ± 0.4	–

Supplementary Information Figure A.8 for a comparison with the as-deposited system).⁵⁰ The appearance of the 2195 cm^{-1} vibration is an indication of Au–NC on the surface because only the ‘infinite’ chain structure of the AuCN solid that contains the Au–NC configuration, as opposed to the solution complex, $\text{Au}(\text{CN})_2^-$, exhibits the Au–NC vibration.^{50,62}

Combining the structural and vibrational characterization, we propose a bonding scheme, shown in Figure 3.9, to describe the annealed CN/Au{111} ribbon structure. The alternating regions of oppositely oriented molecules were constructed using the 0.33 Å difference in apparent height to match the measurement that closely matches the reported distance difference between longer Au–C and shorter Au–N bond lengths in the AuCN crystal.⁵⁰ In the annealed structure, two rows of Au–NC are separated on each side from a row of Au–CN by a single-molecule-wide vacancy row (bottom left of Figure 3.9). In this arrangement, the molecules maintain the pre-annealing lattice spacing³⁸ and match the measured unit cell containing three molecules ($3.8\text{ Å} \times 18.1\text{ Å}$) shown previously in Figure 3.6C. Note that the new structure does not maintain the hexagonal lattice of the as-adsorbed system, but the ribbon direction continues to follow the close-packed direction of the underlying Au{111} substrate (the straight step edges in Fig. 3.6A).

In nitrile SAMs on Au{111}, unfavorable dipole-dipole interactions are minimized when the functional group assumes an orientation almost parallel to the substrate enabling a

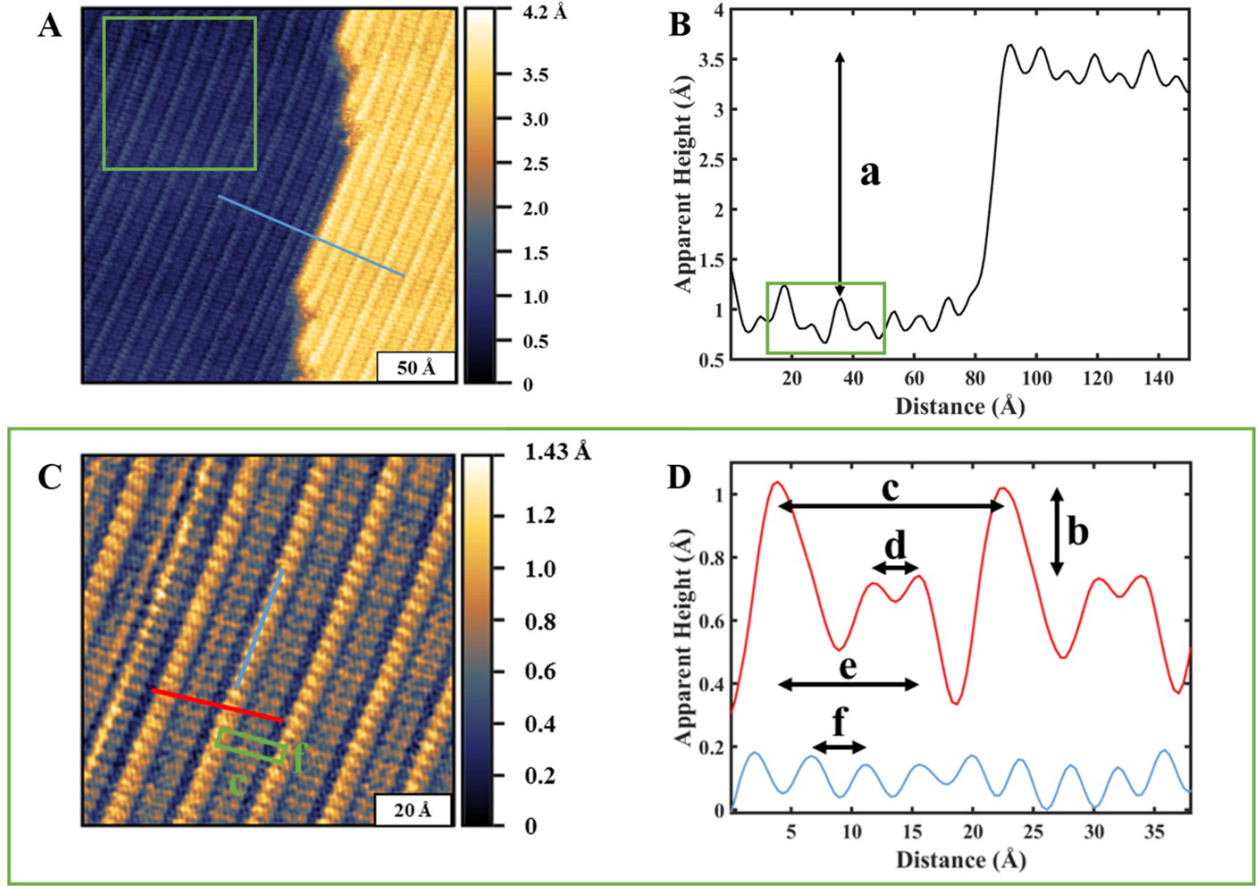


Figure 3.6: (A,C) Scanning tunneling microscope images of the ribbon structures of annealed CN on Au{111} (false colored to highlight the relative apparent height differences and lateral distances). The close-packed substrate lattice direction is indicated by the straight step edge and ribbon orientation in (A). (B) Surface profile shown as the blue line in (A), showing the apparent height variations of the ribbon structure of annealed CN on Au{111} and a step edge, which is used as an internal reference. (C) Higher resolution image of the area indicated in (A), with the unit cell shown as the green box. (D) Corresponding surface profiles along and across the rows shown in (B). Letters a–f correspond to the measured peak-to-peak distances summarized in Table 3.1. Imaging conditions: $V_{\text{sample}} = -1$ V and $I_{\text{tunnel}} = 5$ pA.

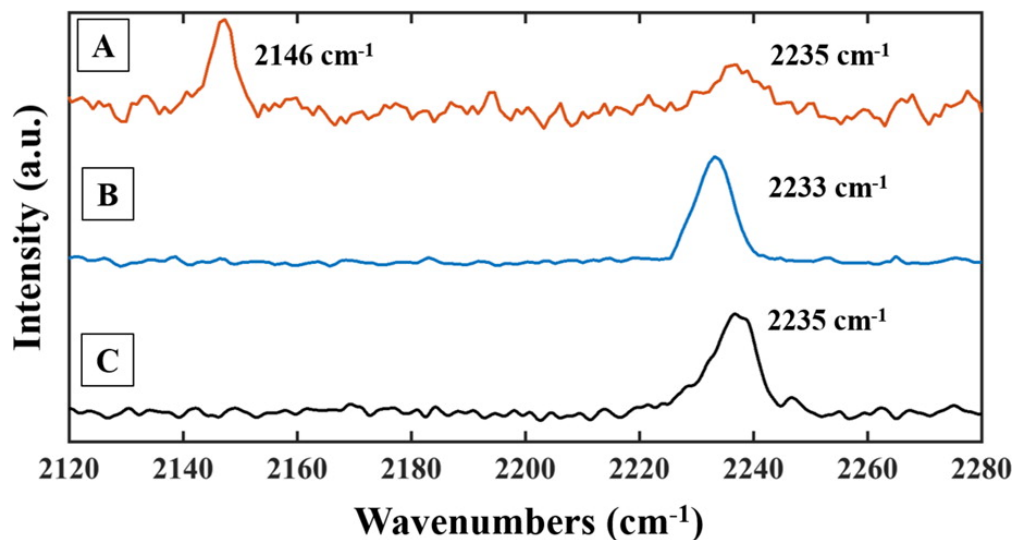


Figure 3.7: Attenuated total reflection infrared spectra of CN/Au{111} (A) after 6 h of thermal annealing at 100 °C and (B) after 24 h of thermal annealing at ~ 100 °C. (C) Polarization-modulation infrared absorption spectroscopy for CN/Au/Si after 24 h of thermal annealing at 100 °C.

tip-to-tail configuration.^{1,14,63,64} This interaction is one possibility for the driving force for the transition between structures here.⁶³ Dipole-dipole interactions between inverted adjacent rows would be favorable after the inversion of the cyanide molecules from Au–CN to Au–NC, but the other energetics have to be considered as well. Only calculations on infinite, linear AuCN chains of the crystalline structure have reported the AuNC vibrational frequency.⁵⁰ Also consistent with this model is the higher frequency CN vibration that is typically associated with a significantly covalent bonding environment, which is reported for gold-cyanide complexes, frequently found in nitriles, and reported for solid, crystalline AuCN.^{50,55,65–67}

3.4 Conclusions and Prospects

Cyanide monolayers that are initially hexagonally close-packed when deposited at room temperature form a ribbon structure after thermal annealing for over 18 h at 100 °C on Au{111}. In this arrangement, molecules assume positions in ‘striped’ regions with stripes that follow the hexagonal symmetry of the underlying gold substrate. Images of annealed

CN/Au{111} reveal regions within the ribbons that have a relative height difference that is in agreement with calculated and experimentally determined differences between bond lengths of the longer Au–CN and shorter Au–NC bonding schemes.⁵⁰ Infrared spectroscopic measurements indicate the CN vibration shifts from 2146 to 2233 cm⁻¹ while maintaining an upright orientation. Surface-enhanced Raman spectroscopy reveals an *additional* substrate-adsorbate bonding mode that is consistent with the observed Au–N bonding mode in linear AuCN crystalline chains along with a doublet in the high frequency region, suggesting another chemical state exists that we attribute to Au–NC. Ribbon regions of similar apparent height measures in multiples of the cyanide molecule lattice constant of ~ 3.8 Å. We conclude by proposing a bonding scheme consisting of a mixed monolayer of upright cyanide and isocyanide molecules on the surface that is the result of a thermally induced process crystallizing the surface similar to what is found in solid AuCN. Such control of orientation may ultimately be of use in templating the growth of one- and two-dimensional materials on substrates.^{68,69}

3.5 Experimental Methods

3.5.1 Monolayer Preparation

Au{111}/mica substrates, 150 nm of Au{111} purchased from Agilent Technologies, (Santa Clara, CA), are hydrogen flame annealed, as described previously, to clean the surface and to increase the size of the atomically flat terraces.^{7,70} Monolayers of cyanide were prepared for STM measurements by placing 0.1 mg of solid KCN ($\geq 96\%$, Sigma Aldrich, St. Louis, MO) stored in a desiccator, without any further purification or treatment, in a glass vial with the Au{111}/mica substrate for 24 h at room temperature.³⁸ **Caution: KCN is highly toxic and produces the volatile and flammable HCN(g) when it reacts with water and oxygen. It should be used with proper personal protective equipment, in a fume hood, and kept out of extreme temperatures.** Afterwards, the Au{111}/mica substrate was removed from the vial with the KCN, transferred to a clean glass vial in order to heat the sample only (not the KCN), and allowed to rest in the fume hood for 1 h before

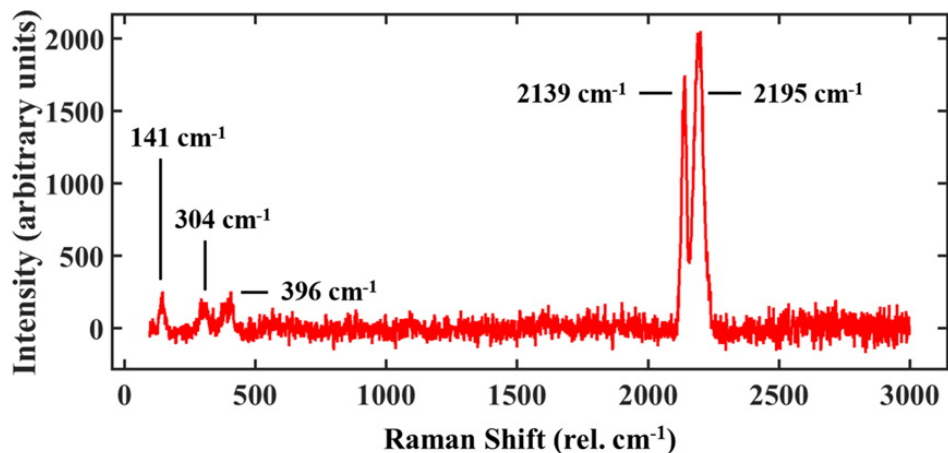


Figure 3.8: Raman spectrum showing both the low- and high-frequency modes of CN/Au{111} after thermal annealing for over 24 h at ~ 100 °C. The most important aspects of the spectrum are the new peaks at 141 and 2195 cm^{-1} without loss of the vibrations that are also detected on the as-adsorbed sample.

being placed in an oven for annealing at 100 °C for either 6, 18, or 24 h. Following annealing, the samples are allowed to cool to room temperature and placed directly into the STM for imaging without further treatment.

3.5.2 Scanning Tunneling Microscopy

A custom-built, Besocke-style STM was used under standard ambient conditions using custom cut Pt/Ir tips (80:20).^{16,71} All STM images were calibrated against known references: Au{111} step edges for height and a decanethiol on Au{111} matrix for lateral distance measurements.¹⁶ Unless otherwise specified, all samples were held at -1 V bias with a 5 pA tunneling current and image resolution of 256×256 pixels.

3.5.3 Infrared Spectroscopy

Infrared (IR) spectroscopy was collected using a Thermo-Fisher Nicolet 8700 Interferometer (Thermo-Fisher Scientific, Waltham, MA) and the packaged OMNIC Software (Thermo-Fisher Scientific). The OMNIC software was also used for processing the spectra and identifying peak positions. All IR samples were incubated with KCN and annealed in the same

manner as described for the STM samples. The entire beam path was purged with flowing N₂ and a liquid-nitrogen-cooled mercury cadmium telluride detector was used to record spectra with a resolution of 2 cm⁻¹. Polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) used custom Au/Cr/Si samples with an 80° grazing incident angle. Shown in the supplementary material (figure A.7) is the evidence that the spectral feature related to the CN bond vibrational frequency is the same on Au{111} and polycrystalline Au/Cr/Si. Silicon substrates were deposited with a 10-nm Cr adhesion layer deposited at 3 Å/s and a 100-nm-thick layer of Au also deposited also at 3 Å/s. For collecting infrared spectrum on Au{111}, we used custom-made Au{111}/sapphire prism substrates. Prism substrates were 0.5-cm radius, 1-cm-high sapphire c-cut half-cylinders with a 2-nm-thick Nb adhesion layer deposited at 0.11 Å/s and a 40-nm-thick layer of Au, which is well below the optical penetration depth for metals in the range of the IR frequencies of interest, deposited at a rate of 0.5 Å/s. A bare Au{111}/sapphire prism sample was used for the background spectrum and an incident angle $\theta = 60^\circ > \theta_c = 34.6^\circ$ as measured relative to surface normal (the critical angle is calculated using $n=1.76$). After incubation and annealing, both STM and IR samples were directly analyzed without rinsing.

3.5.4 Raman Spectroscopy

Surface-enhanced Raman spectroscopy (SERS) was performed on a Renishaw confocal Raman microscope (Renishaw, Inc., Hoffman Estates, Illinois) configured with a laser at 514 nm wavelength, using WiRE 3.2 (Renishaw, Inc.) for spectral processing and analysis. Two substrates designed for surface enhancement were used in this work: Au{111}/mica with nanohole arrays and nanostructured Au on glass. The nanohole arrays (175 nm diameter, 300 nm periodicity) on Au{111}/mica were fabricated using a focused ion beam.²⁵ The nanostructured Au on glass substrates were made by evaporating 50 Å thick Au at 1 Å/s onto a glass slide and annealing at 400 °C for 24 h. All the SERS substrates were incubated with solid KCN and annealed in the same manner as the STM/IR samples.

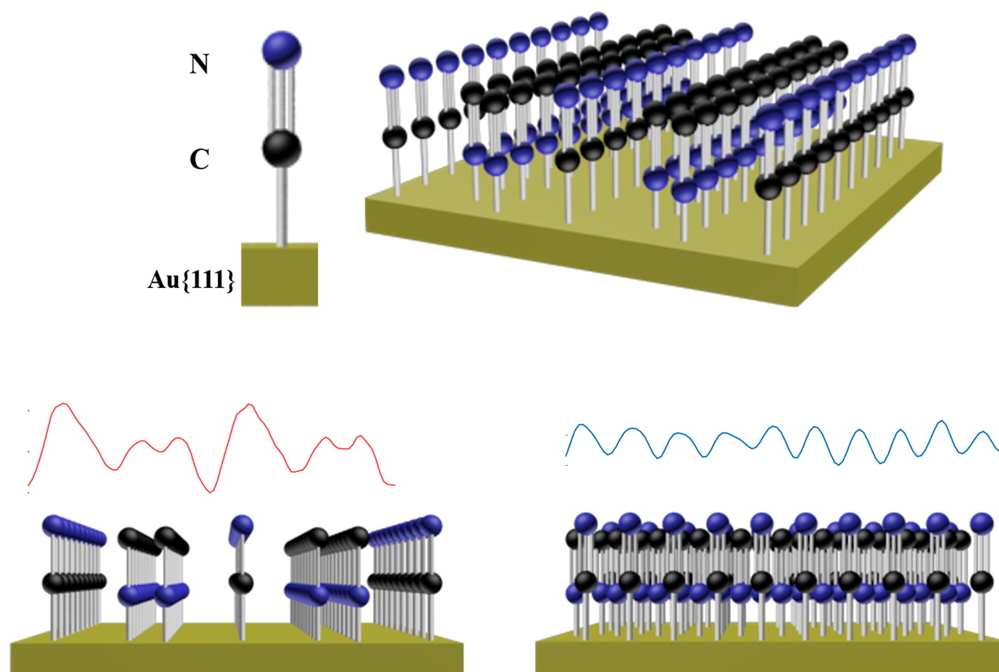


Figure 3.9: Proposed bonding scheme for annealed cyanide SAMs on Au{111} composed of a mixture of Au–CN and Au–NC bound molecules. Surface profiles that match the scanning tunneling microscope image shown in Figure 3.6 are aligned with the schematic for comparison.

3.5.5 Image Analysis

All image analyses were performed with either our custom software,⁷¹ Gwyddion (<http://gwyddion.net/>), or Matlab. The segmentation utilizing the empirical wavelet transform and variational methods as described in the supplementary information. The empirical wavelet toolbox is available online through the Mathworks file exchange, “Empirical Wavelet Toolbox”.^{46–48}

3.6 References

- (1) Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A. Characterization of X-Ray Induced Damage in Alkanethiolate Monolayers by High-Resolution Photoelectron Spectroscopy. *Langmuir* **2001**, *17*, 8–11.

- (2) Weiss, P. S. Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements. *Accounts of Chemical Research* **2008**, *41*, 1772–1781.
- (3) Han, P.; Weiss, P. S. Electronic Substrate-Mediated Interactions. *Surface Science Reports* **2012**, *67*, 19–81.
- (4) Pathem, B. K.; Claridge, S. A.; Zheng, Y. B.; Weiss, P. S. Molecular Switches and Motors on Surfaces. *Annual Review of Physical Chemistry* **2013**, *64*, 605–630.
- (5) Abendroth, J. M.; Bushuyev, O. S.; Weiss, P. S.; Barrett, C. J. Controlling Motion at the Nanoscale: Rise of the Molecular Machines. *ACS Nano* **2015**, *9*, 7746–7768.
- (6) Yamada, R.; Wano, H.; Uosaki, K. Effect of Temperature on Structure of the Self-Assembled Monolayer of Decanethiol on Au(111) Surface. *Langmuir* **2000**, *16*, 5523–5525.
- (7) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chemical Reviews* **2005**, *105*, 1103–1170.
- (8) Moore, A. M.; Yeganeh, S.; Yao, Y.; Claridge, S. A.; Tour, J. M.; Ratner, M. A.; Weiss, P. S. Polarizabilities of Adsorbed and Assembled Molecules: Measuring the Conductance Through Buried Contacts. *ACS Nano* **2010**, *4*, 7630–7636.
- (9) Zhang, Z.; Kim, H.; Noh, J.; Ahn, Y.; Son, J. Y.; Jang, J. Thermal Curing of a Self-Assembled Monolayer at the Nanoscale. *Nanoscale* **2015**, *8*, 1133–1139.
- (10) Joo, S.-W.; Kim, W.-J.; Yun, W. S.; Hwang, S.; Choi, I. S. Binding of Aromatic Isocyanides on Gold Nanoparticle Surfaces Investigated by Surface-Enhanced Raman Scattering. *Applied Spectroscopy* **2004**, *58*, 218–223.
- (11) Monnell, J. D.; Stapleton, J. J.; Jackiw, J. J.; Dunbar, T.; Reinert, W. A.; Dirk, S. M.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Ordered Local Domain Structures of Decaneselenolate and Dodecaneselenolate Monolayers on Au{111}. *Journal of Physical Chemistry B* **2004**, *108*, 9834–9841.

- (12) Swanson, S. A.; McClain, R.; Lovejoy, K. S.; Alamdari, N. B.; Hamilton, J. S.; Scott, J. C. Self-Assembled Diisocyanide Monolayer Films on Gold and Palladium. *Langmuir* **2005**, *21*, 5034–5039.
- (13) Crudden, C. M.; Horton, J. H.; Ebraliidze, I. I.; Zenkina, O. V.; McLean, A. B.; Drevniok, B.; She, Z.; Kraatz, H.-B.; Mosey, N. J.; Seki, T.; Keske, E. C.; Leake, J. D.; Rousina-Webb, A.; Wu, G. Ultra Stable Self-Assembled Monolayers of *N*-Heterocyclic Carbenes on Gold. *Nature Chemistry* **2014**, *6*, 409–414.
- (14) Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort, A.; Cyganik, P.; Zharnikov, M. Thiolate Versus Selenolate: Structure, Stability, and Charge Transfer Properties. *ACS Nano* **2015**, *9*, 4508–4526.
- (15) Parikh, A. N.; Allara, D. L.; Azouz, I. B.; Rondelez, F. An Intrinsic Relationship Between Molecular Structure in Self-Assembled *N*-Alkylsiloxane Monolayers and Deposition Temperature. *Journal of Physical Chemistry* **1994**, *98*, 7577–7590.
- (16) Bumm, L. A.; Arnold, J. J.; Charles, L. F.; Dunbar, T. D.; Allara, D. L.; Weiss, P. S. Directed Self-Assembly to Create Molecular Terraces with Molecularly Sharp Boundaries in Organic Monolayers. *Journal of the American Chemical Society* **1999**, *121*, 8017–8021.
- (17) Hohman, J. N.; Kim, M.; Schüpbach, B.; Kind, M.; Thomas, J. C.; Terfort, A.; Weiss, P. S. Dynamic Double Lattice of 1-Adamantaneselenolate Self-Assembled Monolayers on Au{111}. *Journal of the American Chemical Society* **2011**, *133*, 19422–19431.
- (18) Chen, D.; Sarid, D. Temperature Effects of Adsorption of C₆₀ Molecules on Si(111)-(7 × 7) Surfaces. *Physical Review B* **1994**, *49*, 7612–7619.
- (19) Delamarche, E.; Michel, B.; Kang, H.; Gerber, C. Thermal Stability of Self-Assembled Monolayers. *Langmuir* **1994**, *10*, 4103–4108.
- (20) Schönherr, H.; Feng, C.; Shovskiy, A. Interfacial Reactions in Confinement: Kinetics and Temperature Dependence of Reactions in Self-Assembled Monolayers Compared to Ultrathin Polymer Films. *Langmuir* **2003**, *19*, 10843–10851.

- (21) Furst, E. M. Directed Self-Assembly. *Soft Matter* **2013**, *9*, 9039–9045.
- (22) Han, P.; Akagi, K.; Federici Canova, F.; Shimizu, R.; Oguchi, H.; Shiraki, S.; Weiss, P. S.; Asao, N.; Hitosugi, T. Self-Assembly Strategy for Fabricating Connected Graphene Nanoribbons. *ACS Nano* **2015**, *9*, 12035–12044.
- (23) Hoffmann, H.; Mayer, U.; Brunner, H.; Krischanitz, A. Reflection-Absorption Infrared Spectroscopy of Self-Assembled Monolayers on Gold and Silicon Surfaces. *Vibrational Spectroscopy* **1995**, *8*, 151–157.
- (24) Dunbar, T. D.; Cygan, M. T.; Bumm, L. A.; McCarty, G. S.; Burgin, T. P.; Rein-erth, W. A.; Jones, L.; Jackiw, J. J.; Tour, J. M.; Weiss, P. S.; Allara, D. L. Com-bined Scanning Tunneling Microscopy and Infrared Spectroscopic Characterization of Mixed Surface Assemblies of Linear Conjugated Guest Molecules in Host Alkanethio-late Monolayers on Gold. *Journal of Physical Chemistry B* **2000**, *104*, 4880–4893.
- (25) Zheng, Y. B.; Payton, J. L.; Chung, C.-H.; Liu, R.; Cheunkar, S.; Pathem, B. K.; Yang, Y.; Jensen, L.; Weiss, P. S. Surface-Enhanced Raman Spectroscopy to Probe Reversibly Photoswitchable Azobenzene in Controlled Nanoscale Environments. *Nano Letters* **2011**, *11*, 3447–3452.
- (26) Jiang, N.; Foley, E. T.; Klingsporn, J. M.; Sonntag, M. D.; Valley, N. A.; Dieringer, J. A.; Seideman, T.; Schatz, G. C.; Hersam, M. C.; Van Duyne, R. P. Observation of Multiple Vibrational Modes in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy Combined with Molecular-Resolution Scanning Tunneling Microscopy. *Nano Letters* **2012**, *12*, 5061–5067.
- (27) Stranick, S. J.; Parikh, A. N.; Tao, Y.-T.; Allara, D. L.; Weiss, P. S. Phase Separation of Mixed-Composition Self-Assembled Monolayers Into Nanometer Scale Molecular Domains. *Journal of Physical Chemistry* **1994**, *98*, 7636–7646.
- (28) Poirier, G. E. Characterization of Organosulfur Molecular Monolayers on Au(111) Using Scanning Tunneling Microscopy. *Chemical Reviews* **1997**, *97*, 1117–1128.

- (29) Han, P.; Kurland, A. R.; Giordano, A. N.; Nanayakkara, S. U.; Blake, M. M.; Pochas, C. M.; Weiss, P. S. Heads and Tails: Simultaneous Exposed and Buried Interface Imaging of Monolayers. *ACS Nano* **2009**, *3*, 3115–3121.
- (30) Hohman, J. N.; Zhang, P.; Morin, E. I.; Han, P.; Kim, M.; Kurland, A. R.; McClanahan, P. D.; Balema, V. P.; Weiss, P. S. Self-Assembly of Carboranethiol Isomers on Au{111}: Intermolecular Interactions Determined by Molecular Dipole Orientations. *ACS Nano* **2009**, *3*, 527–536.
- (31) Hostetler, M. J.; Stokes, J. J.; Murray, R. W. Infrared Spectroscopy of Three-Dimensional Self-Assembled Monolayers: *N*-Alkanethiolate Monolayers on Gold Cluster Compounds. *Langmuir* **1996**, *12*, 3604–3612.
- (32) Dubois, L. H.; Nuzzo, R. G. Synthesis, Structure, and Properties of Model Organic Surfaces. *Annual Review of Physical Chemistry* **1992**, *43*, 437–463.
- (33) Allara, D. L.; Parikh, A. N.; Rondelez, F. Evidence for a Unique Chain Organization in Long Chain Silane Monolayers Deposited on Two Widely Different Solid Substrates. *Langmuir* **1995**, *11*, 2357–2360.
- (34) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H.-P. Adsorbate-Substrate Vibrational Modes of Benzene on Ag(110) Resolved with Scanning Tunneling Spectroscopy. *Physical Review Letters* **2001**, *86*, 1050–1053.
- (35) Rosenbaum, A. W.; Freedman, M. A.; Darling, S. B.; Popova, I.; Sibener, S. J. Surface Vibrations in Alkanethiol Self-Assembled Monolayers of Varying Chain Length. *Journal of Chemical Physics* **2004**, *120*, 3880–3886.
- (36) Haensch, C.; Hoeppener, S.; Schubert, U. S. Chemical Modification of Self-Assembled Silane Based Monolayers by Surface Reactions. *Chemical Society Reviews* **2010**, *39*, 2323–2334.
- (37) Elliott, A. B. S.; Horvath, R.; Gordon, K. C. Vibrational Spectroscopy as a Probe of Molecule-Based Devices. *Chem. Soc. Rev.* **2012**, *41*, 1929–1946.

- (38) Guttentag, A. I.; Wächter, T.; Barr, K. K.; Abendroth, J. M.; Song, T.-B.; Sullivan, N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}. *Journal of Physical Chemistry C* **2016**, *120*, 26736–26746.
- (39) Iguchi, K. Dipole Moment of the HCN Molecule. *J. Chem. Phys.* **1956**, *25*, 217–219.
- (40) Keedy, C. R. The Rotational-Vibrational Spectra of HCN and DCN: A Physical Chemistry Experiment. *Journal of Chemical Education* **1992**, *69*, A296.
- (41) Han, P.; Sykes, E. C. H.; Pearl, T. P.; Weiss, P. S. A Comparative Scanning Tunneling Microscopy Study of Physisorbed Linear Quadrupolar Molecules: C₂N₂ and CS₂ on Au{111} at 4 K. *Journal of Physical Chemistry A* **2003**, *107*, 8124–8129.
- (42) Van Deventer, J. S. J.; van der Merwe, P. F. The Effect of Temperature on the Desorption of Gold Cyanide from Activated Carbon. *Thermochimica Acta* **1993**, *221*, 99–113.
- (43) Cherevko, S.; Zeradjianin, A. R.; Topalov, A. A.; Keeley, G. P.; Mayrhofer, K. J. J. Effect of Temperature on Gold Dissolution in Acidic Media. *Journal of the Electrochemical Society* **2014**, *161*, H501.
- (44) Snyders, C. A.; Bradshaw, S. M.; Akdogan, G.; Eksteen, J. J. The Effect of Temperature, Cyanide and Base Metals on the Adsorption of Pt, Pd and Au onto Activated Carbon. *Hydrometallurgy* **2014**, *149*, 132–142.
- (45) Akhtar, M. N.; Isab, A. A.; Hassan, A. Thermal Decomposition of Trialkyl/Arylphosphine Gold(I) Cyanide Complexes. *Journal of Thermal Analysis and Calorimetry* **2000**, *61*, 119–125.
- (46) Gilles, J. Empirical Wavelet Transform. *IEEE Transactions on Signal Processing* **2013**, *61*, Conference Name: IEEE Transactions on Signal Processing, 3999–4010.
- (47) Gilles, J.; Heal, K. A Parameterless Scale-Space Approach to Find Meaningful Modes in Histograms—Application to Image and Spectrum Segmentation. *International Journal of Wavelets, Multiresolution and Information Processing* **2014**, *12*, 1450044.

- (48) Gilles, J.; Tran, G.; Osher, S. 2D Empirical Transforms. Wavelets, Ridgelets, and Curvelets Revisited. *SIAM Journal on Imaging Sciences* **2014**, *7*, 157–186.
- (49) Bui, K. V.; Fauman, J. N.; Kes, D. D.; Torres, L. F. *Unpublished*.
- (50) Bowmaker, G. A.; Kennedy, B. J.; Reid, J. C. Crystal Structures of AuCN and AgCN and Vibrational Spectroscopic Studies of AuCN, AgCN, and CuCN. *Inorganic Chemistry* **1998**, *37*, 3968–3974.
- (51) Eigler, D. M.; Weiss, P. S.; Schweizer, E. K.; Lang, N. D. Imaging Xe with a Low-Temperature Scanning Tunneling Microscope. *Physical Review Letters* **1991**, *66*, 1189–1192.
- (52) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. Are Single Molecular Wires Conducting? *Science* **1996**, *271*, 1705–1707.
- (53) Bumm, L. A.; Arnold, J. J.; Dunbar, T. D.; Allara, D. L.; Weiss, P. S. Electron Transfer Through Organic Molecules. *Journal of Physical Chemistry B* **1999**, *103*, 8122–8127.
- (54) Monnell, J. D.; Stapleton, J. J.; Dirk, S. M.; Reinert, W. A.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Relative Conductances of Alkaneselenolate and Alkanethiolate Monolayers on Au{111}. *Journal of Physical Chemistry B* **2005**, *109*, 20343–20349.
- (55) Jobe, D. J.; Westaway, K. C. Fourier Transform Infrared Spectroscopy Studies of Cyanide Ion Solutions of Dimethylformamide and Aqueous Dimethylformamide. *Canadian Journal of Chemistry* **1993**, *71*, 1353–1361.
- (56) Häkkinen, H. The Gold-Sulfur Interface at the Nanoscale. *Nature Chemistry* **2012**, *4*, 443–455.
- (57) Beltramo, G. L.; Shubina, T. E.; Mitchell, S. J.; Koper, M. T. M. Cyanide Adsorption on Gold Electrodes: a Combined Surface Enhanced Raman Spectroscopy and Density Functional Theory Study. *Journal of Electroanalytical Chemistry* **2004**, *563*, 111–120.
- (58) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chemical Reviews* **1996**, *96*, 1533–1554.

- (59) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J. The Infrared Spectra of Nitriles and Related Compounds Frozen in Ar and H₂O. *The Astrophysical Journal* **1997**, *476*, 932.
- (60) Buffeteau, T.; Desbat, B.; Turllet, J. M. Polarization Modulation FT-IR Spectroscopy of Surfaces and Ultra-Thin Films: Experimental Procedure and Quantitative Analysis. *Applied Spectroscopy* **1991**, *45*, 380–389.
- (61) Pettinger, B.; Picardi, G.; Schuster, R.; Ertl, G. Surface-Enhanced and STM Tip-Enhanced Raman Spectroscopy of CN[−] Ions at Gold Surfaces. *Journal of Electroanalytical Chemistry* **2003**, *554-555*, 293–299.
- (62) Senapati, D.; Dasary, S. S. R.; Singh, A. K.; Senapati, T.; Yu, H.; Ray, P. C. A Label-Free Gold-Nanoparticle-Based SERS Assay for Direct Cyanide Detection at the Parts-Per-Trillion Level. *Chemistry – A European Journal* **2011**, *17*, 8445–8451.
- (63) Hautman, J.; Bareman, J. P.; Mar, W.; Klein, M. L. Molecular Dynamics Investigations of Self-Assembled Monolayers. *Journal of the Chemical Society-Faraday Transactions* **1991**, *87*, 2031–2037.
- (64) Frey, S.; Shaporenko, A.; Zharnikov, M.; Harder, P.; Allara, D. L. Self-Assembled Monolayers of Nitrile-Functionalized Alkanethiols on Gold and Silver Substrates. *Journal of Physical Chemistry B* **2003**, *107*, 7716–7725.
- (65) Neelakantan, P. Raman Spectrum of Acetonitrile. *Proceedings of the Indian Academy of Sciences-Section A* **1964**, *60*, 422–424.
- (66) Kunitatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G.; Philpott, M. R. A Study of the Gold/Cyanide Solution Interface by In Situ Polarization-Modulated Fourier Transform Infrared Reflection Absorption Spectroscopy. *Langmuir* **1988**, *4*, 337–341.
- (67) Wang, X.-B.; Wang, Y.-L.; Yang, J.; Xing, X.-P.; Li, J.; Wang, L.-S. Evidence of Significant Covalent Bonding in Au(CN)₂[−]. *Journal of the American Chemical Society* **2009**, *131*, 16368–16370.

- (68) Bhimanapati, G. R.; Lin, Z.; Meunier, V.; Jung, Y.; Cha, J.; Das, S.; Xiao, D.; Son, Y.; Strano, M. S.; Cooper, V. R.; Liang, L.; Louie, S. G.; Ringe, E.; Zhou, W.; Kim, S. S.; Naik, R. R.; Sumpter, B. G.; Terrones, H.; Xia, F.; Wang, Y.; Zhu, J.; Akinwande, D.; Alem, N.; Schuller, J. A.; Schaak, R. E.; Terrones, M.; Robinson, J. A. Recent Advances in Two-Dimensional Materials Beyond Graphene. *ACS Nano* **2015**, *9*, 11509–11539.
- (69) Zhang, H. Ultrathin Two-Dimensional Nanomaterials. *ACS Nano* **2015**, *9*, 9451–9469.
- (70) Porath, D.; Millo, O.; Gersten, J. I. Scanning Tunneling Microscopy Studies and Computer Simulations of Annealing of Gold Films. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **1996**, *14*, 30–37.
- (71) Mantooth, B. A. Nanoscopic Analyses: Single Molecule Characterization in Molecular Electronics and Surface Science., Ph.D. Thesis, University Park, PA, USA: The Pennsylvania State University, 2004.

CHAPTER 4

Surface-Mediated Crystal Growth of Aurous Cyanide from Molecular Self-Assembled Monolayers

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4.1 Introduction

In previous chapters, we discussed the development and characterization of two types of well-ordered cyanide self-assembled monolayer systems (*i.e.*, monolayers that were hexagonally close-packed (HCP) or formed ribbon structures).^{1,2} These monolayers not only had different surface structures, but also different vibrational modes corresponding to differing chemical environments. Understanding how to control and to tailor surface properties can lead to better understanding of material properties and fabrication. For example, we and others have shown that changing monolayers on surfaces can affect the work function of the underlying substrate.³⁻⁷ With regards to gold cyanide (AuCN), the semiconducting nature of this compound may have applications in designing new scaffolding for nanofabrication.^{8,9}

AuCN structures have recently been applied in a variety of studies including in the creation of 1D and 2D nanostructures (e.g., nanowires, nanosheets),^{8,10} as model systems for instrumentation and technique development, ([11] and Chapter 5) to simulate effects of heavy elements on chemical systems,¹² and for enhancing lithium ion batteries.¹³ The band structure and chemical reactivity of AuCN arise, in part, from its crystal structure and simple molecular structure. AuCN crystals are composed of repeating gold and cyanide units in linear chains.¹⁴⁻¹⁶ These chains are hexagonal close-packed with the gold atoms in the same plane across the unit cell. Compared with silver or copper cyanide systems, the gold cyanide unit cell is simpler than the other metal cyanide structures because aurophilic interactions between neighboring gold atoms are strong compared with that of other group 11 atoms.^{14,15,17,18} This relatively simple crystal structure limits variability in crystal growth, which allows for a straightforward investigative approach to characterize and to understand potential growth mechanisms of AuCN. However, while AuCN is a relatively simple system, there are still opportunities to elucidate growth pathways towards engineering systems with designed properties.

Several techniques have been developed for the growth of AuCN structures. To form monolayers, researchers have previously electrodeposited cyanide on gold substrates to create well-ordered cyanide systems in the aqueous phase.¹⁹ We have described methods to

create self-assembled monolayers (SAMs) of AuCN by exposing gold surfaces to dilute concentrations of cyanide vapor (Chapter 2) and we were able to modify the surfaces through thermal annealing (Chapter 3), which changed the hexagonally close-packed monolayers into ribbon-like structures.^{1,2} Kim and coworkers have recently synthesized nanowires of AuCN on graphene substrates through drop casting dilute AuCN, extending this system to 1D structures.⁸ The formation of bulk cyanide structures has been described using simple acid base chemistry, however, this method did not enable localized growth as the cyanide structures precipitated out of solution.¹⁴

Controlling the growth and, in turn, chemical bonding properties of AuCN can lead to the development of these systems towards applications in materials and nanoscience. To assess the chemical environments of these systems, various spectroscopic methods have been employed. Specifically, by using vibrational spectroscopy, the measured vibrational energy of AuCN can be related to the ensemble-average chemical environment and bonding of its composing molecules. Cyanide compounds have strong infrared (IR) and Raman scattering signals between 2100 and 2300 cm^{-1} (C–N stretch).^{14,20–24} However, literature values for the C–N stretch of cyanide on surfaces vary based upon deposition methods and experimental conditions. Even for AuCN, some sources indicate a C–N vibration stretching mode between 2140 and 2160 cm^{-1} while other sources indicate it being at 2230 cm^{-1} . This discrepancy suggests there are varying electronic and bonding states associated with AuCN and that the local chemical environment of the C–N stretching mode can be tuned via different synthetic methods as well as surface arrangement, which can result in greater control over the band structure and chemical reactivity of these compounds.

In this work, we describe a method to create AuCN crystals through substrate-mediated growth on gold substrates. We characterized these crystals using a variety of surface sensitive and microscopy techniques including confocal Raman spectroscopy, scanning electron microscopy (SEM), and contact profilometry. These techniques were used to categorize the chemical environments as well as the bulk properties of the AuCN crystals. Understanding the growth properties of AuCN will enable us better control over the growth of these structures for micron and nano-scale applications.

4.2 Methods

4.2.1 Sample preparation

Gold cyanide crystals were grown using a similar method to previous work by first rinsing gold substrates (described below) with ethanol and then flame annealing with a hydrogen flame. This process not only cleaned the substrates, but also smoothed the gold surfaces. Gold substrates were then placed in a vessel that was surrounded by potassium cyanide (KCN) powders ($\geq 96\%$, Sigma Aldrich, St. Louis, MO) stored in a desiccator without any further purification or treatment. The vessel was kept in a fume hood and opened to the atmosphere only to replace the KCN or to place or remove the gold substrates. All crystal morphologies formed independently of the underlying Au substrates used (*i.e.*, Au on mica, Au on silicon, Au on sapphire).

Caution: KCN is highly toxic and produces the volatile and flammable HCN(g) when it reacts with water and oxygen. It should be used with proper personal protective equipment, in a fume hood, and kept out of extreme temperatures.

The 100-nm-thick Au substrates were created by depositing gold onto the silicon wafer using electron beam evaporation at a rate of 3 Å/s with a 10-nm-thick chromium adhesion layer deposited at 3 Å/s on top of a silicon wafer (University Wafer, South Boston, Massachusetts). The gold-limited samples were composed of 2 nm of gold (0.02 Å/s) on silicon borosilicate glass prepared using an electron beam evaporator at 300 °C. The thermally annealed AuCN crystal samples were prepared in a sealed scintillation vial held at 100 °C in an oven. For partial transitions, we used short term exposures of 18 hours. For complete transitions, samples were kept in the oven for up to one week—samples with larger crystal densities required more time. Raman spectroscopy measurements were used to monitor the progress of the transitions.

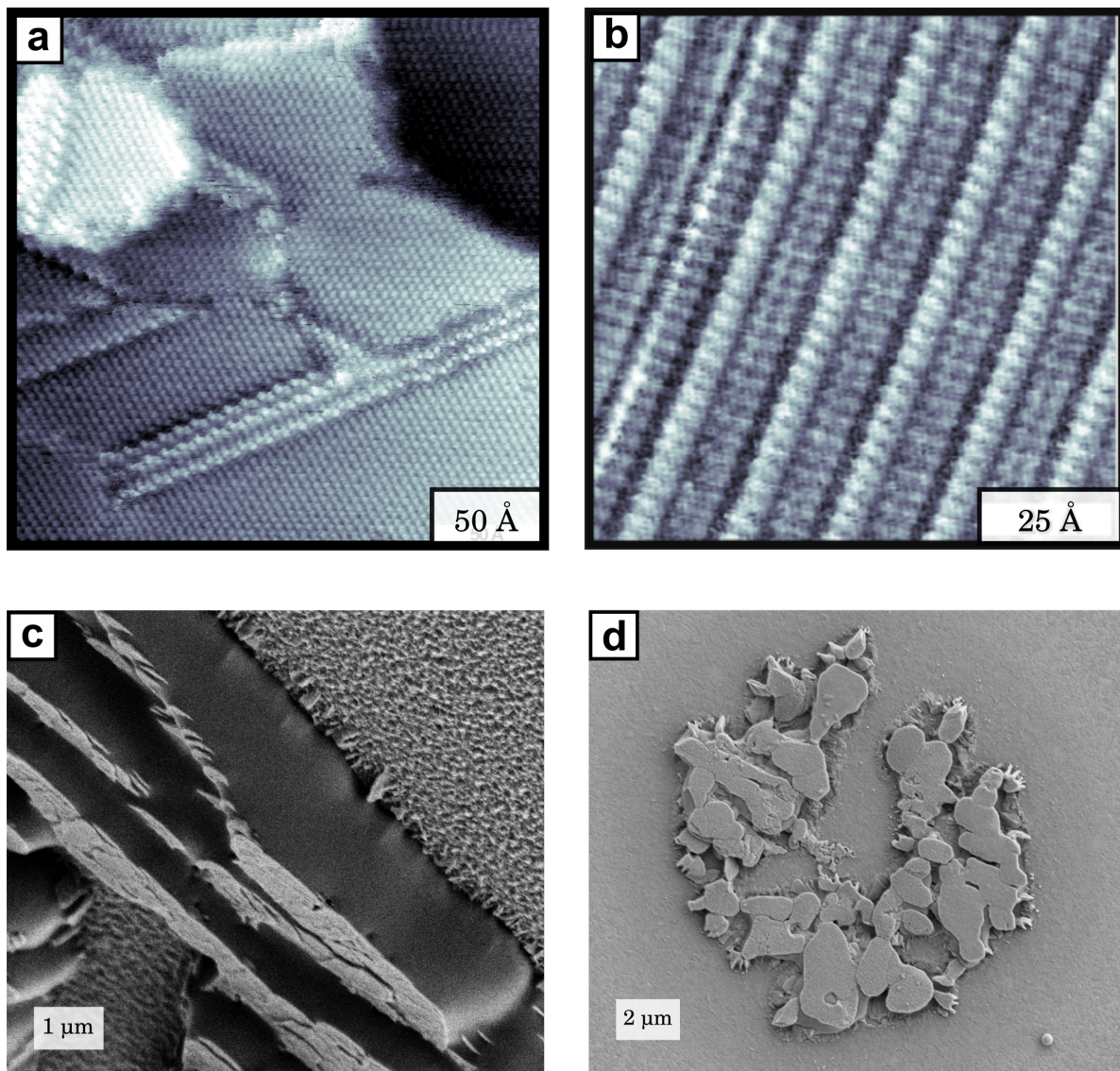


Figure 4.1: a,b) Well-ordered monolayers of cyanide on Au{111} using a custom-built scanning tunneling microscope. The tunneling current was 5 pA with a sample bias voltage of 1 V with respect to the tip. Upon thermal annealing, at 100 °C, the surface would rearrange forming the ribbon structure b). c) Scanning electron microscopy image of a crystal prior to thermal annealing taken at a 45° angle with respect to the electron beam (layout shown in supplemental information figure A.10a). d) After thermal annealing treatment of the crystal.

4.2.2 Raman and optical microscopy

Optical and Raman measurements were performed on a WITec confocal Raman microscope (Alpha300, Knoxville, Tennessee) equipped with a 532 nm laser. Most samples were scanned at 5 mW with an integration time of 50 ms and a 100 $\times$ lens to avoid degradation. The WITec Project5.5 software (Alpha300, Knoxville, Tennessee) was used to create 2D Raman maps as well as for signal processing. Signal processing included removing cosmic rays, background subtraction, and component analysis to separate the 2160 cm^{-1} peak from the 2220 cm^{-1} peak.

The depth scan image was created by stitching together multiple 2D scans of the surface at incremental depths of 200 nm per scan. Integrated intensity from the 2160 and 2220 cm^{-1} regions is used to show Raman mode spatial distribution in the crystals.

4.2.3 Scanning electron microscopy

Most scanning electron microscope images were collected using a ZEISS Supra 40VP SEM (White Plains, NY). Samples were collected using a 3 kV acceleration voltage. The Energy-dispersive X-ray spectroscopy (EDX) measurements used a TESCAN VEGA3 SEM (Fuveau, France) on the 2-nm AuCN samples described above.

4.3 Results and Discussion

We previously demonstrated the growth of cyanide monolayers on top of gold substrates, and that under different thermal conditions, we could create two different monolayer morphologies as shown from the scanning tunneling microscope images in figure 4.1a and 4.1b.^{1,2} However, when gold substrates were exposed to KCN for longer than 40 hours, larger crystal structures were observed (figure 4.1c). These AuCN crystals grew in a reproducible manner and produced consistent structures. Crystals became more numerous as the KCN exposure time increased, starting from a low surface coverage of crystals after 6 hours of exposure. Figure 4.2a shows an optical microscope image recorded after 45 hours of KCN exposure. How-

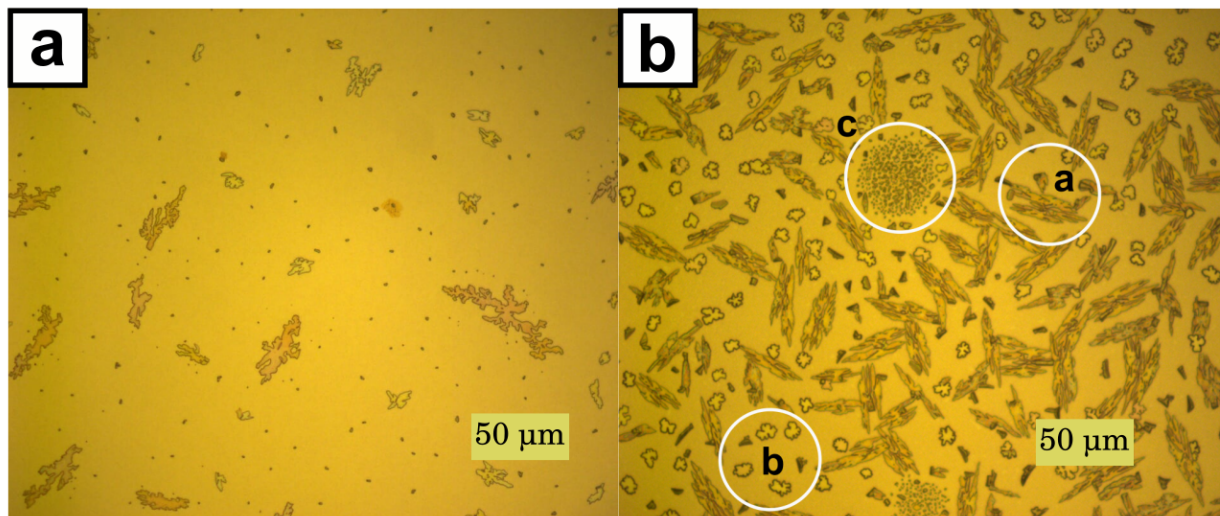


Figure 4.2: Optical microscope image of a) sparse (2 days) and b) high-crystal density structures (90 days). In b), Circle **a** corresponds to examples of the elongated crystals. They grow to lengths of $50\ \mu\text{m}$ and widths of $15\ \mu\text{m}$. Circle **b** contains examples of the amorphous crystals. They tend to grow to $20\ \mu\text{m}$ in diameter. Circle **c** highlights examples of sunbursts made from smaller particulates that collectively have diameters of $50\ \mu\text{m}$.

ever, the terminal length of the crystal—in the long direction—remained constant ($\sim 50\ \mu\text{m}$) even upon prolonged exposure of up to 90 days.

The crystals grew in three basic shapes, herein referred to as: elongated, small, and sunburst (figure 4.2b). Crystal size distributions are described in figure A.14 and table A.1. Elongated crystals (*ca.* $10\ \mu\text{m} \times 50\ \mu\text{m}$) were the most prominent type of crystal grown on Au surfaces (figure 4.2b, circle **a**). The small crystals were the second most apparent crystals and were amorphous in shape, with diameters typically less than $20\ \mu\text{m}$ (figure 4.2, circle **b**). Lastly, sunburst crystals were composed of small amorphous crystalites packed closely together in a circular shape (figure 4.2b, circle **c**). Sunburst crystals had diameters of *ca.* $50\ \mu\text{m}$. We note that the gold substrates next to the crystals likely have AuCN monolayers on their surface because our measurements in Chapter 2 did not find regions lacking the cyanide monolayer, though not visible from SEM (figure A.11).¹

Crystals appeared to prefer growth directions parallel to the surface normal. The SEM images (figure 4.1c) indicated that crystal surfaces perpendicular to the growth direction had

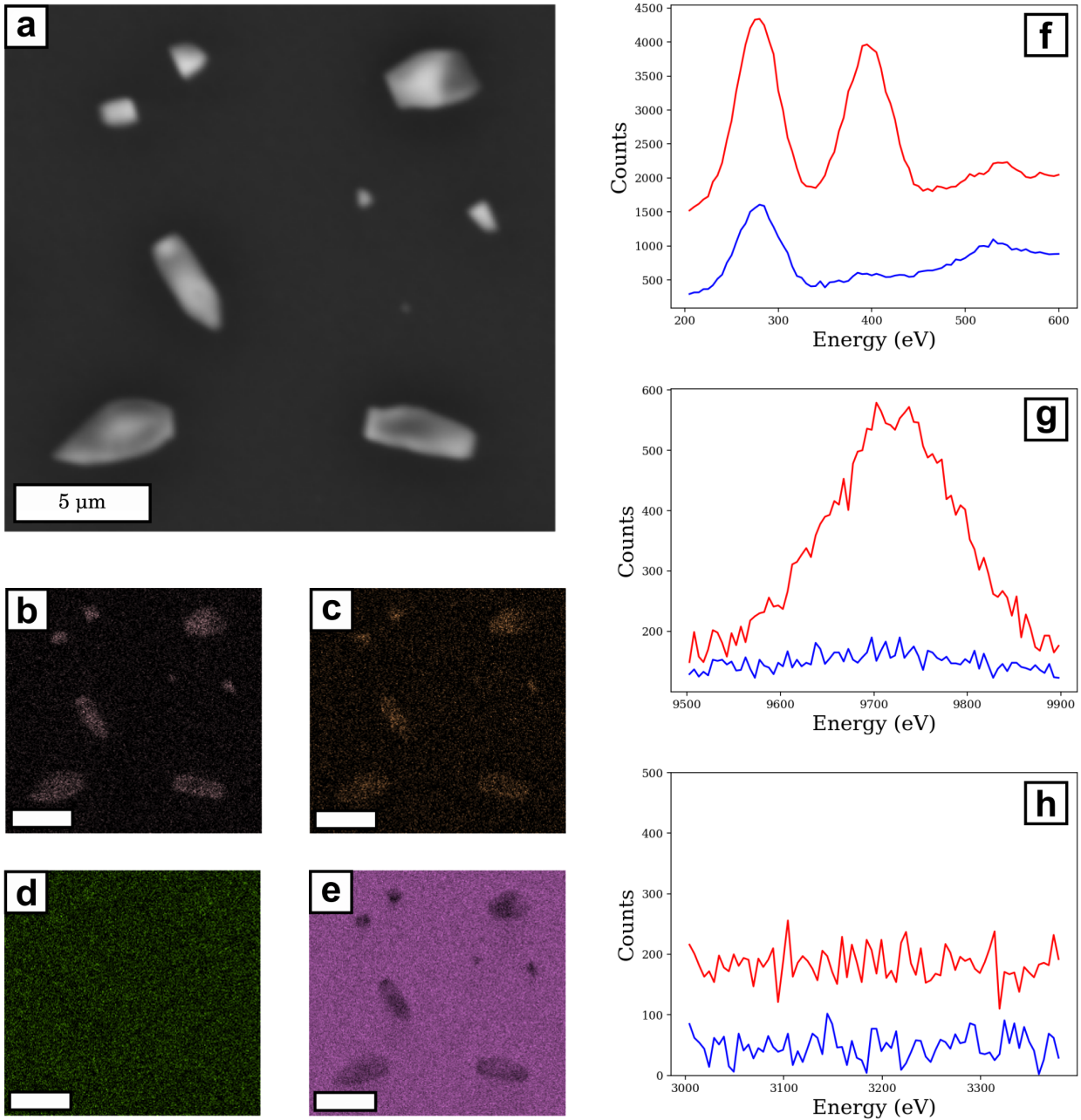


Figure 4.3: a) Scanning electron microscopy image of AuCN crystals made from 2-nm-thick Au substrate. The scale bar on each of the images is 5 μm across. Images below a) correspond to element channels: b) nitrogen, c) gold, d) oxygen, and e) silicon. f), g), and h) Correspond to the X-ray spectrum on the crystal (red) and off the crystal (blue). Counts are offset for clarity. The C and N K_{α} are shown in f) at 277 and 392 eV respectively. The Au K_{α} is shown in g) and is minimized off of the crystal as seen in c). There were no potassium K_{α} signals at 3314 eV visible in h).

minimal defects, suggestive of a potential layer-by-layer growth mechanism. The heights of the AuCN crystals were typically 1–2 μm , measured from the SEM images and via contact profilometry (in figures 4.1c and A.12 respectively). The profilometry and SEM data showed flat profiles (nanoscale roughness) along the plateaus of the crystal surface.

Upon thermal annealing at 100 °C, the morphology of the crystal structures changed as the sharp edges became smoother and neighboring crystals joined together (figure 4.1d). Considering that the packing structures of cyanide SAMs change after thermal annealing, we hypothesize that the crystal arrangements also change. For cyanide SAMs, the density of molecules in the ribbon structures is lower than that of the HCP structure, so the unit cell must change. This change correlates to the structural rearrangement we find on the crystal surfaces, as seen in figure 4.1d, in that the molecules are rearranging, resulting in more rounded crystal appearances.²

As for the formation of these crystals, we hypothesize that charged cyanide molecules react with gold in a surface-mediated growth mechanism, where surrounding Au atoms are absorbed and incorporated into the crystal structure. Gold grain densities were measured via SEM to be substantially lower around areas where AuCN crystals grew (figures 4.3c and 4.3g). Additionally, the crystals consisted only of Au, C, and N as observed via EDX spectroscopy (figures 4.3b–h). We found that EDX signals corresponding to nitrogen absorptions were colocalized with crystal locations (figures 4.3b). Elemental peaks corresponding to potassium and oxygen were notably absent (figures 4.3f and 4.3g) and diminished for silicon (figure 4.3e), the most likely impurities for these crystals; silicon and oxygen from the underlying substrates from which the crystals are grown and potassium from the solid KCN used to produce the cyanide vapor.

Furthermore, we investigated the effects of a gold-limited system versus a cyanide-limited system on the subsequent growth of crystals. In the aforementioned studies, a dilute cyanide vapor was deposited onto 100-nm-thick Au substrates, and crystal growth was performed where Au was in large excess. In order to study a gold-limited system, a 2-nm-thick layer of gold was deposited onto silicon substrates and these substrates were used for crystal growth. Cyanide crystals grew to similar sizes even when a 2-nm-thick layer of gold was used to

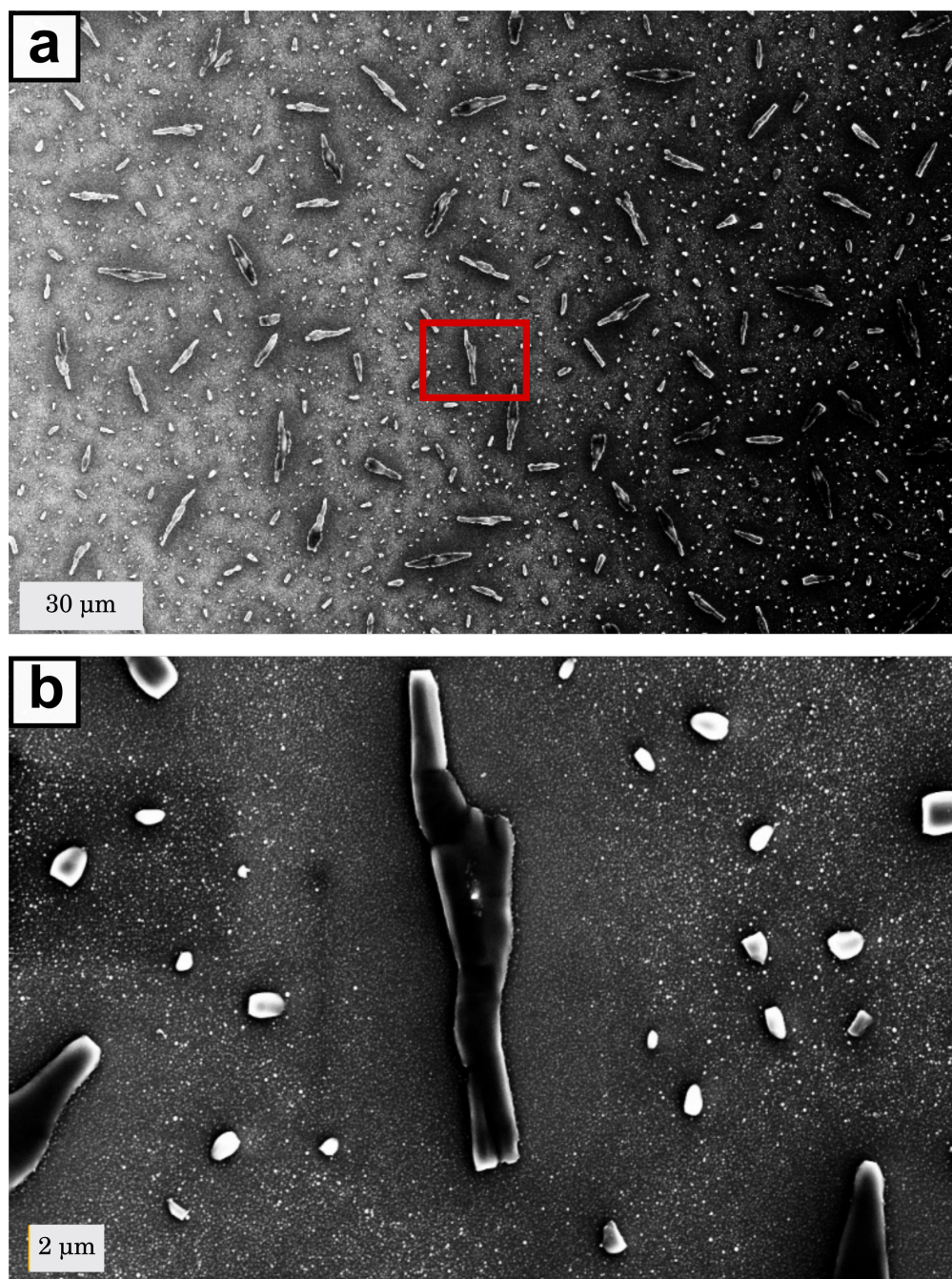


Figure 4.4: Scanning electron microscope images of AuCN crystals made from 2-nm Au substrates. a) Wide view image. The red outline corresponds to the location of figure b). Similarly to 100-nm-thick Au substrates, there are elongated and small crystals.

produce AuCN, suggesting that the terminal size of the crystals were independent of the thickness of gold from the underlying substrate.

Similar crystal morphologies (*i.e.*, elongated and small crystals) were observed for the Au-limited system compared to that of the cyanide-limited system (figure 4.4a). In contrast to the cyanide-limited crystals, the Au-limited crystals appeared to have rounded surfaces across the entire crystal (figure 4.4b). Considering that these crystals were grown from 2-nm gold on silicon substrates, it was surprising that the sizes of crystals were far larger than those of the substrate gold grains.

Thus, to understand the structures and chemical compositions of the crystals, we investigated the chemical interactions (*i.e.*, vibrational energies) of molecules in the crystals. Previously, we showed that cyanide monolayer surfaces were not able to produce detectable Raman scattering without using plasmonic enhancement.¹ However, the AuCN crystals have large Raman scattering cross-sections in an otherwise spectroscopically silent region, enabling straightforward mapping of crystal structures using confocal Raman mapping. Figure 4.5a, 4.5b show spatially resolved CN vibrational normal modes of the crystals. As grown, these crystals had a strong vibrational normal mode at 2160 cm^{-1} from the cyanide C–N stretch (figure A.16). Crystal morphologies had similar Raman signatures (*i.e.*, a C–N stretch and metal-ligand stretches around 300 cm^{-1} though metal-ligand stretches were not always visible (figure A.16).

Similar to our previous work on cyanide monolayers on Au, upon sample heating, the 2160 cm^{-1} peak of the crystals shifted to a higher energy of 2220 cm^{-1} (figure A.17). Previously, we attributed this observed shifts in the C–N peak as a result of a change in the chemical environment from heat-induced structural rearrangements. We hypothesize that the previously observed rearrangements and the crystal morphology change are both due to rearrangements in bonding from a primarily $\text{Au}(\text{CN})_2^-$ state to AuCN. The lower energy vibrational modes (*i.e.*, 2140 and 2160 cm^{-1}) correlate well to the charged $\text{Au}(\text{CN})_2^-$ species while the higher vibrational energy mode (*i.e.*, 2220 cm^{-1}) is consistent with spectra measured from bulk AuCN powder.¹⁴ Additionally, similar to vibrational spectra measured from the molecular monolayer, the peak did not translate from 2160 to 2220 cm^{-1} , but rather,

the shift occurred with one peak decreasing and the other increasing.

However, unlike cyanide monolayers, some crystals exhibited the higher energy peak even without heating. We also observed locations that had both peaks present. The spot size of the 532 nm laser used for Raman spectroscopy was *ca.* 300 nm across, which enabled single-crystal imaging experiments without measuring signals from neighboring crystals. We also observed that certain regions of crystals were more likely to have the lower energy peak versus the higher energy peak. Notably, these measurements revealed that morphologically similar crystals indiscernible via optical microscopy were structurally (*i.e.*, chemically) different.

To investigate the vibrational structures of these crystals further, we performed confocal Raman mapping at different depths of the surface. The 3D z-stack Raman map indicated that outer crystal layers were more likely to have the lower energy vibrational feature when compared to the inner layers (figure 4.5d). This difference could be due to a multitude of factors, including how heat moves through the crystal during thermal annealing, the ability of the gold surface to dissipate energy more effectively, or the surface molecules being confined in only one direction while the molecules within the bulk are confined in two directions with respect to their linear arrangement. Regardless, by heating the crystals, we demonstrate the ability to tune the vibrational modes (*i.e.*, chemical interactions within the crystal) and potentially the structures and morphologies of the crystals grown.

4.4 Conclusions and Prospects

We have demonstrated a straightforward method for creating AuCN crystals by physical vapor deposition under ambient conditions. Similar to our monolayer surfaces, we found that heating the crystals changes the CN arrangements within the crystals and shifts Raman peaks to a higher vibrational energy. Better understanding of the growth mechanism of AuCN structures will enable the construction of new nanoscale semiconducting materials. Previous work has shown the efficacy of creating one-dimensional semiconducting AuCN nanowires, and has described an orthogonal method to produce AuCN crystals. Prospective works could assess the effects of the structures of the underlying monolayer, by initially

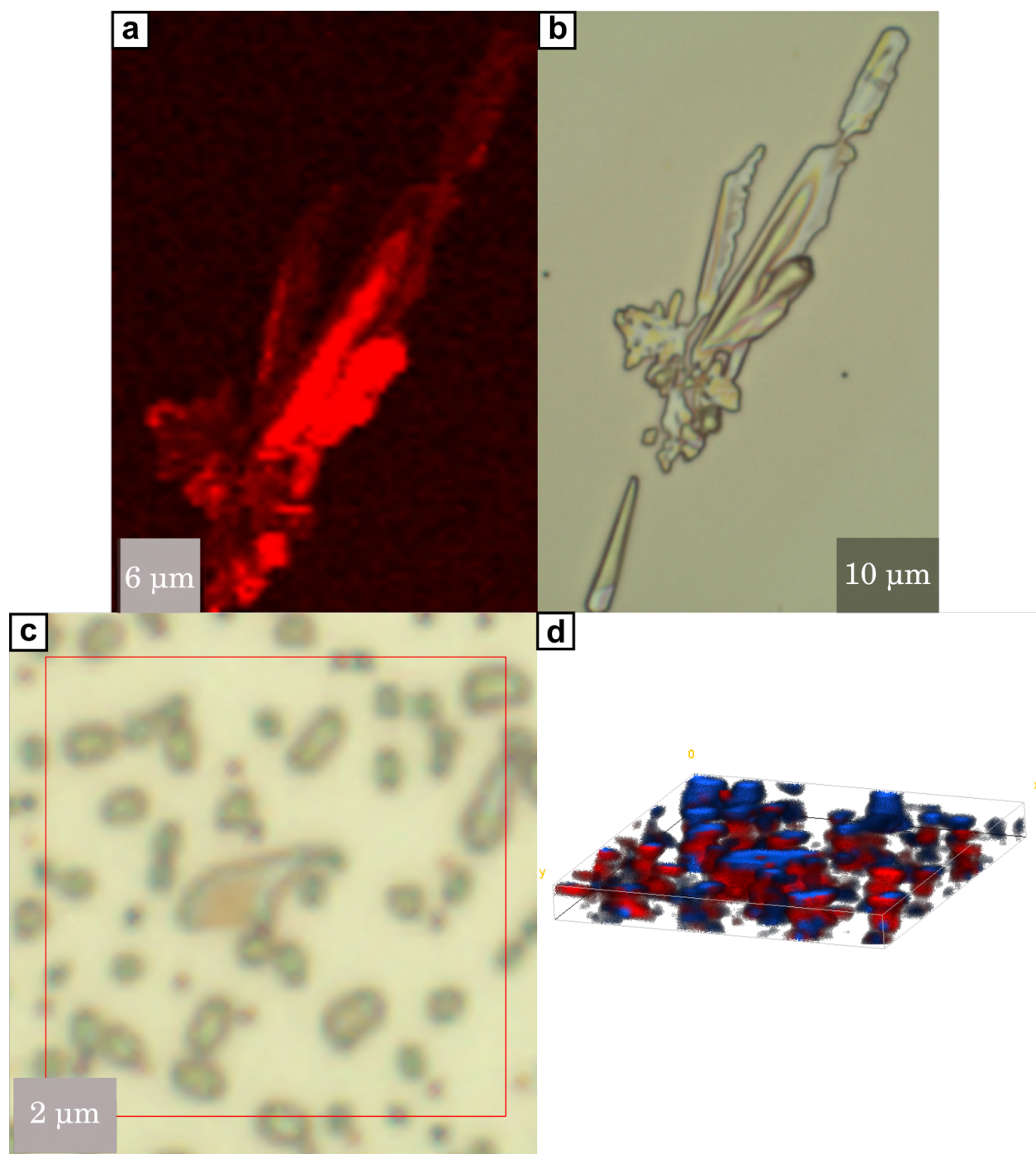


Figure 4.5: a) 2D Raman mapping of the surface where the intensity of the color corresponds to the location of the 2160 cm^{-1} peak. The 2D mapping correlates well to b) the optical microscope image. A depth scan was performed on the sample in c) resulting in the stitched image d). The blue region in d) relates to the 2160 cm^{-1} peak while the red region corresponds to the 2220 cm^{-1} peaks.

creating SAMs, heating the samples, and then putting the samples back into the cyanide environment to determine how the growth changes under those conditions. Experiments can also use complementary lithographic techniques, such as soft lithography, to force directional growth in the crystals to control where and in which direction the gold cyanide is formed.²⁵ Using this methodology, a semiconducting architecture can be built ranging from self-assembled monolayers to bulk micron-sized crystals.

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***Acknowledgments to be placed at the beginning of dissertation**

4.5 References

- (1) Guttentag, A. I.; Wächter, T.; Barr, K. K.; Abendroth, J. M.; Song, T.-B.; Sullivan, N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}. *Journal of Physical Chemistry C* **2016**, *120*, 26736–26746.
- (2) Guttentag, A. I.; Barr, K. K.; Song, T.-B.; Bui, K. V.; Fauman, J. N.; Torres, L. F.; Kes, D. D.; Ciomaga, A.; Gilles, J.; Sullivan, N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Hexagons to Ribbons: Flipping Cyanide on Au{111}. *Journal of the American Chemical Society* **2016**, *138*, 15580–15586.
- (3) De Boer, B.; Hadipour, A.; Mandoc, M. M.; van Woudenberg, T.; Blom, P. W. Tuning of Metal Work Functions with Self-Assembled Monolayers. *Advanced Materials* **2005**, *17*, 621–625.
- (4) Chen, C.-Y.; Wu, K.-Y.; Chao, Y.-C.; Zan, H.-W.; Meng, H.-F.; Tao, Y.-T. Concomitant Tuning of Metal Work Function and Wetting Property with Mixed Self-Assembled Monolayers. *Organic Electronics* **2011**, *12*, 148–153.
- (5) Wu, K.-Y.; Yu, S.-Y.; Tao, Y.-T. Continuous Modulation of Electrode Work Function with Mixed Self-Assembled Monolayers and Its Effect in Charge Injection. *Langmuir* **2009**, *25*, 6232–6238.
- (6) Kim, J.; Rim, Y. S.; Liu, Y.; Serino, A. C.; Thomas, J. C.; Chen, H.; Yang, Y.; Weiss, P. S. Interface Control in Organic Electronics Using Mixed Monolayers of Carboranethiol Isomers. *Nano Letters* **2014**, *14*, 2946–2951.
- (7) Serino, A. C.; Anderson, M. E.; Saleh, L. M. A.; Dziedzic, R. M.; Mills, H.; Heidenreich, L. K.; Spokoyny, A. M.; Weiss, P. S. Work Function Control of Germanium through Carborane-Carboxylic Acid Surface Passivation. *ACS Applied Materials & Interfaces* **2017**, *9*, 34592–34596.
- (8) Jang, J.; Lee, Y.; Yoon, J.-Y.; Yoon, H. H.; Koo, J.; Choe, J.; Jeon, S.; Sung, J.; Park, J.; Lee, W. C.; Lee, H.; Jeong, H. Y.; Park, K.; Kim, K. One-Dimensional Assembly on

- Two-Dimensions: AuCN Nanowire Epitaxy on Graphene for Hybrid Phototransistors. *Nano Letters* **2018**, *18*, 6214–6221.
- (9) Jia, C.; Lin, Z.; Huang, Y.; Duan, X. Nanowire Electronics: From Nanoscale to Macroscale. *Chemical Reviews* **2019**, *119*, 9074–9135.
 - (10) Lee, Y.; Koo, J.; Lee, S.; Yoon, J.-Y.; Kim, K.; Jang, M.; Jang, J.; Choe, J.; Li, B.-W.; Le, C. T.; Ullah, F.; Kim, Y. S.; Hwang, J. Y.; Lee, W. C.; Ruoff, R. S.; Cheong, H.; Cheon, J.; Lee, H.; Kim, K. Universal Oriented van der Waals Epitaxy of 1D Cyanide Chains on Hexagonal 2D Crystals. *Advanced Science* **2020**, *7*, 1900757.
 - (11) Rossi, F.; Bevilacqua, M.; Busson, B.; Corva, M.; Tadjeddine, A.; Vizza, F.; Vesselli, E.; Bozzini, B. An In Situ IR-Vis Sum Frequency Generation Spectroscopy Study of Cyanide Adsorption during Zinc Electrodeposition. *Journal of Electroanalytical Chemistry* **2019**, *855*, 113641.
 - (12) Demissie, T. B.; Ruud, K. Darmstadtium, Roentgenium, and Copernicium Form Strong Bonds with Cyanide. *International Journal of Quantum Chemistry* **2018**, *118*, e25393.
 - (13) Kang, H. S. Electronic Structures and Li Intercalation of AuCN and CuCN Crystals and Nanowires. *Computational and Theoretical Chemistry* **2013**, *1020*, 157–162.
 - (14) Bowmaker, G. A.; Kennedy, B. J.; Reid, J. C. Crystal Structures of AuCN and AgCN and Vibrational Spectroscopic Studies of AuCN, AgCN, and CuCN. *Inorganic Chemistry* **1998**, *37*, 3968–3974.
 - (15) Cano, A.; Avila, Y.; Avila, M.; Reguera, E. Structural Information Contained in the XPS Spectra of nd^{10} Metal Cyanides. *Journal of Solid State Chemistry* **2019**, *276*, 339–344.
 - (16) Harris, K. J.; Wasylishen, R. E. A ^{13}C and ^{15}N Solid-State NMR Study of Structural Disorder and Auophilic Bonding in Au^{I} and Au^{III} Cyanide Complexes. *Inorganic Chemistry* **2009**, *48*, 2316–2332.

- (17) Katz, M. J.; Sakai, K.; Leznoff, D. B. The Use of Auophilic and Other Metal–metal Interactions as Crystal Engineering Design Elements to Increase Structural Dimensionality. *Chemical Society Reviews* **2008**, *37*, 1884–1895.
- (18) Schmidbaur, H.; Schier, A. Auophilic Interactions as a Subject of Current Research: an Update. *Chemical Society Reviews* **2012**, *41*, 370–412.
- (19) Yamada, T.; Sekine, R.; Sawaguchi, T. Ultrahigh-Vacuum Multitechnique Study of AuCN Monolayers on Au(111) Formed by Electrochemical Deposition. *The Journal of Chemical Physics* **2000**, *113*, 1217–1227.
- (20) Pettinger, B.; Picardi, G.; Schuster, R.; Ertl, G. Surface-Enhanced and STM Tip-Enhanced Raman Spectroscopy of CN[−] Ions at Gold Surfaces. *Journal of Electroanalytical Chemistry* **2003**, *554-555*, 293–299.
- (21) Gao, P.; Weaver, M. J. Metal-Adsorbate Vibrational Frequencies as a Probe of Surface Bonding: Halides and Pseudohalides at Gold Electrodes. *The Journal of Physical Chemistry* **1986**, *90*, 4057–4063.
- (22) Chadwick, B. M.; Frankiss, S. G. Vibrational Spectra and Structures of Some Dicyanoaurate(I) Complexes. *Journal of Molecular Structure* **1976**, *31*, 1–9.
- (23) Zaleski-Ejgierd, P.; Patzschke, M.; Pyykkö, P. Structure and Bonding of the MCN Molecules, M=Cu,Ag,Au,Rg. *The Journal of Chemical Physics* **2008**, *128*, 224303.
- (24) Bozzini, B.; Fanigliulo, A. An in Situ Spectroelectrochemical Raman Investigation of Au Electrodeposition and Electrodissolution in KAu(CN)₂ Solution. *Journal of Applied Electrochemistry* **2002**, *32*, 1043–1048.
- (25) Liao, W.-S.; Cheunkar, S.; Cao, H. H.; Bednar, H. R.; Weiss, P. S.; Andrews, A. M. Subtractive Patterning via Chemical Lift-Off Lithography. *Science* **2012**, *337*, 1517–1521.

CHAPTER 5

Fourier Transform Infrared Scanning Tunneling Microscopy: Probing Molecular Vibrations at the Nanoscale

Adapted from a manuscript being prepared for publication:

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5.1 Introduction

In the previous chapters, we explored how we can create self-assembled monolayers of gold cyanide on gold substrates, modify the compounds into new rearrangements, and build off of those substrates to form micron-sized crystals. This chapter focuses on instrumentation advances for investigating the vibrational interactions of molecules at scales far below the diffraction limit of light. Being able to assess the chemical interactions of the surface-bound molecules at this scale, is of vast importance to many fields including molecular electronics and heterogeneous catalysis.¹⁻⁹ To achieve this goal, we use scanning tunneling microscopy (STM), which has been shown to probe a variety of surface interactions with atomic resolution.¹⁰⁻¹²

Researchers have used STM for almost 40 years for characterizing conductive and semi-conducting surfaces with unprecedented spatial resolution.^{3,13} STM is capable of measuring the topography of the atomic and molecular arrangements at temperatures ranging from milli Kelvin to hundreds of Kelvin.^{14,15} Except under very specific conditions, STM is unable to measure chemical information about a system. This omission is important because the topography measured cannot be chemically distinguished without further information, (simple systems, known mixtures, etc.). To improve upon this limitation, researchers have combined the strengths of scanning probe microscopies with optical spectroscopic techniques that enable unambiguous molecular identification.¹⁶⁻¹⁸

Due to the nanoscale confinement of electromagnetic fields at the tunneling junction, tip-enhanced optical spectroscopies, such as UV-vis absorption, Raman scattering, and infrared absorption have been demonstrated recently.^{18,19} Herein, I will focus on the implementation of infrared (IR) absorption measurements into STM that can directly probe the vibrational modes in the tip-sample junction. These molecular vibrations are sensitive to the surrounding chemical environment, including isotopic effects, oxidation state,²⁰ and the packing of the surface.^{21,22} Conventional IR spectroscopic techniques generally interrogate these chemical effects averaged over the excitation spot-size. Infrared techniques use photon wavelengths of up to 5 μm , so the spatial resolution is limited to *ca.* 2 μm , orders of magnitude larger than

the molecular dimensions. However, combining with scanning probe techniques, researchers have been able to use tip-enhanced optical effects to localize the IR absorption sites. For example, using a tunable IR laser, atomic force microscopy has shown promise in this field. However, challenges remain with STM techniques.¹⁹

Back in the early 1990s, Ho and coworkers reported the first inelastic electron tunneling spectroscopy (IETS) scanning tunneling microscope capable of distinguishing different isotopes of acetylene on a surface, which, from the STM images only, were indistinguishable.²³ This opened the door for using the STM tip as a detector for measuring vibrational normal modes. Though STM-IETS created a new paradigm for the exploration of chemical features on molecular surfaces, there are multiple drawbacks. First, the selection rules for IETS are not well defined.²⁴ Generally, one needs to perform the experiment to discover if a vibrational mode is active. The second issue is the ultrahigh vacuum and low temperatures (<10 K) required to perform these measurements. In order to cool down to such low temperatures, one needs to use liquid helium, which has become scarcer with time.

In 2013, Crommie and co-workers were able to create an infrared scanning tunneling microscope using a quantum cascade laser.²⁵ In their design, when the laser’s frequency was the same as the vibrational modes of the adsorbates, the molecular vibration would heat up the system and consequently expand. This thermal expansion was on the pm scale but nevertheless measurable by the STM tip. Similarly to IETS, this IR-STM technique has drawbacks including the low temperature needed to perform these measurements as well as only being able to use the vibrations within the frequency range of the laser.

Instead of using a laser for excitation, we designed an instrument that utilizes the chemical identification capability of Fourier transform infrared (FTIR) spectroscopy with the spatial localization of STM. The goal is to produce an instrument that can simultaneously measure the local vibrational modes of adsorbates while scanning the surface topography. Specifically, we explore the possibility of using the tunneling junction as a nanoamplifier to measure the vibrational modes of the surface. This arrangement uses a broadband, IR source enabling measurements that cover a wide energy range simultaneously using the multiplex advantage of FTIR.²⁶ This FTIR-STM design mitigates the cost of cooling down the system while

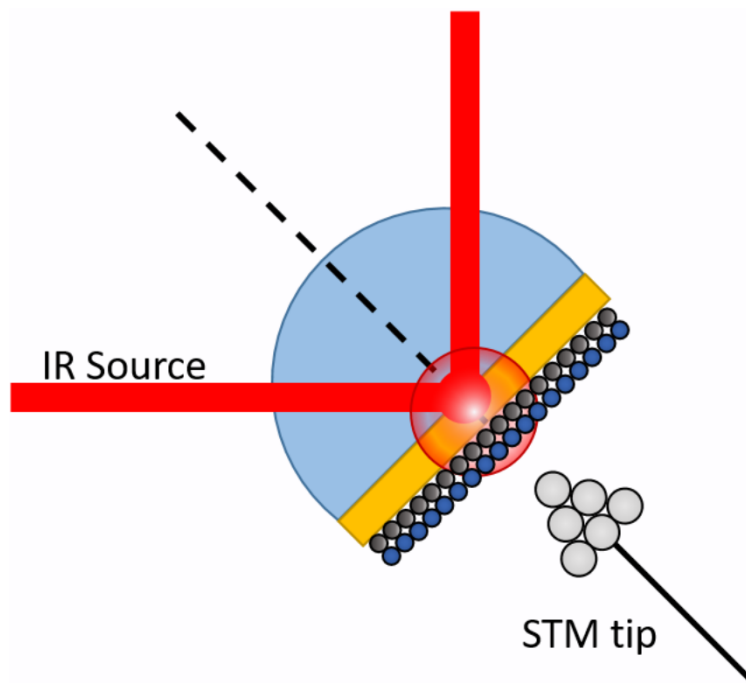


Figure 5.1: A 40-nm-thick layer of gold atop a sapphire substrate forms the crystalline substrate surface. Self-assembled monolayers are adsorbed on the gold substrate. Using a back-illuminated geometry, the surface is illuminated evanescently without significantly thermally heating the scanning tunneling microscope tip.

also obtaining chemical information under ambient temperatures and pressures, which may differ from observations made at UHV and liquid helium temperatures and also has broader potential applications.²⁷

5.2 Experimental Layout

5.2.1 Scanning Tunneling Microscopy Background

Scanning tunneling microscopy, along with other scanning probe techniques, has given us the capability to probe subnanometer surface features. Generally, this technique is based upon the following setup: a conductive/semiconducting surface and an atomically sharp metal tip are brought into close proximity while an electric potential is applied between the two surfaces. When the distance between the two materials is within a few nanometers,

electrons are able to tunnel quantum mechanically across the tunneling gap. This tunneling probability is directly proportional to the current within the tunneling gap (labeled I in equation 5.1). By moving the tip closer to the surface (decreasing the tunneling distance x), the probability of electrons tunneling from one side to the other increases exponentially. Due to the exponentiality of tunneling junction, one Ångstrom closer to the surface increases the current by an order of magnitude for common surface and probe tip materials in a vacuum.²⁸

$$I \propto \exp(-Cx) \tag{5.1}$$

By using a feedback loop that maintains a constant tunneling current, the tip-sample distance is automatically adjusted to compensate for nanoscale changes in surface electron density of states. Then, by rastering the tip across the surface, one can map out the topography landscape of the surface as a convolution of the geometric and electronic structure.¹⁰ The STM topography is a convolution of the tunneling distance and the local electron density of states (DOS). Different atoms and molecules have different electronic structures, which changes the tunneling probability. In constant-current mode, these changes in tunneling manifests as changes in height. For example, a metal with fewer states available, would lead to larger tip-surface distances and the tip would move closer until the current equilibrated to the set-point of the feedback loop. Our FTIR-STM takes advantage of this feedback mechanism directly.

Generally, spontaneous absorption and emission from molecules changing states is assumed to follow the Born-Oppenheimer approximation.²⁹ Infrared, Raman, and fluorescence spectroscopies use this assumption to separate the nuclei’s energy states from the electrons. However these structures do not adhere to this approximation due to vibronic coupling.^{29–32} In these vibronic coupling modes, one cannot separate the electronic and vibrational states. Density-functional theory calculations (unpublished), indicate coupling between the gold surface electronic state and the C–N vibrational mode. Therefore, there may be enhanced strength in the vibrational transition of the adsorbed cyanide. Using a harmonic oscillator model, one can approximate the vibrational displacement as the molecule changes vibrational states. AuCN has a vibrational normal mode of 2140 cm^{-1} , so the molecule-tip separation at

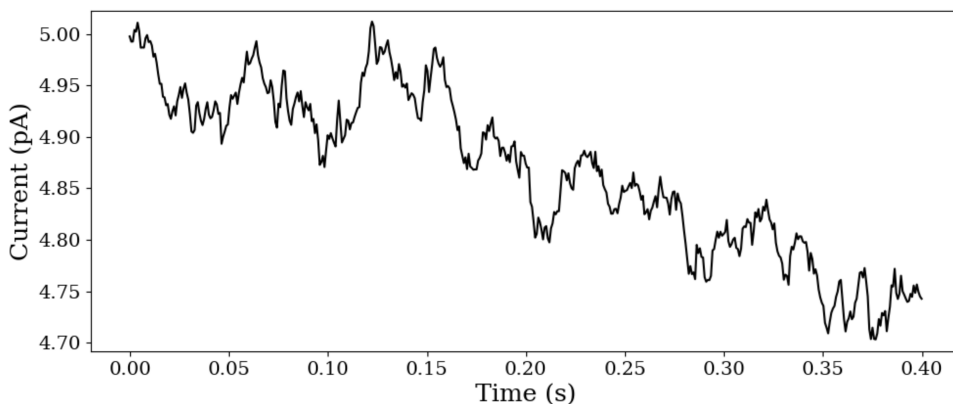


Figure 5.2: Simulated scan of current modulation by a random normal distribution of noise for 400 ms. The standard deviation of the noise per step was 0.01 pA.

the outer vibrational turning point can decrease by ~ 10 pm when compared to the ground state turning-point distance.^{26,33} Using the workfunction of gold to be 4.5 eV and a tunneling distance of 1 nm, the current would change by approximately 10% in the first excited vibrational state *vs.* the ground vibrational state, which is readily measurable in our system.²⁶

I designed the following FTIR-STM experiment to assess the Au–CN vibronic coupling described above. Using Au/sapphire prism substrates, we formed AuCN SAMs on the surface, as described in Chapter 2.³³ These cyanide monolayers are robust, air-stable, modifiable, and have a vibrational mode that overlaps with the gold surface electronic states. Using an attenuated total reflection (ATR) geometry, we excite the surface evanescence (figure 5.1). This geometry has previously been shown to minimize the thermal expansion of the STM tip.³⁴ By measuring the tunneling current *vs.* time response at a constant tip-sample distance with IR irradiation, we can perform an inverse Fourier transform of the time-lapse current signal to obtain single-molecule cyanide IR absorption spectra. Moreover, the AuCN monolayer possesses favorable properties to serve as a model system for the FTIR-STM, including cyanide’s strong C–N normal stretching mode residing outside of the water and carbon dioxide absorption windows, and the well-ordered monolayers of the AuCN. In the following section, I describe a simulation used to assess the sensitivity of the described FTIR-STM instrument.

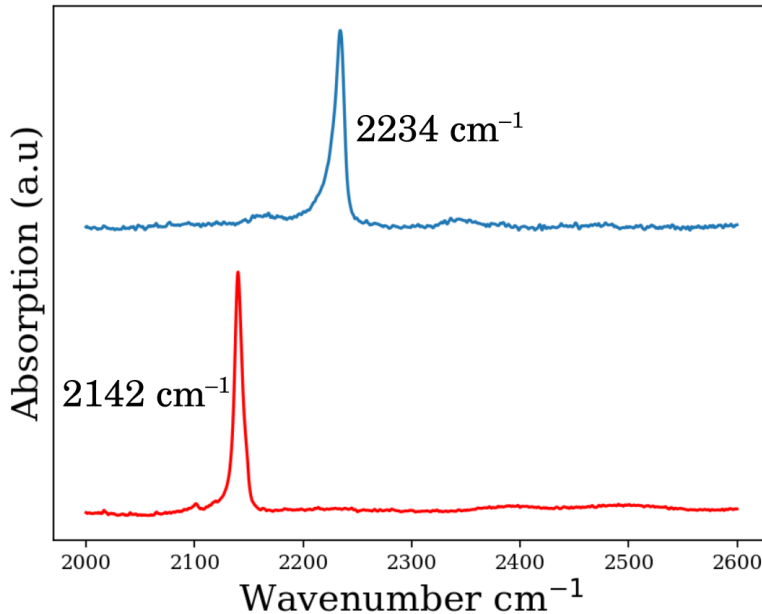


Figure 5.3: Fourier transform infrared attenuated total reflection measurements of hexagonally close-packed AuCN (2142 cm^{-1}) and ribbon AuCN (2134 cm^{-1}) on Au/Si substrates.

5.2.2 Simulation of Fourier Transform Infrared Scanning Tunneling Microscopy Performance

We modeled the interferometer at the tunneling junction with Python 3. First, we assumed a 5 pA current, similar to our experimental setup (figure 5.2).^{33,35} Then, using a normal distribution, we simulated a random walk to model the drift seen at the tunneling junction under ambient conditions. We processed the time lapse for 400 ms, which is comparable to typical STM experimental measurements. Note, the longer the scan, the higher the spectral resolution of our output spectrum.^{26,29,36}

We simulated IR absorption spectra, similar to the absorption observed for hexagonal close-packed cyanide model layers (figure 5.3).³³ The signal from the interferometer is composed of a broadband multiplex source illuminating the surface at once. The Gaussian absorption curve in figure 5.4a, using equation 5.2, had a standard deviation (σ) of 10 cm^{-1} centered at 2142 cm^{-1} used as μ in equation 5.2. Though our infrared measurements have peaks that are sharper, a broader peak will have a lower signal at each wavenumber, thus

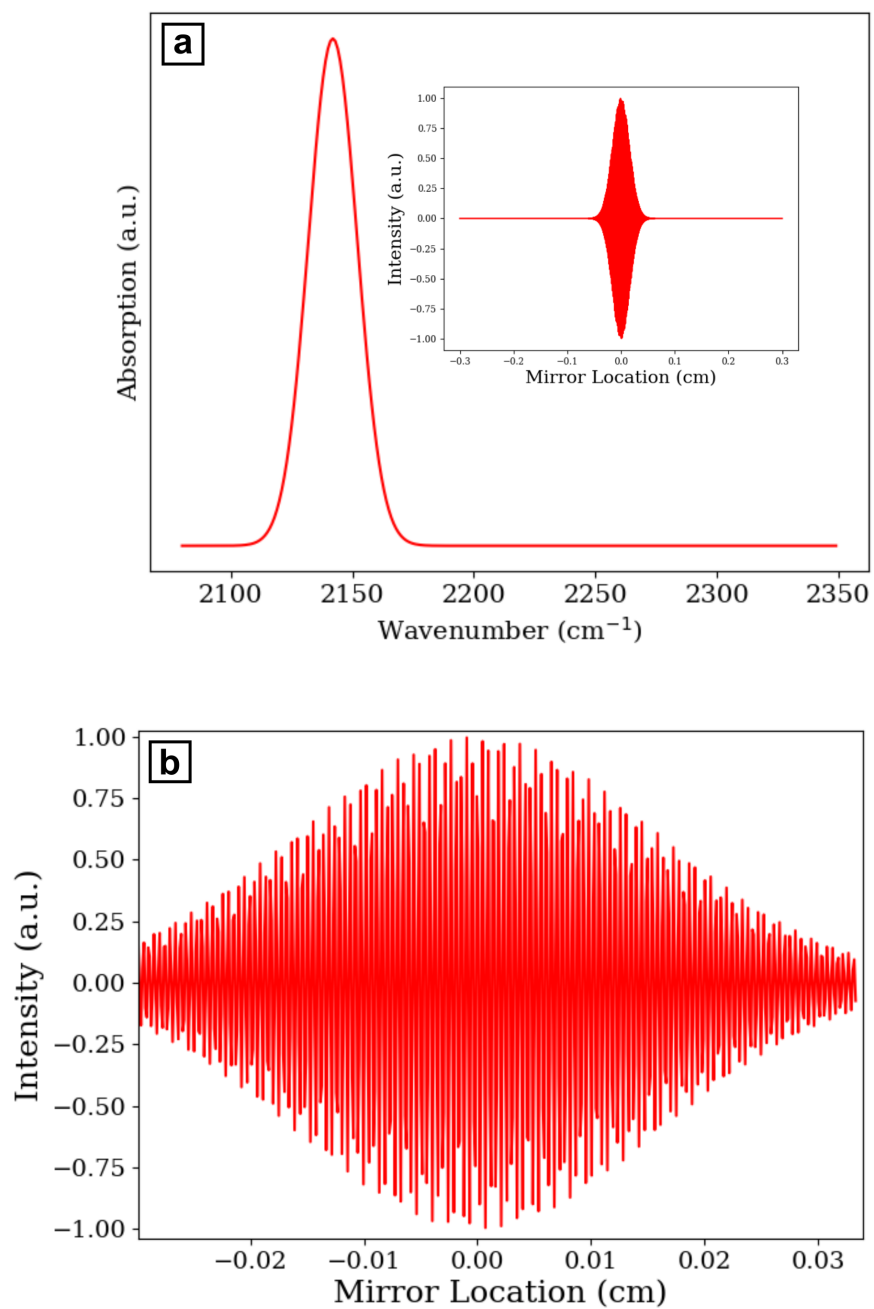


Figure 5.4: a) Normal distribution used to create the simulated absorption spectrum at 2142 cm^{-1} with a σ of 10 cm^{-1} . The inlet is the constructed interferogram from the absorption profile in a). b) The portion of the interferogram used to simulate the mirror motion during the data acquisition phase. This simulation starts with t_0 at the mirror at -0.03 cm compared to the center position.

minimizing the signal that can be used to assess the limitations of this measurement.

$$B(\tilde{\nu}) = \exp \left(- \left(\frac{(\tilde{\nu} - \mu)}{\sigma} \right)^2 \right) \quad (5.2)$$

Next, I created a model interferogram based on the aforementioned absorption spectrum. It was composed of an array of cosine waves at 1 cm^{-1} increments from 500 to 3000 cm^{-1} (equation 5.3). The amplitude of each cosine wave, B , was equal to the magnitude of the gaussian curve at that particular frequency calculated from equation 5.2. Therefore, the majority of the cosine waves below 2100 and above 2200 cm^{-1} played no part in the overall intensity of the converted spectrum from equation 5.3. The inset in figure 5.4a, shows the result of the interferogram produced. The range of this graph is -0.3 cm to $+0.3 \text{ cm}$. Our experimental start time is based on obtaining the information-rich centerburst.

$$S(\delta) = \sum_{\tilde{\nu}_i=500}^{3000} B(\tilde{\nu}_i) \cos(2\pi\tilde{\nu}_i\delta) \quad (5.3)$$

To obtain the highest intensity at the surface, we want to measure the centerburst as shown in figure 5.4b. Sources with narrow distributions, such as from laser signals, have an oscillating interferogram. However broadband sources, containing photons with a range of frequencies, tend to cancel out quickly outside of the centerburst, and thus, have narrow interferograms.²⁶ The Nicolet 6700 FTIR spectrometer, used in our design, uses a constant mirror velocity in its interferometer. Therefore, the spacings for our calculated spectrum are correlated to the mirror motion. The slowest mirror velocity this instrument utilizes is 0.158 cm/s . Using a current sampling frequency of 1.25 kHz , the individual spacing for each data point is $1.26 \mu\text{m}$. Due to this fairly narrow absorption distribution, the simulated interferogram is wide compared to broadband sources.

Under the assumption that the current is changing with respect to the mirror position, we used the data range from figure 5.4b, and correlated that to the mirror velocity. Next, we added the intensity multiplied by a scaling factor—for clarity, we used a factor of 2% though values less than 1% were nonetheless distinguishable. This newly modeled current was composed of signals from the interferometer as well as the noise of the system (figure 5.5a).

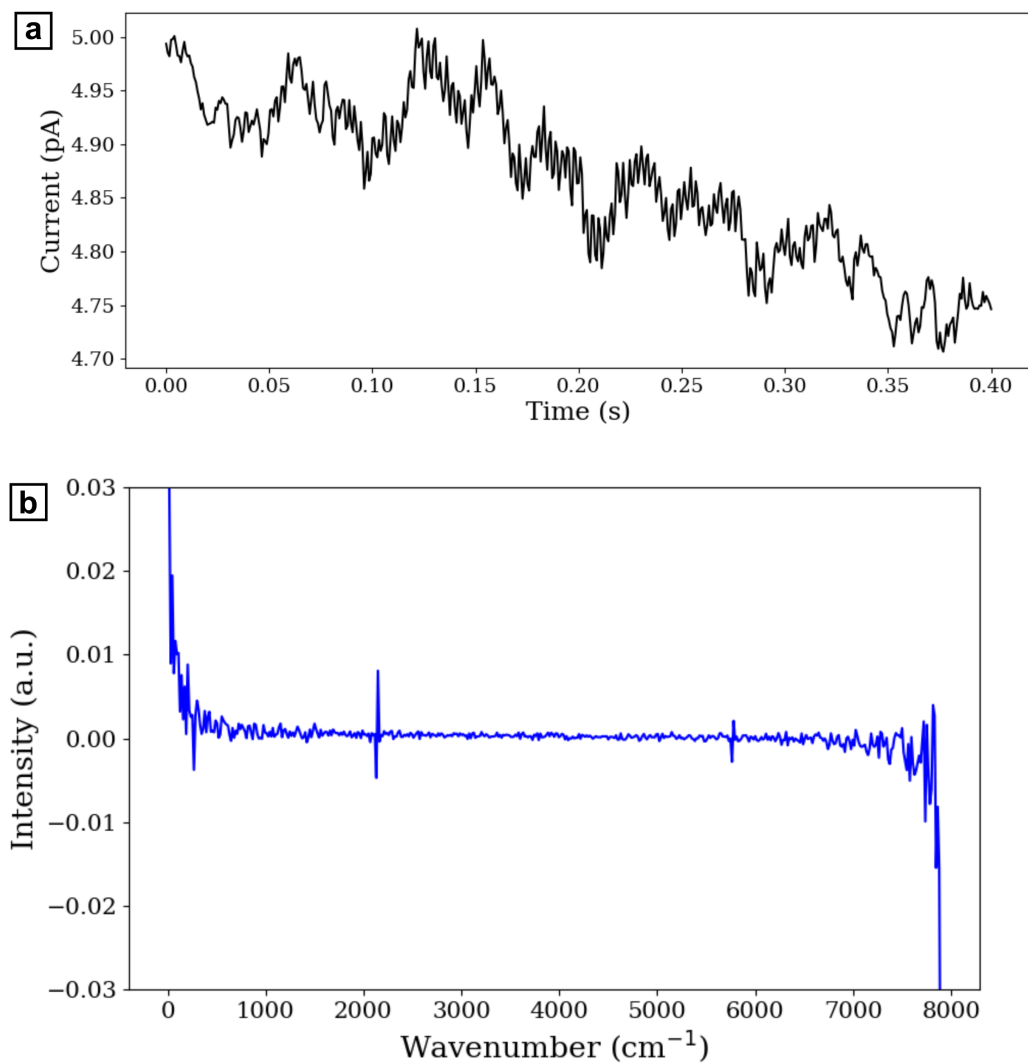


Figure 5.5: a) The simulated scan with vibronic components, both real and imaginary, added in at 2% intensity. b) The resulting inverse fast Fourier transform of the current found in a) with respect to the mirror velocity.

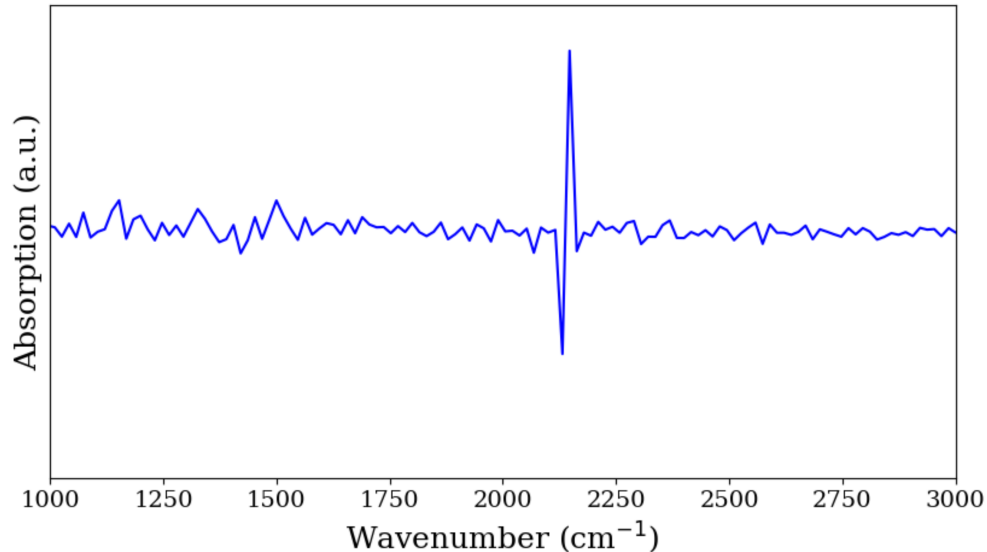


Figure 5.6: Simulated absorption spectrum from 2142 cm^{-1} normal mode. Maximum peak found at 2131 cm^{-1} .

By taking the inverse fast Fourier transform of the current in figure 5.5a, and correlating that to the current acquisition frequency and the mirror velocity, we obtained a complex set of spectra. We merged the resulting spectra together, as is performed with an FTIR interferometer, creating the blue trace in figure 5.5b.²⁶ The signal is symmetric about the maximum measured frequency, and as such only the lower half will be explored. Taking this spectrum and focusing on the region of interest, we find a peak at 2130 cm^{-1} (figure 5.6). The resolution of this measurement, dictated by the acquisition time, is *ca.* 16 cm^{-1} . This resolution can easily distinguish the as-adsorbed AuCN *vs.* the heated AuCN (figure 5.3).

5.3 Experimental Results

5.3.1 Concurrent Attenuated Total Reflection Data Collection and Scanning Tunneling Microscope Images

Using the instrument described in figure 5.7, we were able to obtain the surface vibrational spectrum and molecular resolution STM topography simultaneously. We find that the STM

images on the Au-sapphire prism have higher levels of disorder when compared with the gold on mica substrates on other measurements. We did, however, achieve molecular resolution STM images of AuCN monolayers as shown in figure 5.8.

Using FTIR-STM, we simultaneously acquire that the infrared absorption spectrum of the AuCN SAM via ATR geometry. The signal is less prominent than our previous ATR methods without the addition of the STM (due to more optical elements, longer path length, greater atmospheric absorption from the pathlength and minimal purging, and alignment).²⁶ The IR absorption was still strong enough to distinguish the two cyanide C–N absorption configurations. This dual measurement technique offers unique capabilities for *in situ* and *operando* studies of heterogeneous materials with strong IR absorption cross-sections with the atomic-resolution STM surface characterization.

5.3.2 Analyzing the Current Spectrum

Using Matlab code similar to the Python code mentioned prior, we were able to analyze the experimental current spectrum using the same method as in the simulation above. Though no observable peak has yet been measured, we created a process capable of discerning this measurement. With the experimental settings described herein, the acquisition resolution is roughly 20 cm^{-1} . In comparison with other current-based vibrational spectroscopies (*e.g.*, IETS) at room temperature, there is a vast improvement in spectral resolution since the resolution is not dictated by the homogeneous broadening that results from the broadened Fermi distribution of electrons.

5.4 Conclusions and Prospects

We developed an ambient condition FTIR scanning tunneling microscope capable of simultaneously measuring the vibrational modes of the surface and the topography of the molecular arrangement. We showed that we could distinguish normal modes with similar resolution to that of common ATR equipment. This instrument is designed to expand beyond its mercury cadmium telluride (MCT) detector to use the tunneling junction STM tip as a nanoscale

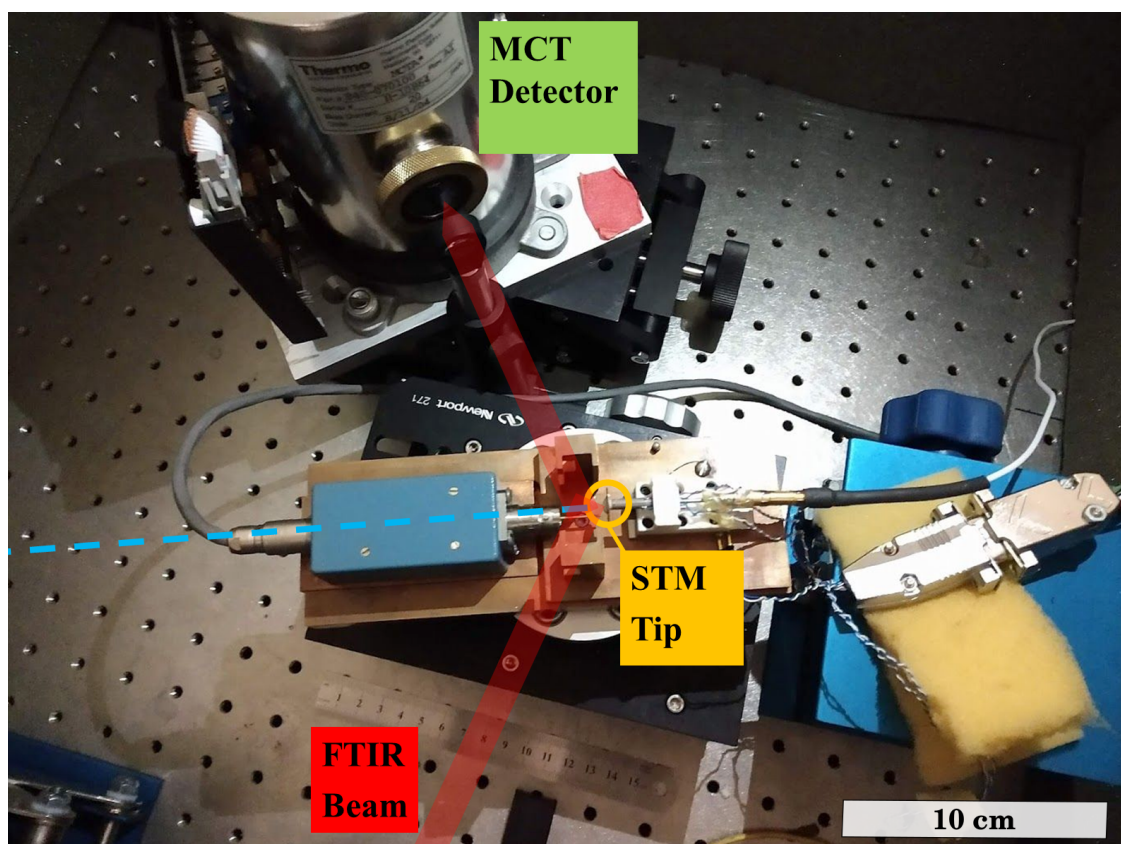


Figure 5.7: Photograph of the experimental system. This design uses a multiplex signal from a broadband infrared source with attenuated total reflection geometry. We evanescently excite the surface molecules on the back of the prism into vibration. The reflected beam then heads to a mercury cadmium telluride (MCT) detector to be analyzed. As we bring the scanning tunneling microscope probe tip within tunneling distance of the surface, we can measure the change in the tunneling current due to the and can use that to measure the change in conductance at the tunneling junction.

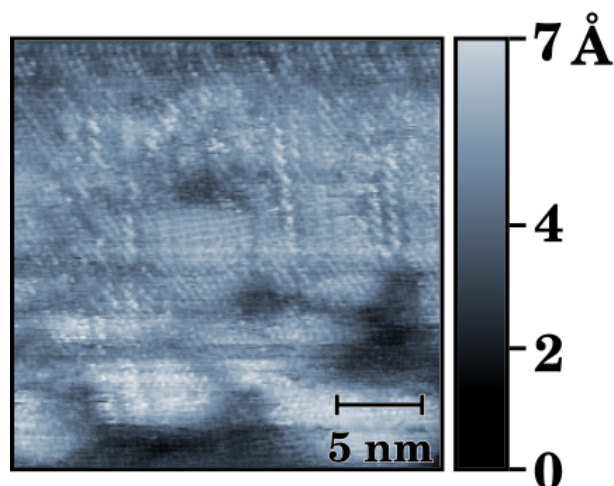


Figure 5.8: Scanning tunneling microscope image of AuCN on a Au/sapphire substrate, while simultaneously being irradiated evanescently by a broadband infrared source. The tunneling current was 10 pA with a sample bias voltage of 1 V with respect to the tip. Image adapted from reference [37].

amplifier. Measuring at this scale will enable us to study chemical features much below the diffraction limit, and thus give us unrivaled chemical specificity under ambient conditions. We have shown how these measurements are possible within the limitations of the resolution and signal intensity. To improve this instrument further, several modifications can be employed with the simplest being a high-throughput mechanism that could take “live” signal analysis during the data acquisition phase, which is the slowest step currently. This instrument will enable us to study surface and chemical features at the nanoscale, as needed to probe chemical interactions and molecular stability. Being able to study systems under ambient conditions will enable viewing those systems under realistic environments that go beyond idealized settings.

5.5 Experimental Methods

The scanning tunneling microscope is a custom-built instrument with National Instrument electronics using a microslider tip assembly.³⁸ The FTIR-STM instrument layout is shown in figure 5.7. Using Au/sapphire prism substrates, we back illuminate the prisms using an

ATR geometry. We use a proprietary program called WinSTM to control the motion of the STM tip, acquire images, and collect current *vs.* time data.

We use a Nicolet 6700 FTIR interferometer from Thermo Fisher Scientific (Waltham, MA) to produce our broadband infrared radiation and use the company’s software, OMNIC, to view and subtract the background of our infrared data from an MCT detector (Thermo Fisher Scientific, Waltham, MA). The beam is sent from the instrument onto our optical table where we use an ATR geometry to excite the surface evenly (figure 5.7).

Samples are deposited on half-cylindrical sapphire prisms produced by Princeton Scientific Corp. (Easton, PA), and are 1 cm in length. A photograph of the sapphire is shown in supplemental figure A.18. A 4-nm-thick adhesion Nb layer is added before a 40-nm-thick Au layer is deposited on top at 300 °C. Sapphires were then annealed at 500 °C for 18 h then 400 °C for 24 h.³⁹ Once substrates were cooled to room temperature, AuCN SAMs were created using the methods described in Chapters 2 and 3.^{33,35}

5.6 References

- (1) Bergfield, J. P.; Ratner, M. A. Forty Years of Molecular Electronics: Non-Equilibrium Heat and Charge Transport at the Nanoscale. *Physica Status Solidi B* **2013**, *250*, 2249–2266.
- (2) Ratner, M. A brief history of molecular electronics. *Nature nanotechnology* **2013**, *8*, 378–381.
- (3) Weiss, P. S. Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements. *Accounts of Chemical Research* **2008**, *41*, 1772–1781.
- (4) Mantooth, B. A.; Weiss, P. S. Fabrication, Assembly, and Characterization of Molecular Electronic Components. *Proceedings of the IEEE* **2003**, *91*, 1785–1802.
- (5) Kim, M.; Hohman, J. N.; Cao, Y.; Houk, K. N.; Ma, H.; Jen, A. K.-Y.; Weiss, P. S. Creating Favorable Geometries for Directing Organic Photoreactions in Alkanethiolate Monolayers. *Science* **2011**, *331*, 1312–1315.

- (6) Bell, A. T. The Impact of Nanoscience on Heterogeneous Catalysis. *Science* **2003**, *299*, 1688–1691.
- (7) Zhang, H.; Liu, G.; Shi, L.; Ye, J. Single-Atom Catalysts: Emerging Multifunctional Materials in Heterogeneous Catalysis. *Advanced Energy Materials* **2018**, *8*, 1701343.
- (8) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H.-P. Adsorbate-Substrate Vibrational Modes of Benzene on Ag (110) Resolved with Scanning Tunneling Spectroscopy. *Physical Review Letters* **2001**, *86*, 1050.
- (9) Goronzy, D. P.; Ebrahimi, M.; Rosei, F.; Arramel; Fang, Y.; De Feyter, S.; Tait, S. L.; Wang, C.; Beton, P. H.; Wee, A. T.; Weiss, P. S.; Perepichka, D. F. Supramolecular Assemblies on Surfaces: Nanopatterning, Functionality, and Reactivity. *ACS Nano* **2018**, *12*, 7445–7481.
- (10) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. Surface Studies by Scanning Tunneling Microscopy. *Physical Review Letters* **1982**, *49*, 57–61.
- (11) Kuk, Y.; Silverman, P. J. Scanning Tunneling Microscope Instrumentation. *Review of Scientific Instruments* **1989**, *60*, 165–180.
- (12) Bonnell, D. A.; Basov, D.; Bode, M.; Diebold, U.; Kalinin, S. V.; Madhavan, V.; Novotny, L.; Salmeron, M.; Schwarz, U. D.; Weiss, P. S. Imaging Physical Phenomena with Local Probes: From Electrons to Photons. *Reviews of Modern Physics* **2012**, *84*, 1343.
- (13) Claridge, S. A.; Schwartz, J. J.; Weiss, P. S. Electrons, Photons, and Force: Quantitative Single-Molecule Measurements from Physics to Biology. *ACS Nano* **2011**, *5*, 693–729.
- (14) Song, Y. J.; Otte, A. F.; Shvarts, V.; Zhao, Z.; Kuk, Y.; Blankenship, S. R.; Band, A.; Hess, F. M.; Stroscio, J. A. Invited Review Article: A 10 mK Scanning Probe Microscopy Facility. *Review of Scientific Instruments* **2010**, *81*, 121101.

- (15) Arias, P.; Tesař, J.; Kavner, A.; Šikola, T.; Kodambaka, S. In Situ Variable-Temperature Scanning Tunneling Microscopy Studies of Graphene Growth Using Benzene on Pd(111). *ACS Nano* **2020**, *14*, 1141–1147.
- (16) Schultz, J. F.; Li, S.; Jiang, S.; Jiang, N. Optical Scanning Tunneling Microscopy Based Chemical Imaging and Spectroscopy. *Journal of Physics: Condensed Matter* **2020**, *32*, 463001.
- (17) Böckmann, H.; Müller, M.; Hammud, A.; Willinger, M.-G.; Pszona, M.; Waluk, J.; Wolf, M.; Kumagai, T. Near-Field Spectral Response of Optically Excited Scanning Tunneling Microscope Junctions Probed by Single-Molecule Action Spectroscopy. *The Journal of Physical Chemistry Letters* **2019**, *10*, 2068–2074.
- (18) Centrone, A. Infrared Imaging and Spectroscopy Beyond the Diffraction Limit. *Annual Review of Analytical Chemistry* **2015**, *8*, 101–126.
- (19) Kurouski, D.; Dazzi, A.; Zenobi, R.; Centrone, A. Infrared and Raman chemical imaging and spectroscopy at the nanoscale. *Chemical Society Reviews* **2020**, *49*, 3315–3347.
- (20) Dujardin, C.; Mamede, A.-S.; Payen, E.; Sombret, B.; Huvenne, J.-P.; Granger, P. Influence of the Oxidation State of Rhodium in Three-Way Catalysts on Their Catalytic Performances: An in Situ FTIR and Catalytic Study. *Topics in Catalysis* **2004**, *30*, 347–352.
- (21) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. Spontaneously Organized Molecular Assemblies. 3. Preparation and Properties of Solution Adsorbed Monolayers of Organic Disulfides on Gold Surfaces. *Journal of the American Chemical Society* **1987**, *109*, 2358–2368.
- (22) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. Spontaneously Organized Molecular Assemblies. 4. Structural Characterization of *n*-Alkyl Thiol Monolayers on Gold by Optical Ellipsometry, Infrared Spectroscopy, and Electrochemistry. *Journal of the American Chemical Society* **1987**, *109*, 3559–3568.

- (23) Stipe, B. C.; Rezaei, M. A.; Ho, W. Single-Molecule Vibrational Spectroscopy and Microscopy. *Science* **1998**, *280*, 1732–1735.
- (24) Blake, M. M.; Nanayakkara, S. U.; Claridge, S. A.; Fernández-Torres, L. C.; Sykes, E. C. H.; Weiss, P. S. Identifying Reactive Intermediates in the Ullmann Coupling Reaction by Scanning Tunneling Microscopy and Spectroscopy. *The Journal of Physical Chemistry A* **2009**, *113*, 13167–13172.
- (25) Pechenezhskiy, I. V.; Hong, X.; Nguyen, G. D.; Dahl, J. E. P.; Carlson, R. M. K.; Wang, F.; Crommie, M. F. Infrared Spectroscopy of Molecular Submonolayers on Surfaces by Infrared Scanning Tunneling Microscopy: Tetramantane on Au(111). *Phys. Rev. Lett.* **2013**, *111*, 126101.
- (26) Griffiths, P. R.; de Haseth, J. A., *Fourier Transform Infrared Spectrometry*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2007.
- (27) Weeks, B. L.; Durkan, C.; Kuramochi, H.; Welland, M. E.; Rayment, T. A High Pressure, High Temperature, Scanning Tunneling Microscope for in Situ Studies of Catalysts. *Review of Scientific Instruments* **2000**, *71*, 3777–3781.
- (28) Coombs, J.; Pethica, J. Properties of Vacuum Tunneling Currents: Anomalous Barrier Heights. *IBM Journal of Research and Development* **1986**, *30*, 455–459.
- (29) McHale, J. L., *Molecular Spectroscopy*, 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.
- (30) Fulton, R. L.; Gouterman, M. Vibronic Coupling. I. Mathematical Treatment for Two Electronic States. *The Journal of Chemical Physics* **1961**, *35*, 1059–1071.
- (31) Nafie, L. A.; Freedman, T. B. Vibronic Coupling Theory of Infrared Vibrational Transitions. *The Journal of Chemical Physics* **1983**, *78*, 7108–7116.
- (32) Abraham, B.; Rego, L. G. C.; Gundlach, L. Electronic–Vibrational Coupling and Electron Transfer. *The Journal of Physical Chemistry C* **2019**, *123*, 23760–23772.

- (33) Guttentag, A. I.; Wächter, T.; Barr, K. K.; Abendroth, J. M.; Song, T.-B.; Sullivan, N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Surface Structure and Electron Transfer Dynamics of the Self-Assembly of Cyanide on Au{111}. *Journal of Physical Chemistry C* **2016**, *120*, 26736–26746.
- (34) Wang, S. Submolecular Resolution Spectroscopic Imaging for Photoactive Molecules and Assemblies., Ph.D. Thesis, Los Angeles, CA, USA: University of California, Los Angeles, 2019.
- (35) Guttentag, A. I.; Barr, K. K.; Song, T.-B.; Bui, K. V.; Fauman, J. N.; Torres, L. F.; Kes, D. D.; Ciomaga, A.; Gilles, J.; Sullivan, N. F.; Yang, Y.; Allara, D. L.; Zharnikov, M.; Weiss, P. S. Hexagons to Ribbons: Flipping Cyanide on Au{111}. *Journal of the American Chemical Society* **2016**, *138*, 15580–15586.
- (36) Perkins, W. D. Fourier Transform-Infrared Spectroscopy: Part I. Instrumentation. *Journal of Chemical Education* **1986**, *63*, A5.
- (37) Guttentag, A. I. From Poison to Small-Molecule Probe: Cyanide Self-Assembly on Au{111} for the Development of Room-Temperature Single-Molecule Spectroscopy., Ph.D. Thesis, University of California, Los Angeles, 2016.
- (38) Saavedra Garcia, H. M. Controlling Adsorbate Interactions For Advanced Chemical Patterning., Ph.D. Thesis, University Park, PA, USA: The Pennsylvania State University, 2010.
- (39) Zhao, Y. Interface Properties of Functional Molecules on Au{111}: From Photoinduced Charge Transfer to Exchange Reactions., Ph.D. Thesis, University of California, Los Angeles, 2014.

CHAPTER 6

Conclusions and Prospects

6.1 Summary

The work discussed herein describes the growth mechanisms and chemical interactions of cyanide materials and how these systems were used to develop a new scanning tunneling spectroscopic imaging method with broad vibrational spectroscopic capabilities. As is with most works, the initial questions that I asked expanded to new ones—changing from understanding how gold cyanide (AuCN) molecules self-assemble and arrange atop gold substrates, to learning how to apply these properties and growth mechanisms to probe and to understand the structure and assembly of alternative chemical systems. Herein, I will start with a summary of the major conclusions and new science that we learned throughout these chapters, and then I will expand on how to apply this research to new systems for us to explore and why these systems are relevant.

This dissertation reports the mechanism, growth, and study of AuCN substrates from the molecular level to micron-sized crystals. I created two distinct self-assembled monolayers (SAMs) of AuCN on gold substrates with a transformation occurring upon thermal annealing of the samples. These monolayers had different physical morphologies (hexagonal close-packed (HCP) for the as-adsorbed and a ribbon structure for the heated sample) and these morphologies had different C–N stretches, measured through attenuated total reflection, of 2142 cm^{-1} for the HCP structure and 2234 cm^{-1} for the ribbon structure. This vibrational change is indicative of differences in the strengths of the bonds interacting with the gold substrate and allows us to probe the local chemical environment.

When the AuCN monolayers underwent prolonged exposure to the cyanide environment, I discovered that AuCN crystals grew directly atop the SAM substrate. Understanding this growth mechanism could help create the scaffolding needed to improve ultrathin materials. Here, I probed the growth mechanism *via* scanning electron microscopy imaging and found that the growth direction was primarily perpendicular to the surface. Similarly with the monolayers, I found that as the samples were heated, the C–N vibrational normal mode blue shifted from 2160 cm^{-1} to 2234 cm^{-1} showing that heating the sample changes the local chemical environment around the cyanide. This shift is most likely due to a transformation

from $\text{Au}(\text{CN})_2^-$ to AuCN , though it is unknown where the charge balance occurs and is subject to rather arbitrary boundaries for adsorbate on surfaces in any case. We discovered that the crystals grow in size-consistent repeating structures regardless of the quantity of gold present. Energy dispersive X-ray spectroscopic characterization of the AuCN crystals formed atop Au/Si substrates indicated that the crystals contained carbon, nitrogen, and gold and lacked potassium (silicon was also found though with lower intensity within the regions of the crystals).

Lastly, to probe the chemical interactions at the scale of molecules, we developed and constructed a scanning tunneling microscope (STM) that can collect image data while simultaneously measuring the vibrational energy of the surface adsorbates using a Fourier transform infrared (FTIR) interferometer as an excitation source. By using the multiplexed signal from a broadband IR source, we have demonstrated the capabilities of measuring vibrational modes at the subnanometer scale by using the STM tip as a nanoamplifier. Because the tunneling current is exponentially related to the tunneling distance, the turning points of the vibrationally excited molecules result in larger currents than the ground energy vibrational states. By measuring this change in current with time we probe the vibrational changes. The STM tip resolves spatial and spectroscopic information far below the diffraction limit of light, relaying a richer picture of the chemical properties of the surface.

6.2 New Applications and Experiments for AuCN Crystals

With our AuCN systems, we are able to create scaled assemblies from SAMs to micron-sized crystals. Finding new mechanisms to bridge the gap between these scales would enable better control and engineering new nanotechnologies. One strategy is to use soft-lithographic techniques, *i.e.*, chemical lift-off lithography, to pattern surfaces of interest then control where the cyanide crystals grow.¹ By patterning the growth of the crystals in specific regions, we could dictate the growth location for nanoelectronics. This experimental setup works because alkanethiols have been shown to out-compete cyanide for binding sites on gold surfaces.² However, if we use chemical lift-off lithography to create domains, we can

subtractively form regions lacking the alkanethiols and can then dictate where crystals grow on surfaces. We can determine the growth dynamics by measuring the crystal coverage in the regions of interest, elucidating the limits of this growth mechanism.

Another question pertaining to the monolayer growth concerns how AuCN crystals are deposited on the HCP backbone—does changing the AuCN monolayer change the crystal structure? To answer this question, the size, shape, and structure of AuCN grown on the HCP lattice can be compared to that of the crystals grown from the ribbon structure. This research would enable us to evaluate the roles of the underlying SAM in the crystal formation and can be extended to other surface-mediated systems. Overall, this knowledge would provide us with additional tools for achieving precise control over the final crystal structure. The experimental process to assess this question is as follows. One could create a surface and confirm its structure *via* STM and IR spectroscopy, then thermally anneal the sample until the conversion is complete. Next, one could re-expose the sample to the KCN environment and then wait until the crystals have become visible. If the crystals formed through this method are similar in size, shape, and abundance to the ones grown in Chapter 4, then the underlying substrate is not as influential in dictating the growth of the material. Deviations from our prior crystals would show the opposite. This methodology would also be relevant to thin (2-nm-thick) samples to discover if they also produced similar-sized crystals. These experiments would determine whether the ribbon structure monolayer played a role in the growth mechanism of the gold-limited crystals.

6.3 Fourier Transform Infrared-Scanning Tunneling Microscopy: New Systems and Outlook

6.3.1 Isocyanide Systems

Though the potential for the FTIR-STM is high, the capabilities and limitations of the system needs to be further explored. The limitations should be interrogated through the study of monolayer assemblies of compounds whose structures exhibit intense infrared absorption,

specifically, those with vibrational modes similar in energy to that of AuCN. The next sets of compounds to assess *via* FTIR should be isocyanide molecules. Work has been done to show how di-isocyanide structures create linear chain-like patterns atop Au{111} substrates.³ However, to assess the length dependence on the vibrational modes, researchers could use a molecule with both a thiol and an isocyanide functional group. As mentioned above, the thiol will outcompete the cyanide for binding to gold surfaces. This experiment would also allow us to assess the distance dependence of our measuring the vibrational modes. By changing the length of the linker chains and measuring the vibrational mode versus the intensity, we can compare the effect of the distances of the molecules to the surface and to the probe tip.

6.3.2 Alkynes

Measuring local chemical vibrations beyond the C–N systems, requires us to assess other types of chemical bonds. Alkynes are similar to cyanide in that both functional groups contain triple bonds with similar vibrational modes. We have previously shown that we can bond alkynes to gold substrates creating a C–Au with a covalent σ bond.⁴ Probing the local chemical interactions of surfaces and utilizing this new air stable method will allow us to design better nanoarchitectures. Using the FTIR–STM, we could probe the vibrational interactions of the $\text{C}\equiv\text{C}$ bonded carbon atoms on the surface. Alkynes, similar to isocyanide, also have vibrational normal modes *ca.* 2200 cm^{-1} . These experiments will allow us to probe the localized $\text{C}\equiv\text{C}$ vibrational modes.⁴

6.3.3 Modifications to the Fourier Transform Infrared Scanning Tunneling Microscope

The modifications we made constructing the FTIR scanning tunneling microscope have enabled simultaneously measuring the vibrational modes while imaging the surface topography. However, several steps can be made to improve the efficacy of this experimental procedure. The first step would be by changing the substrates from sapphire prisms to calcium fluoride (CaF_2) prisms. Researchers have created epitaxially grown Au/ CaF_2 substrates, which have

the distinct advantage of transmitting more of the infrared spectrum than sapphire prisms do.⁵ The sapphire prisms used thus far are robust substrates that we have used in a variety of experiments due to their large optical window within the visible spectrum.^{4,6–8} However, below 1900 cm^{-1} , the sapphire prism absorbs strongly and thus, is not an appropriate substrate for measuring those vibrational modes. This limitation becomes more obvious when studying systems with double bonds or correlating the fingerprint region of an infrared spectrum to a known molecule. Due to the brittleness of the CaF_2 substrate, and the location of the cyanide absorption, we decided to focus our attention on the sapphire prisms first.

With the current design of this scanning tunneling microscope, we use a large area on our optical table. Because of the volume and the purging mechanism, we have only been able to purge about 90% of the atmosphere measured *via* carbon dioxide peaks before and after purging. However, by decreasing the volume of the environment and better insulating our system from atmospheric pressure, we would be able to purge the system more effectively and diminish the carbon dioxide and water signals in our spectra even more. This modification would become relevant when studying systems that have absorption modes within the water or carbon dioxide viewing windows.

Our STM current measurements used for the nanoamplifier experiments are performed through the proprietary software used to control the instrument, WinSTM. However, this process creates a lag time between acquiring the dataset and discovering whether there was a strong absorption in the current spectrum. This step could be sped up with two modifications to our system. First, by using a triggering mechanism from the interferometer, we could implement known times to acquire our current spectrum. This trigger would ensure that all measurements contain the information-rich centerburst, and we would be able to acquire multiple measurements to create averaged spectra increasing the signal-to-noise ratio and increasing the likelihood of measuring the signal. The last modification is on the software side—how we view the current spectrum. We acquire the current versus time spectrum, then process the data utilizing our MatLab program to perform an inverse fast Fourier transform on this data set. This procedure requires 10 minutes to acquire each spectrum. By remodeling the software so that we can measure the current while implementing “live” inverse Fourier

transforms, the ten-minute process could be brought down to the scale of seconds.

6.4 Conclusions

Overall, my research during my time in graduate school has been spent focusing on AuCN systems to understand how they grow and what their molecular scale chemical properties are. Considering how simple the AuCN molecules are, there is still much we do not understand. With the properties of a semiconductor, AuCN can serve as a model system to test a variety of applications, so understanding the growth mechanisms and the localized chemical environments will help us create nanomaterials more effectively. From morphology control to densities in the crystal structure, I found several methods to dictate how these molecules bind and grow. Though AuCN is composed of a lethal poison, our curiosity has found precious insights that can be applied to nanomaterials more broadly.

We keep moving forward—opening new doors and doing new things—because we’re curious. And curiosity keeps leading us down new paths. We’re always exploring and experimenting.

~Walt Disney

6.5 References

- (1) Liao, W.-S.; Cheunkar, S.; Cao, H. H.; Bednar, H. R.; Weiss, P. S.; Andrews, A. M. Subtractive Patterning via Chemical Lift-Off Lithography. *Science* **2012**, *337*, 1517–1521.
- (2) Lewis, G.; Shaw III, C. F. Competition of Thiols and Cyanide for Gold (I). *Inorganic Chemistry* **1986**, *25*, 58–62.
- (3) Boscoboinik, J. A.; Calaza, F. C.; Habeeb, Z.; Bennett, D. W.; Stacchiola, D. J.; Purino, M. A.; Tysoe, W. T. One-Dimensional Supramolecular Surface Structures: 1,4-Diisocyanobenzene on Au(111) Surfaces. *Physical Chemistry Chemical Physics* **2010**, *12*, 11624–11629.
- (4) Wang, S.; Goronzy, D. P.; Young, T. D.; Wattanatorn, N.; Stewart, L.; Baše, T.; Weiss, P. S. Formation of Highly Ordered Terminal Alkyne Self-Assembled Monolayers on the Au{111} Surface through Substitution of 1-Decaboranethiolate. *The Journal of Physical Chemistry C* **2019**, *123*, 1348–1353.
- (5) Semaltianos, N. G.; Wilson, E. G. Investigation of the Surface Morphology of Thermally Evaporated Thin Gold Films on Mica, Glass, Silicon and Calcium Fluoride Substrates by Scanning Tunneling Microscopy. *Thin Solid Films* **2000**, *366*, 111–116.
- (6) Wang, S.; Wattanatorn, N.; Chiang, N.; Zhao, Y.; Kim, M.; Ma, H.; Jen, A. K.-Y.; Weiss, P. S. Photoinduced Charge Transfer in Single-Molecule P--N Junctions. *The Journal of Physical Chemistry Letters* **2019**, *10*, 2175–2181.
- (7) Wang, S.; Chiang, N.; Guo, H.; Wattanatorn, N.; Barr, K. K.; Alexandrova, A. N.; Weiss, P. S. Photoinduced Carrier Generation and Distribution in Solution-Deposited Titanyl Phthalocyanine Monolayers. *Chemistry of Materials* **2019**, *31*, 10109–10116.
- (8) Kim, M.; Hohman, J. N.; Cao, Y.; Houk, K. N.; Ma, H.; Jen, A. K.-Y.; Weiss, P. S. Creating Favorable Geometries for Directing Organic Photoreactions in Alkanethiolate Monolayers. *Science* **2011**, *331*, 1312–1315.

APPENDIX A

Supplemental Information

A.2 Chapter 2 Supplemental Information

Infrared Spectroscopy: Comparison of CN monolayers on Au{111} by Attenuated Total Internal Reflection Fourier Transform Infrared Spectroscopy and Polycrystalline Au/Si Using Polarization-Modulated Fourier Transform Infrared Reflection Absorption Spectroscopy

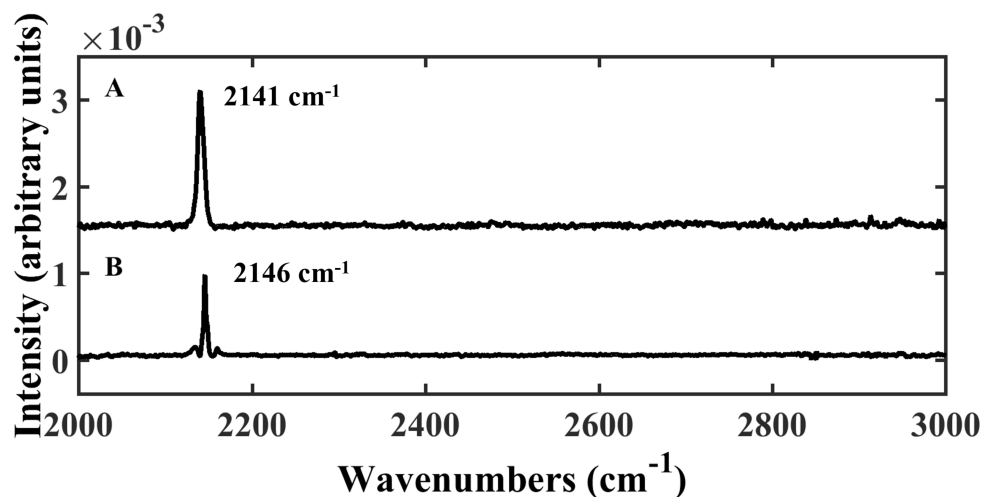


Figure A.1: (A) The polarization-modulated Fourier transform infrared reflection absorption spectrum (PM-IRRAS) of CN as-deposited on polycrystalline Au/Si indicating the CN is still primarily upright on the surface without detection of the C–H stretch associated with HCN. (B) The attenuated total internal reflectance Fourier transform infrared spectrum of as-deposited CN on Au{111} showing the multiplet not detected by PM-IRRAS and a blue shift of 5 cm⁻¹.

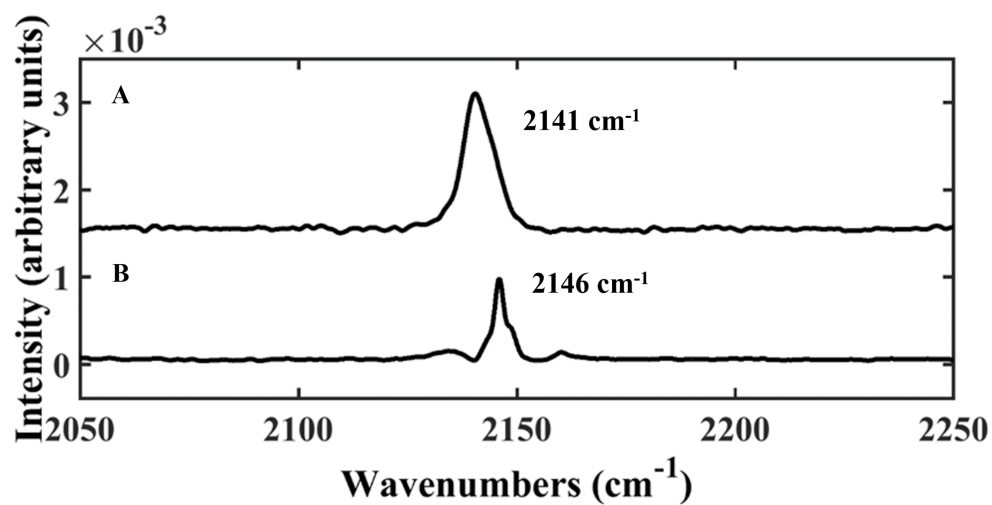


Figure A.2: Detail of the (A) CN region from the polarization-modulated Fourier transform infrared reflection absorption spectrum of CN as-deposited on polycrystalline Au/Si and (B) the attenuated total internal reflectance Fourier transform infrared spectrum of as-deposited CN on Au{111}.

A.3 Chapter 3 Supplemental Information

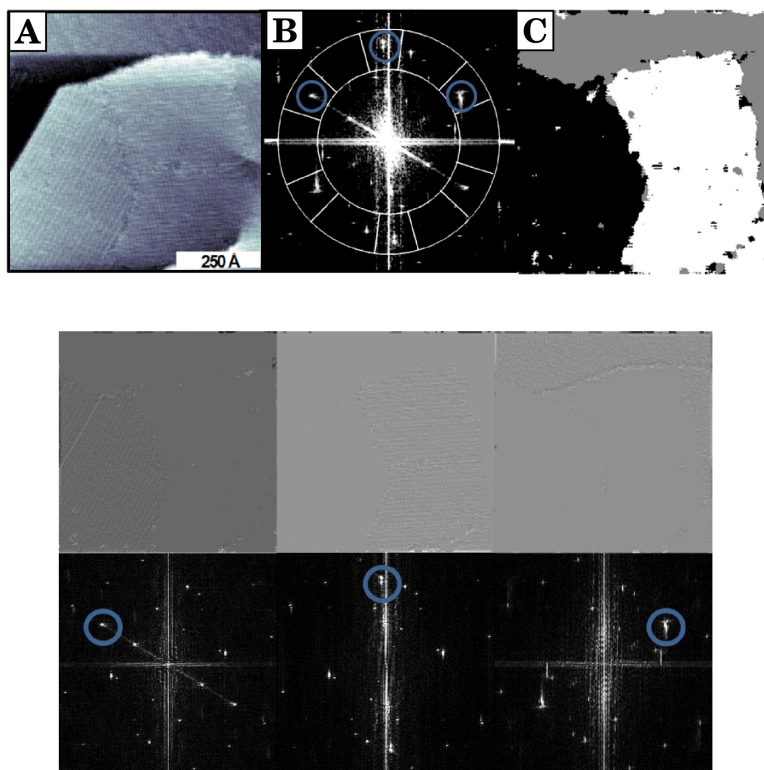


Figure A.3: (A) Scanning tunneling microscope image, (B) associated manual curvelet partitioning of the Fourier domain using the empirical wavelet transformation, and (C) the segmentation results for the domains with different orientations. The bottom panels represent the manual 2D fast Fourier transformation filtering of the circled Fourier coefficients and the corresponding image textures for each segmented domain. Relative stripe domain rotation angles are calculated to be multiples of 60° using the dot product of the displacement vectors of the position of the circled coefficients from the origin. Only one of the Fourier coefficients was used for each segmented texture region because of symmetry in the Fourier domain. The Fourier domain plots take into account all information in the image.

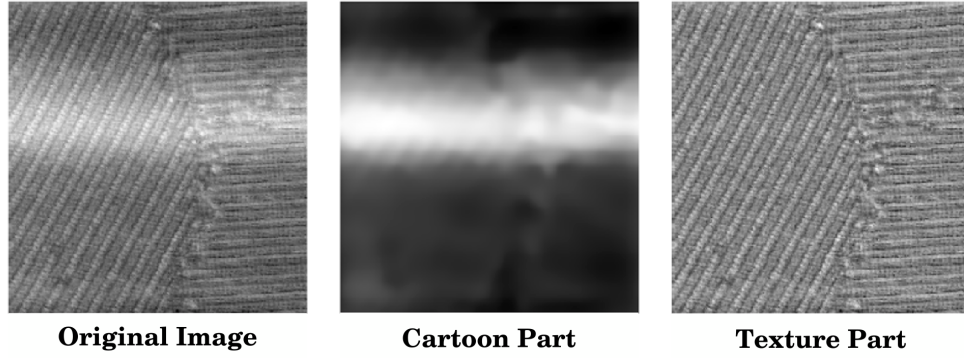


Figure A.4: Scanning tunneling microscope image segmented using a combination of cartoon and texture decomposition. Artifacts associated with the imaging were separated from the analyzed image and stored separately to avoid loss of information.

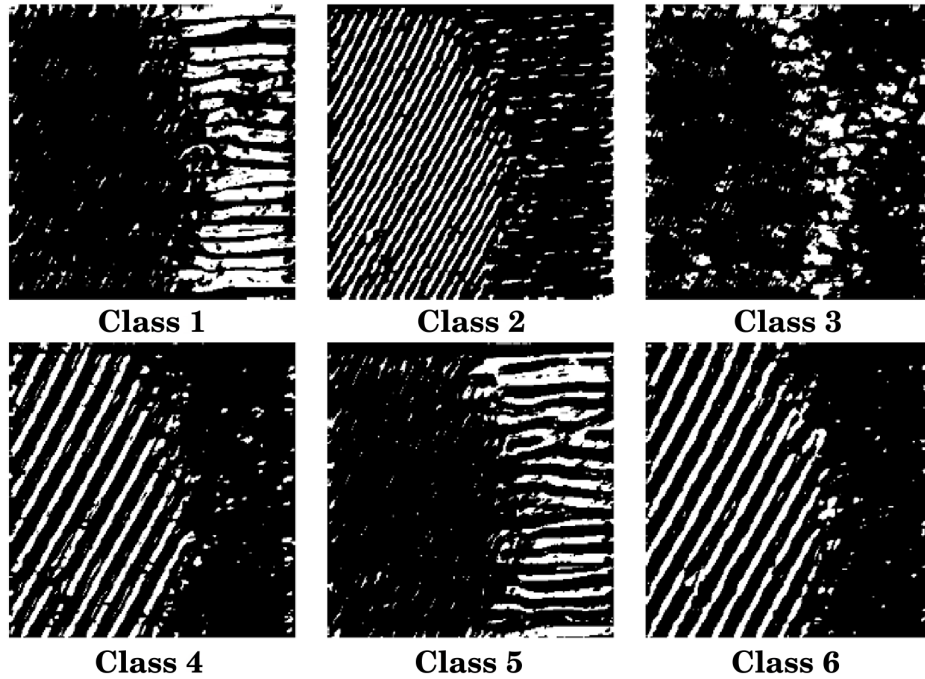


Figure A.5: Classes associated with texture decomposition of the scanning tunneling microscope image shown in Figure A.4 that highlight the different regions of the image associated with the ribbon orientation and domain boundary.

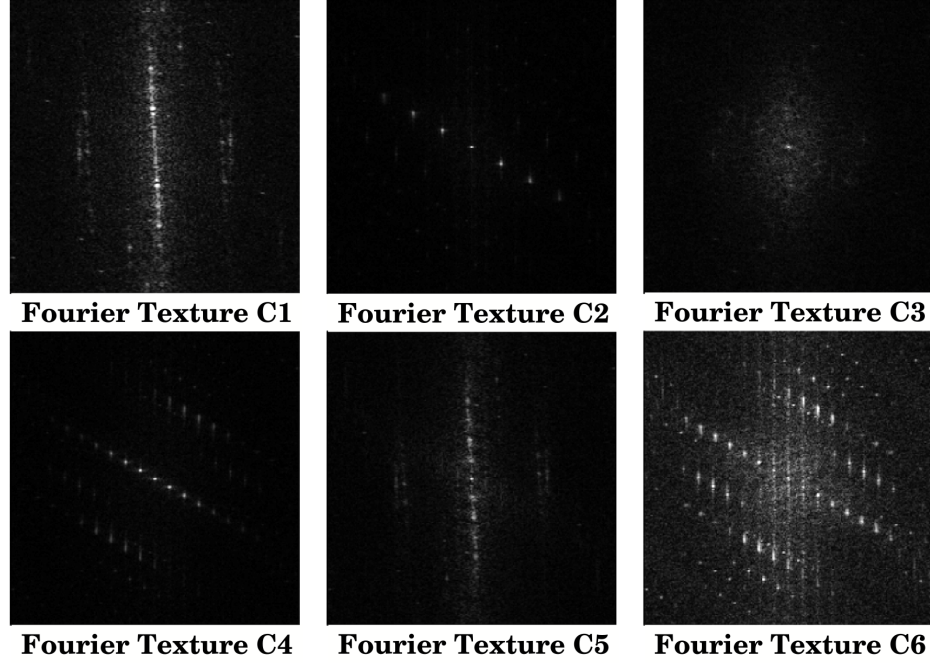


Figure A.6: Fourier domain classes associated with the texture decomposition of the scanning tunneling microscope image shown in Figure A.4. The angles between different orientation domains, as shown in Figure A.3, were calculated using the dot product of the displacement vectors from the farthest and largest Fourier coefficient from the origin. Fourier textures C1 and C2 are examples that represent the two stripe orientation domains, Class 1 and Class 6, highlighted in Figure A.5. Equivalently, the Fourier textures from C4 and C5 could be used to calculate the same angle.

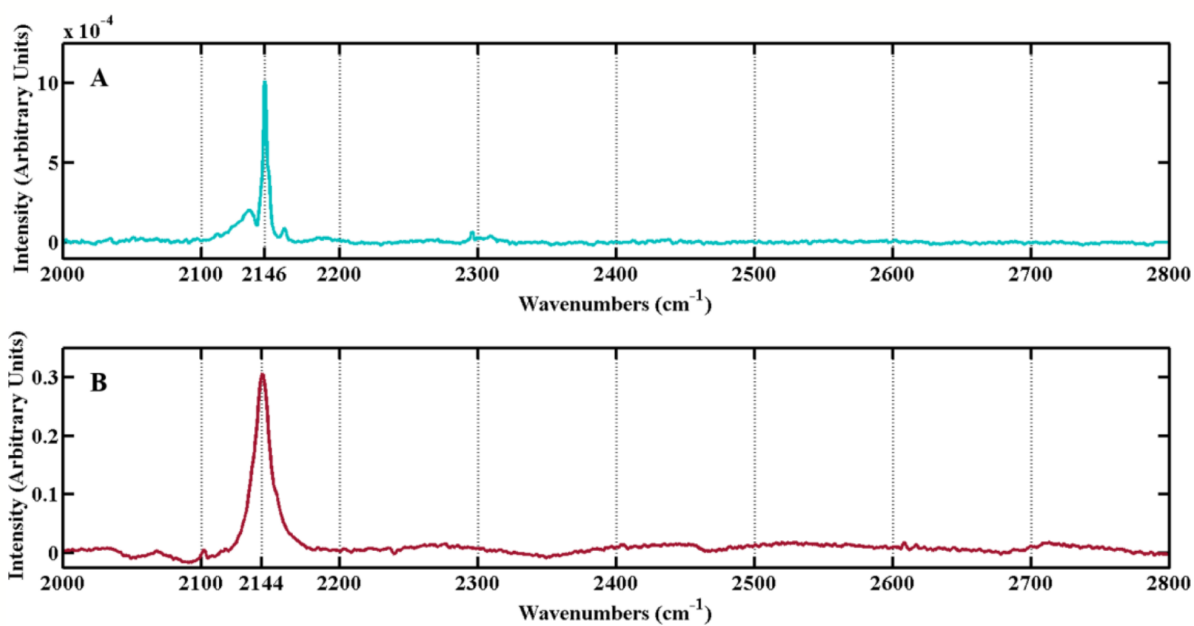


Figure A.7: (A) Attenuated total reflection-infrared spectrum of as-adsorbed CN/Au{111} at room temperature. (B) Polarization-modulation infrared absorption spectrum of room temperature as-deposited CN/Au/Si.

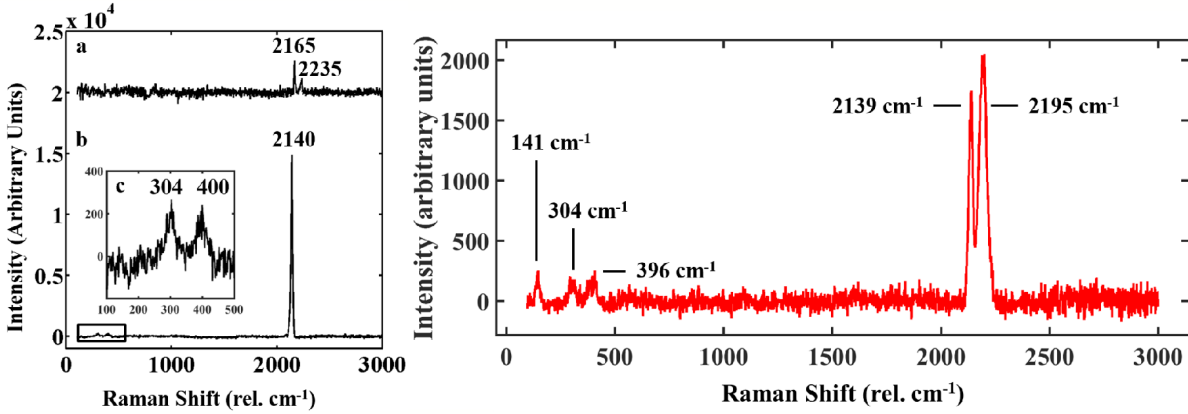


Figure A.8: Surface-enhanced Raman spectrum of as-adsorbed CN/Au{111} at room temperature showing the peaks attributed to the CN vibrations. On the Au{111} surface we were unable to detect the low-frequency modes, but did detect a splitting of the CN vibration. (b) Surface-enhanced Raman spectrum of as-adsorbed CN on a custom roughened polycrystalline Au substrate on glass with the low-frequency vibrations attributed to the AuCN stretch and bend (shown in the inset, c). (d) Surface-enhanced Raman spectrum of CN on Au after annealing using the same custom polycrystalline nanostructured SERS substrate. (As-deposited Raman spectra shown in (a, b, and c) from chapter 2)

A.3.1 Supplemental Raman Spectroscopy

Raman spectra for the as-deposited and annealed cyanide on gold systems are shown in Figure A.8. The splitting of the high-frequency peak on the as-deposited CN/Au{111}, shown in Figure A.8a, are similar to the vibrations for the annealed CN sample. The 2195 and 2235 cm^{-1} are close to the values reported for the crystalline high-frequency vibration, while the lower 2140 and 2165 cm^{-1} are closer to the reported value for cyanide adsorbed on the surface of gold. It is unknown why the Au{111} value is shifted by 25 cm^{-1} . We do not observe the CN vibration at a lower frequency for the weaker Au–NC vibration, however, the appearance of the 2195 cm^{-1} vibration is an indication of the presence of isocyanide coupled with the appearance of a new low-frequency mode. In the spectra for the annealed adsorbed CN, we detected the additional low-frequency mode at 141 cm^{-1} that is close to the Au–N vibration detected in crystalline AuCN (see Figure A.9 for structural schematic of AuCN crystals). Note that only the infinite chain model reports this Au–NC vibrational

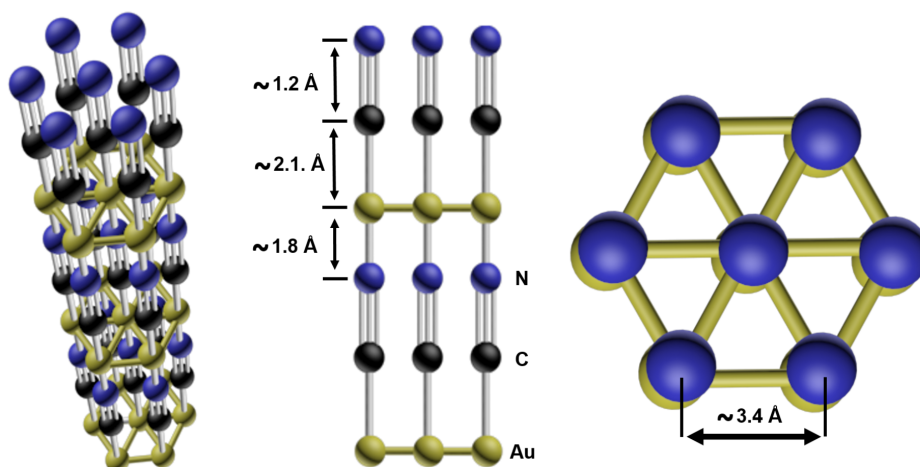


Figure A.9: Schematic of the crystal structure and distance measurements for solid AuCN, which is composed of hexagonally bundled, linear AuCN chains with alternating Au–C and Au–N bonds (distances from ref [5]).

because the individual complexes of $\text{Au}(\text{CN})_2^-$ typically found in solution do not contain Au–N bonding. One explanation for the observation of the mode on the $\text{Au}\{111\}$ surface is that the single-crystal face enables greater packing and order that results in some stochastic ‘flipping’ of the cyanide from exposure to the thermal energy at room temperature. (see ref [5] for the AuCN crystalline vibration characterization and ref [6] for the as-adsorbed CN on Au).

A.3.2 References

- (1) Gilles, J. Empirical Wavelet Transform. *IEEE Transactions on Signal Processing* **2013**, *61*, Conference Name: IEEE Transactions on Signal Processing, 3999–4010.
- (2) Gilles, J.; Tran, G.; Osher, S. 2D Empirical Transforms. Wavelets, Ridgelets, and Curvelets Revisited. *SIAM Journal on Imaging Sciences* **2014**, *7*, 157–186.
- (3) Gilles, J.; Heal, K. A Parameterless Scale-Space Approach to Find Meaningful Modes in Histograms—Application to Image and Spectrum Segmentation. *International Journal of Wavelets, Multiresolution and Information Processing* **2014**, *12*, 1450044.
- (4) Bui, K. V.; Fauman, J. N.; Kes, D. D.; Torres, L. F. *Unpublished*.
- (5) Bowmaker, G. A.; Kennedy, B. J.; Reid, J. C. Crystal Structures of AuCN and AgCN and Vibrational Spectroscopic Studies of AuCN, AgCN, and CuCN. *Inorganic Chemistry* **1998**, *37*, 3968–3974.
- (6) Senapati, D.; Dasary, S. S. R.; Singh, A. K.; Senapati, T.; Yu, H.; Ray, P. C. A Label-Free Gold-Nanoparticle-Based SERS Assay for Direct Cyanide Detection at the Parts-Per-Trillion Level. *Chemistry – A European Journal* **2011**, *17*, 8445–8451.

A.4 Chapter 4 Supplemental Information

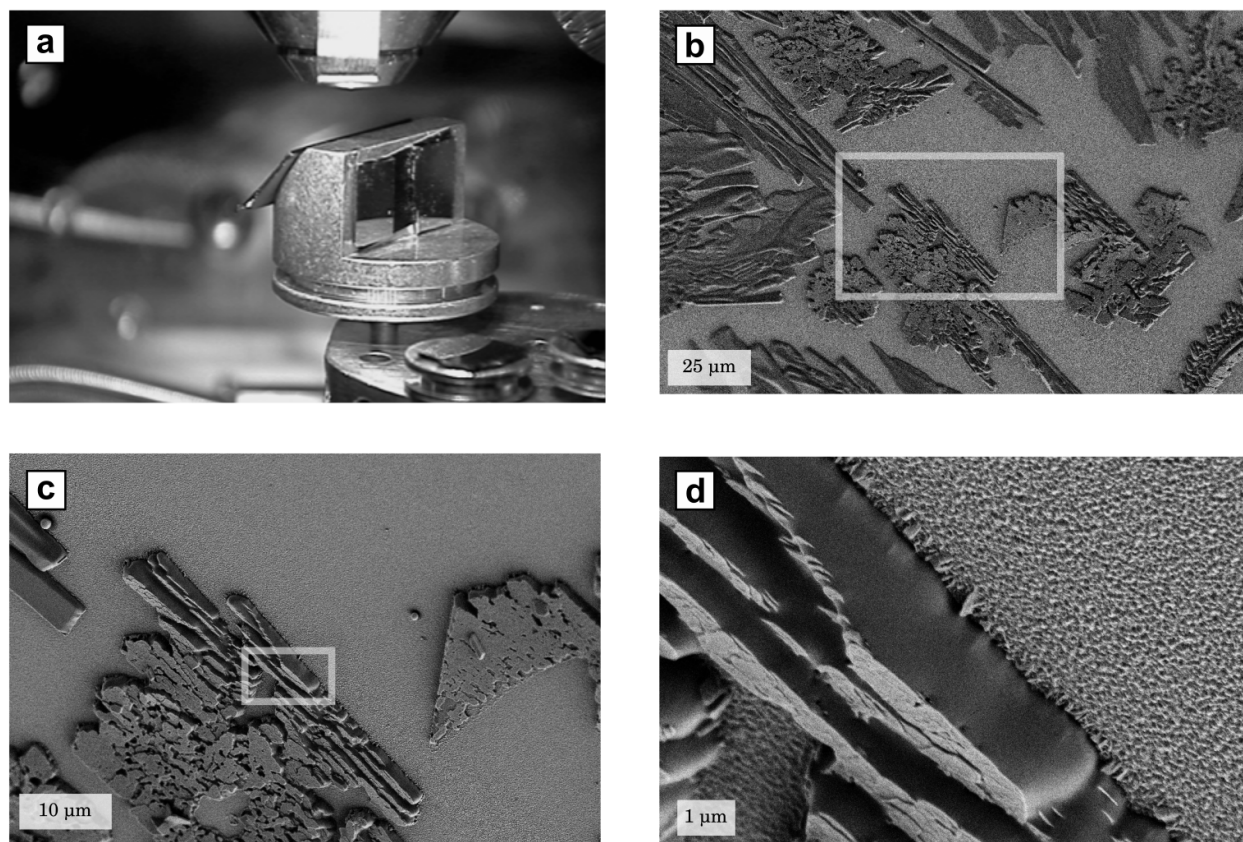


Figure A.10: a) Scanning electron microscope layout. Sample placed on stage at 45° with respect to the electron beam. b,c,d) scanning electron microscope images of AuCN crystals on Au/Si substrate. Grey rectangle inside of b) corresponds to c), and the rectangle in c) corresponds to d) (figure 4.1c).

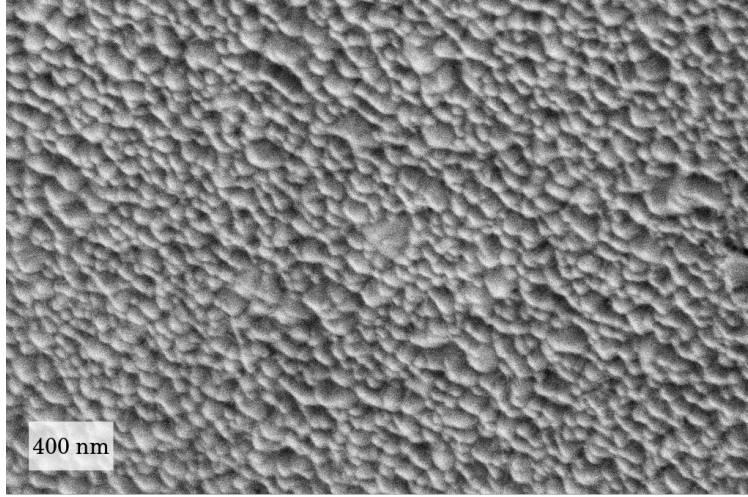


Figure A.11: Scanning electron microscope image of bare Au/Si (without exposure to AuCN). The bare-gold surface is indistinguishable from the off-crystal surfaces in figure A.10b–d.

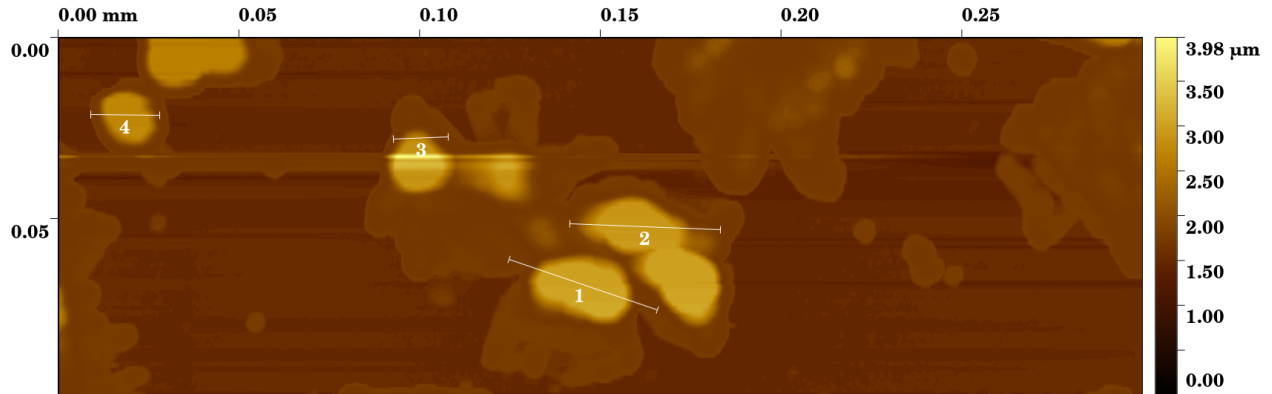


Figure A.12: Contact profilometry measurements of AuCN on a Au/Si substrate. The fast-scan direction is in the horizontal plane. The dimensions of the image are $300\ \mu\text{m} \times 100\ \mu\text{m}$, and the image was processed using background and horizontal slope subtraction. Line profiles of crystals are labeled 1–4 shown in figure A.13.

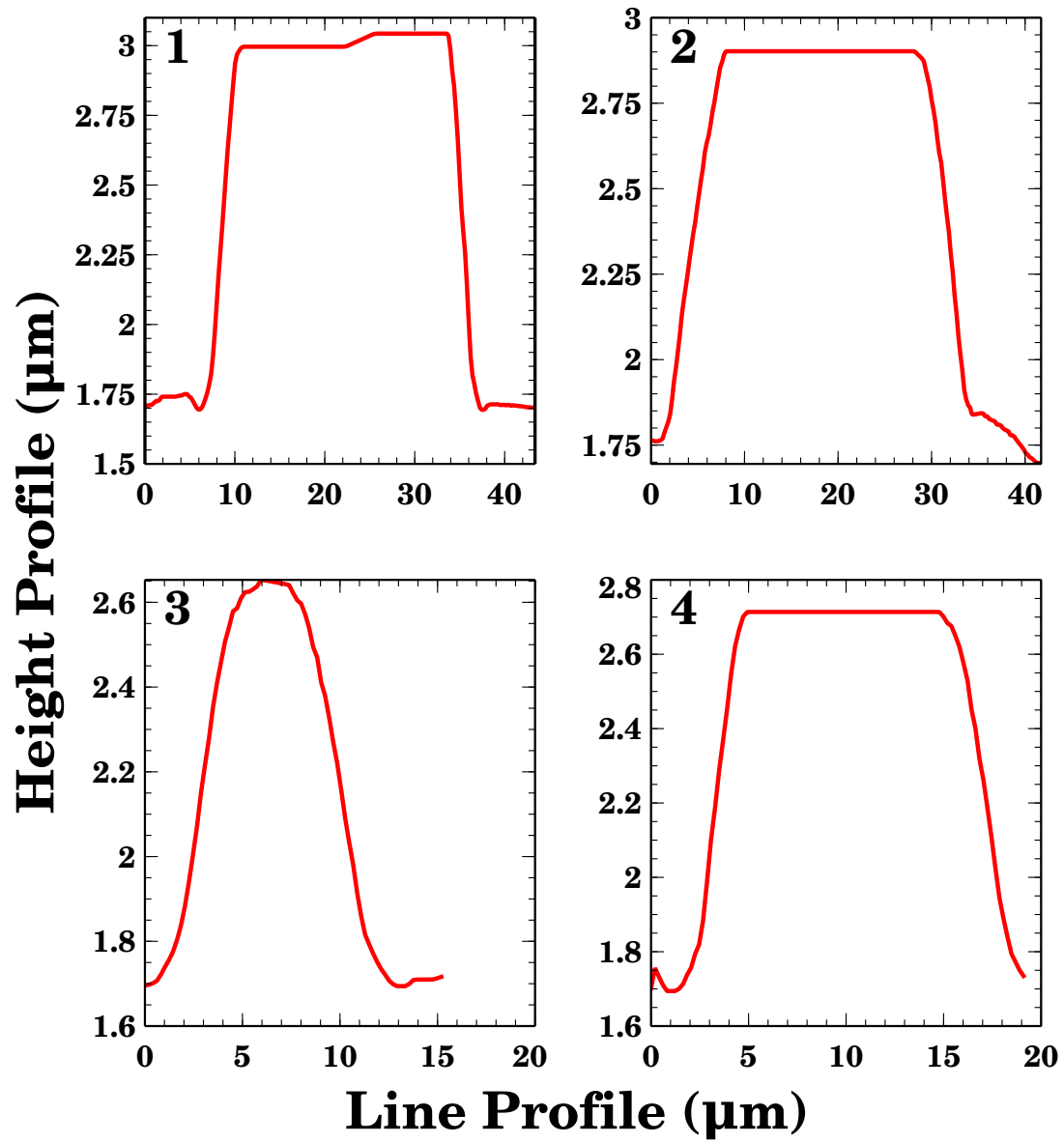


Figure A.13: Line profiles from the profilometry measurements found in figure A.12. The heights of these crystals ranged from 0.9 to 1.5 μm .

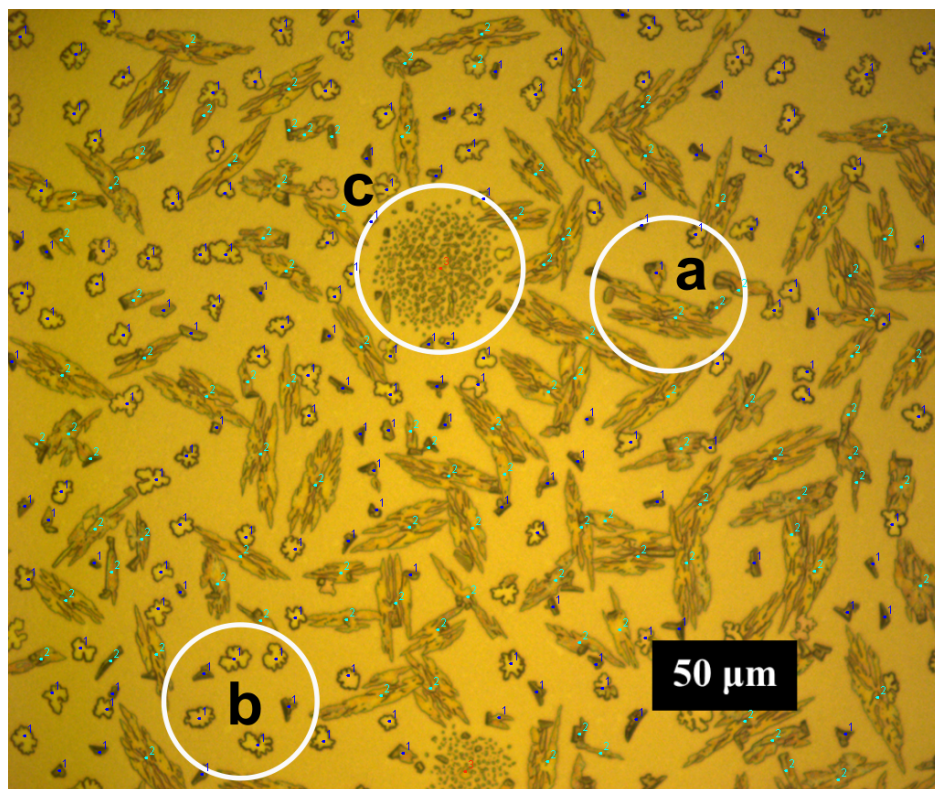


Figure A.14: AuCN crystal counts of cyanide-limited system from figure 4.2b categorized by size and shape. **1**, **2**, and **3** refer to small, elongated and sunburst structures respectively. Results are shown in table A.1.

Table A.1: Surface counts from figures A.14 and A.15

	Small (1)	Elongated (2)	Sunburst (3)	$< 4 \mu$ (4)
Figure A.14	152	107	2	N/A
Figure A.15	24	75	N/A	1576

N/A—Not applicable

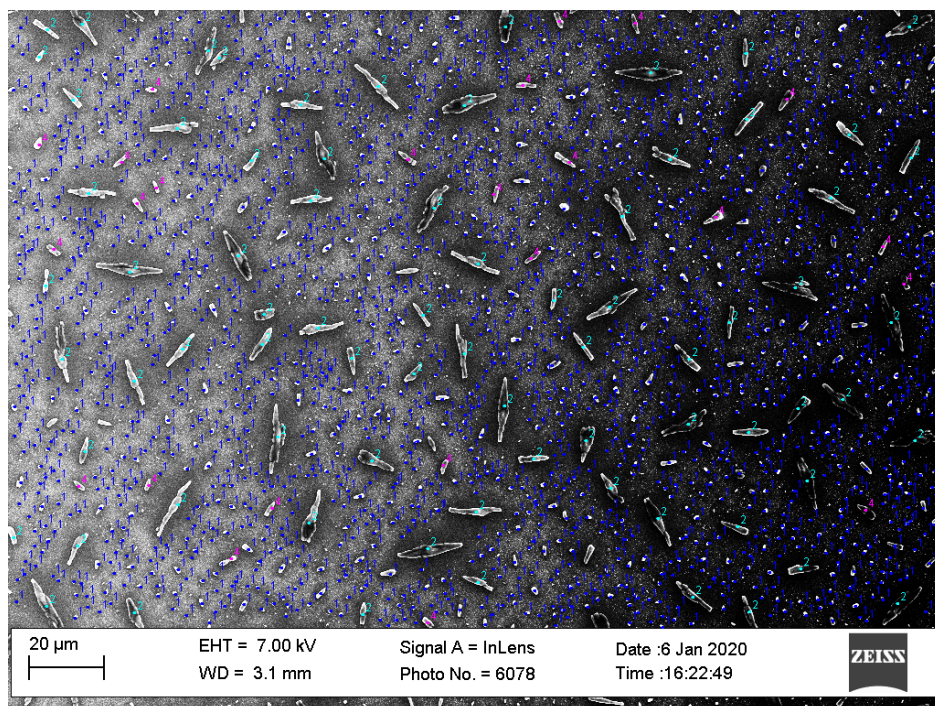


Figure A.15: AuCN crystal counts of gold-limited system from figure 4.4a categorized by size and shape. **1**, **2**, and **4** refer to small, elongated and $<4 \mu\text{m}$ structures respectively. Due to the low quantity of gold on the surface, many particles were less than $4 \mu\text{m}$ long. Results are shown in table A.1.

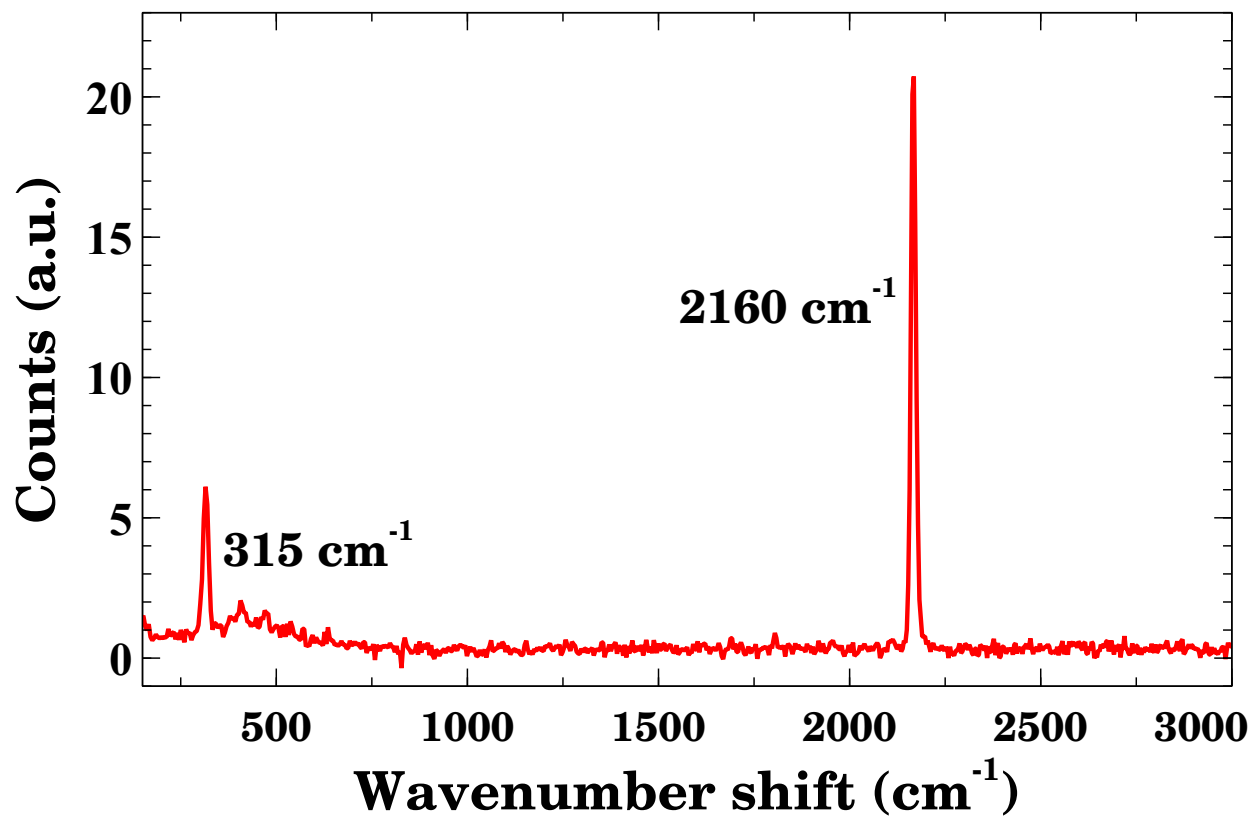


Figure A.16: Representative Raman vibrational spectrum of AuCN crystals on Au/Si substrates. The lower energy vibration mode from Au–CN stretch at 315 cm⁻¹. The spectrum was background subtracted with cosmic rays removed. The spectrum was acquired at a single location.

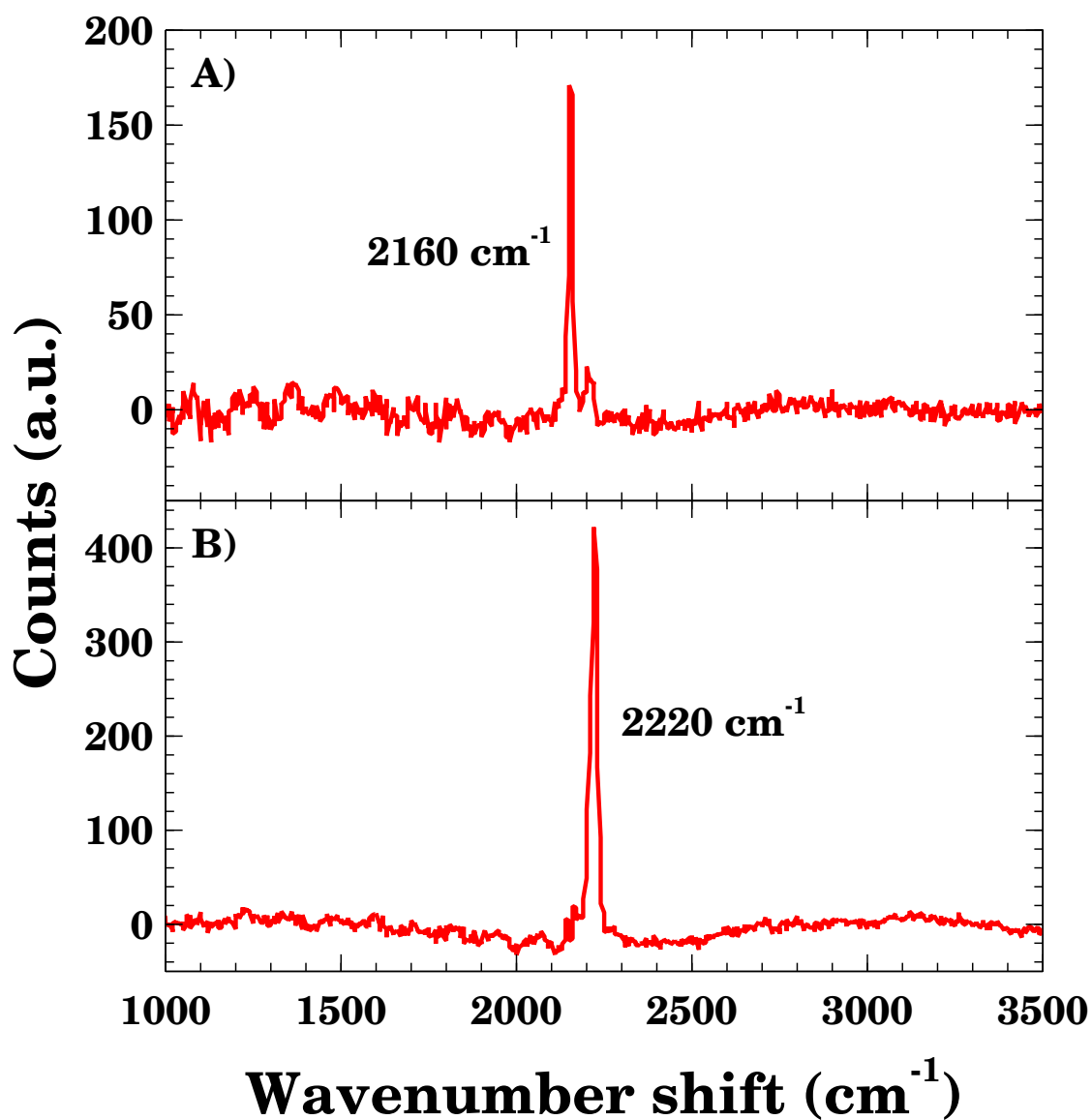


Figure A.17: A,B) Representative Raman vibrational spectra of AuCN crystals on Au/Si substrates. B) Spectrum post thermal annealing at 100 °C. Both spectra are background subtracted with cosmic rays removed. Spectra were averaged over the surface and were demixed true component analysis using the WITec's Suite Five software.

A.5 Chapter 5 Supplemental Information

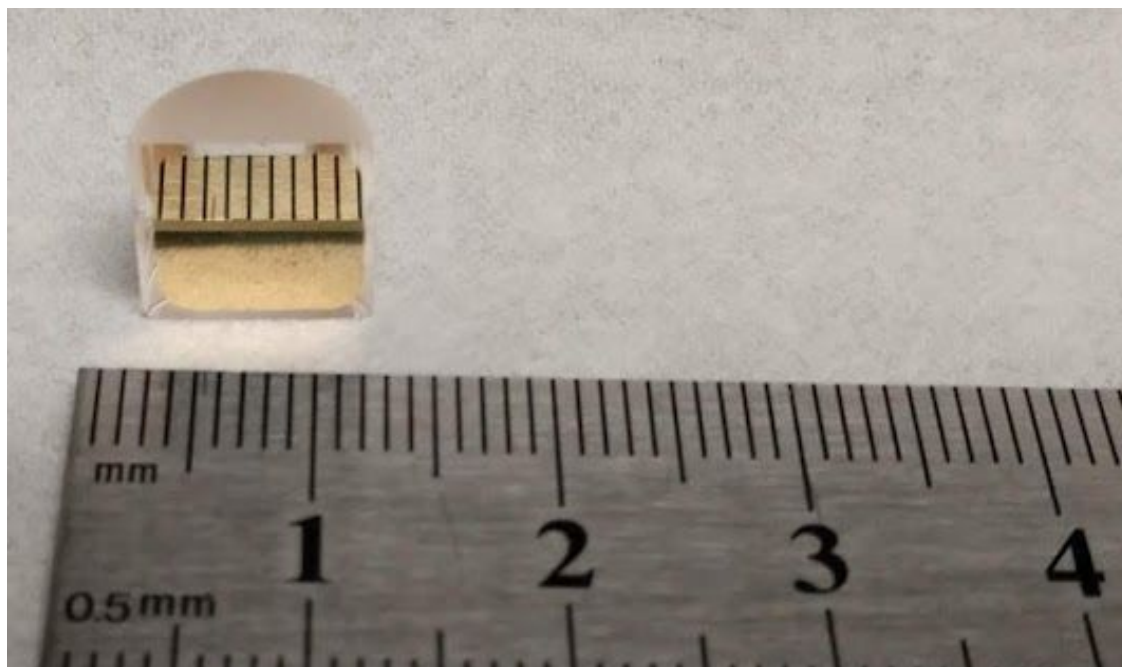


Figure A.18: Digital photograph of 40-nm-thick Au/sapphire substrate.