Time-Resolved IR Studies of Monolayer Self-Assembly on a Gold Substrate Using Planar Array Infrared (PA-IR) Spectroscopy

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Time-resolved and spatially resolved infrared spectra (line images) of self-assembled monolayers of octadecylthiol (ODT) on gold substrates were investigated by planar array infrared (PA-IR) spectroscopy, with a grazing incidence reflection attachment. It was observed that PA-IR spectra with a good signal-to-noise ratio that is comparable to those obtained from Fourier transform infrared spectroscopy could be acquired with a significantly shorter collection time. Focusing on the peak intensities and peak positions of the CH_2 asymmetric stretch (approximately 2918 cm^{-1}) and the CH_3 symmetric stretch (approximately 2960 cm^{-1}), respectively, the molecular orientation and organization of the monolayers were determined. The ODT formed a uniform monolayer on the surface of the gold whether it was deposited within 1–2 s or over a 40 h period. Disordered monolayers formed instantly, and with an increase in dipping time, the monolayer became more ordered, becoming highly ordered after dipping times of many (>24) hours.

Introduction

Self-assembled monolayers (SAMs) are easily prepared and modified and play an important role in biology, microelectronics, lubrication, adhesion, sensors, and catalysis, due to their stable performance under various perturbing conditions.[1] In addition, the ability to engineer functional films at the molecular level provides a wide range of choices for altering chemical architecture. Due to the inert nature of the gold, the strong chemical bonding of Au–S, and the dense packing of crystalline alkanethiol SAMs on gold,[2] researchers have focused on the thiol–gold system as a model to explore the nature of the self-assembly process. Hence the study of SAMs continues to be of interest in almost all fields of science.

From a characterization perspective, SAMs have always been a challenge. Conventional techniques such as NMR do not exhibit the sensitivity for investigating SAMs, while others like X-ray diffraction and IR and Raman spectroscopy take extended periods of time to accumulate data of sufficiently high signal-to-noise (S/N) to allow interpretation of structural details. Elmore et al.[3] recently showed that broadband infrared spectra with very low noise levels can be obtained using a planar array infrared spectrograph (PA-IR spectrograph). The ultrasensitive, high-speed PA-IR instrument can easily record the IR spectrum of a monolayer in a matter of seconds with an acceptable signal-to-noise ratio (SNR). In a recent paper,[4]

spatially resolved spectra and broadband images of monolayer films have been reported for the first time.

The kinetics of self-assembly has been explored[5,6] with ellipsometry, contact angle, and Fourier transform infrared (FT-IR) spectroscopy, but the surface coverage of the monolayer during the self-assembly process has not been investigated. In this paper, we use a PA-IR spectrograph to follow the octadecylthiol (ODT) monolayer formation and organization on the surface of gold; at the same time, the broadband images revealed that the monolayer distribution was macroscopically uniform.

Experimental Section

Optical Setup. A block diagram of the PA-IR spectrograph with a monolayer sampling accessory is shown in Figure 1. Broadband infrared radiation is produced by a globar light source connected to a low-noise, high-voltage power supply. The light is collected and collimated by torroidal mirrors and passed through an adjustable slit and a standard Harrick grazing incidence reflection attachment. It then reflects off a torroidal mirror and is diffracted by a ruled grating; after reflection off another torroidal mirror, the beam is finally collected (with *f*/2.3 condensing optics) and focused onto an InSb 320 × 256 focal plane array (FPA) detector cooled with liquid nitrogen. The InSb camera optics include a 3–5 µm band-pass filter to avoid detector saturation and optimize integration time.

The spectrograph was constructed on a Newport (NRC) optical table and did not require an operational vibration-isolation system. The globar used in this instrument was ~1.2 cm high, with a diameter of ~2 mm. An adjustable slit (0–2 mm), set at ~0.3 mm width, was used to collect spectra at 1.5 ms integration times. The torroidal mirrors were silver-coated on the front surface and had a focal length of 10 cm. The ruled grating had

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(5) Schwarts, D. K. *Annu. Rev. Phys. Chem.* **2001**, *52*, 107–137.

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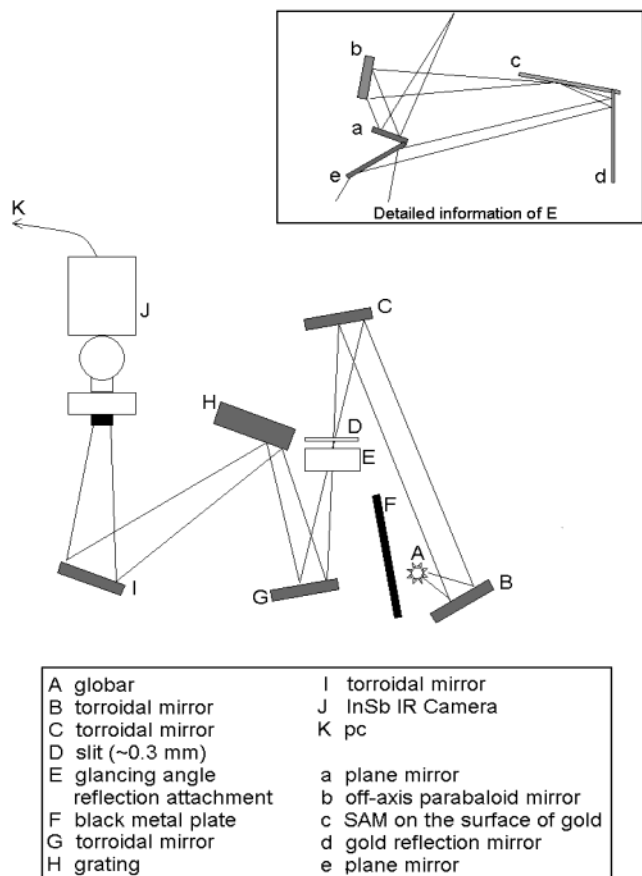
Figure 1. Experimental arrangement of components in the PA-IR spectrograph with monolayer sampling.

Figure 2. Comparison of PA-IR 100% lines with and without polarizer.

Figure 3. Comparison of the PA-IR spectrum of an ODT SAM on the surface of gold with its corresponding FT-IR spectrum.

300 grooves/mm (SPEX, Edison, NJ) and a blaze wavelength of 4.0 μm. The FPA, with 30×30 μm pixels, was housed in a Dewar that was part of a Merlin InSb Laboratory Infrared Camera (Indigo Systems, Santa Barbara, CA). A frequency range of $\sim$5 cm^{-1} illuminated each pixel. The optical configuration had not been optimized, and the PA-IR experiment was run open to the atmosphere.

Grazing Incidence Reflection. In 1965, Greenler first suggested a grazing incidence reflection (GIR) method to obtain IR spectra of thin films on the surfaces of metals.[7] If the polarization of the incoming beam is resolved into two components, one parallel (E$_{//}$) and one perpendicular (E$_{\perp}$) to the surface, the E$_{//}$ component undergoes a phase shift of $\sim$180° on reflection (almost independent of the angle of incidence), and hence the reflected beam will destructively interfere with the incident beam, producing a node in the E$_{//}$ light at the reflective surface. The E$_{\perp}$ component also experiences a phase change on reflection, varying to $\sim$90° at large incident angles (near grazing incidence), but the net result is an enhanced electric field component polarized normal to the reflecting surface. Thus, when the GIR technique is used in conjunction with standard transmission measurements, only those transition dipoles with components perpendicular to the surface will be detected. In many cases,[8–10] spectra observed at two orthogonal polarizations can be used to determine the orientation of the functional groups present in thin films such as SAMs.

Polarization Selection. Using the Greenler method, Rabolt et al.[8,11] compared the GIR method with and without the use of a polarizer. The results suggested that only the E$_{\perp}$ component

of the incident beam contributed to the resulting GIR spectrum and hence no polarizer was required. The authors then went on to demonstrate how this method (without polarizer) could be used in conjunction with standard transmission measurements to study the order and orientation of transferred Langmuir–Blodgett (LB) films.

Sample Preparation and Procedure. *Materials and Reagents.* ODT was obtained from Aldrich at 90+% purity. Reagent alcohol (HPLC grade) was obtained from Fisher Scientific. The solvents used in the cleaning process were 30% H_2O_2, 37.8% HCl, and 29.8% NH_4OH (all certified ACS grade, Fisher Scientific). All chemicals listed above were used as received. In addtion, ultrapure water (resistivity of 18.2 MΩ cm, Millipore Ultrapure water system, Millipore Inc.) was used throughout the cleaning procedure.

Pretreatment of Surfaces. Plain glass microscope slides (3 in. $\times$ 1 in., Fisherbrand, Fisher Scientific) were cleaned according to a standard procedure.[7] The slides (four slides per cleaning batch) were immersed in a $NH_4OH/H_2O_2/H_2O$ (1:1:5) solution at 65 °C for 15 min and rinsed in water for 10 min, followed by immersion in a $HCl/H_2O_2/H_2O$ (1:1:5) solution at 65 °C for 15 min. They were then rinsed in water for 10 min and finally dried in a flow of warm, clean nitrogen gas. Then, immediately after cleaning by a plasma cleaner, these slides were put into the vacuum evaporator. Vapor deposition of 200 Å of chromium under vacuum ($\sim$1 $\times$ 10^{-7} Torr) was followed by evaporation of 2000 Å of gold. The deposition rate for chromium was 1–2 Å/s, and that for gold was 3–5 Å/s. Gold substrates prepared in this manner were put into the plasma cleaner again and then dipped in the solutions as soon as they were removed.

Preparation of the Monolayers. ODT solution was prepared at 1 mM concentration with reagent grade alcohol. Gold substrates, cleaned by plasma cleaner, were immersed into freshly prepared solutions immediately, with dipping times lasting from 1–2 s to

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(8) Swalen, J. D.; Rabolt, J. F. In *Fourier Transform Infrared Spectroscopy: Applications to Chemical Systems 4*; Ferraro, J. R., Basile, L. J., Eds.; Academic Press: New York, 1985.
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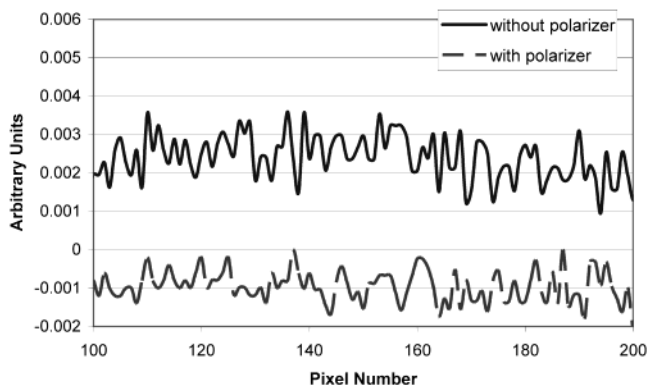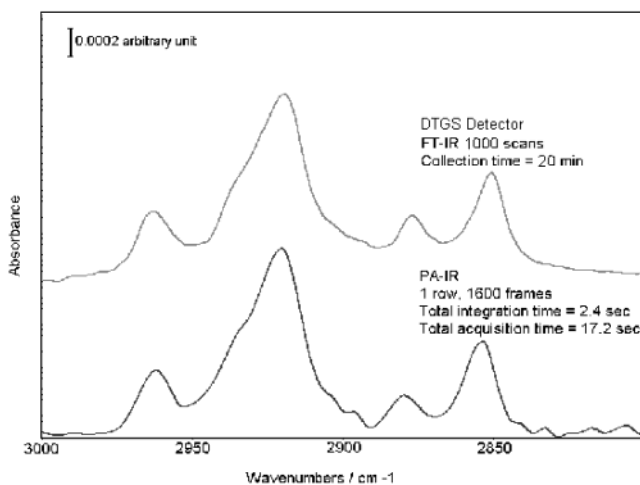(11) Rabolt, J. F.; Jurich, M.; Swalen, J. D. *Appl. Spectrosc.* **1985**, *39*, 269.
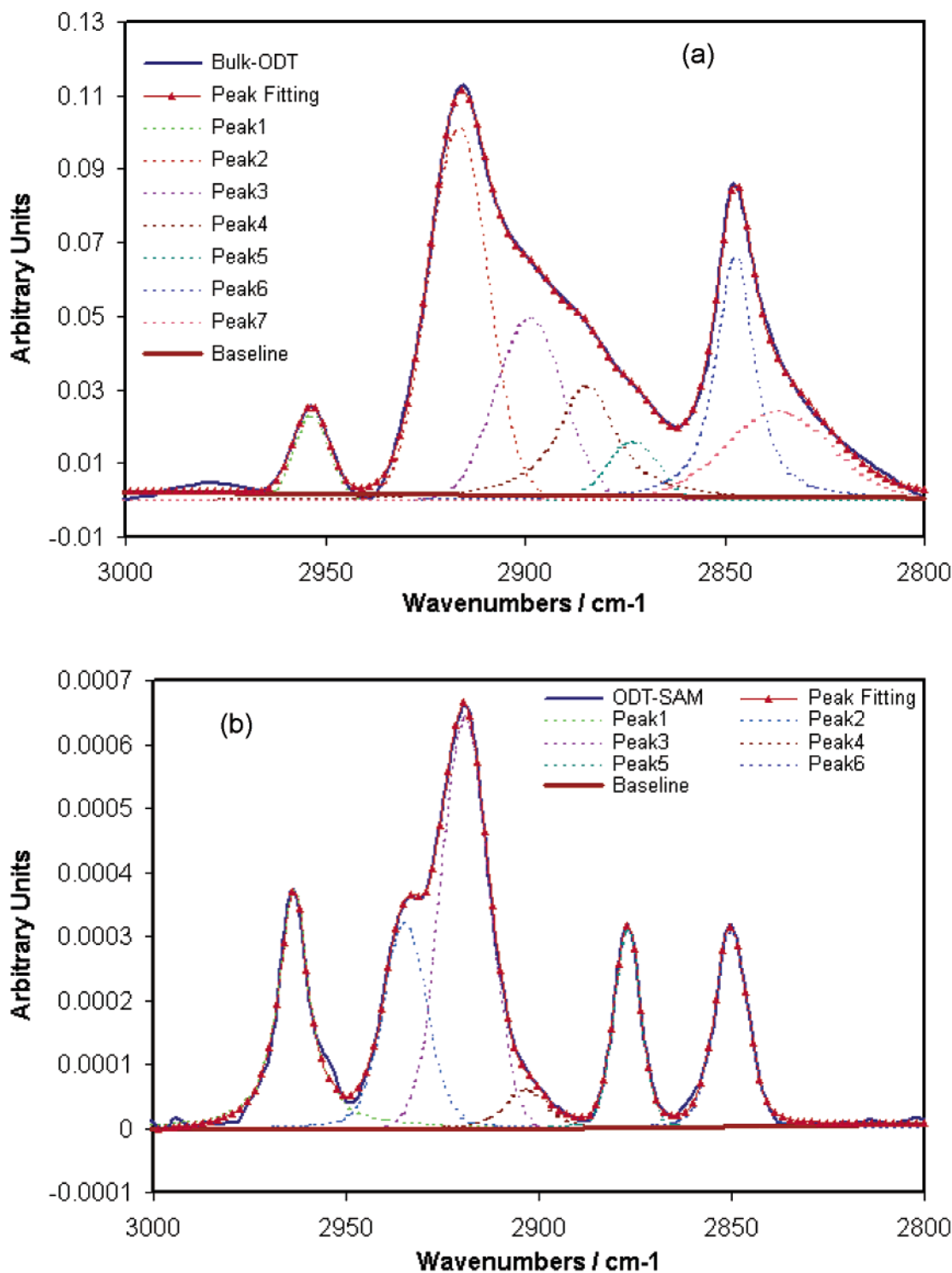
Figure 4. Curve fitting for (a) the isotropic spectrum of bulk ODT and (b) the GIR spectrum of a self-assembled ODT monolayer on gold.

several hours. For longer dipping times, the vials were sealed with Parafilm. After the corresponding dipping time, the slides were rinsed using the reagent alcohol and dried under warm nitrogen.

Deuterated octadecylthiol, which has IR bands isotopically shifted down in frequency from those of its *n*-alkyl analogue, was also used for coating gold substrates that were used to record the "reference". This coating procedure prevents the gold (used as the IR reference) from being contaminated by airborne impurities (e.g., hydrocarbons) that will interfere with the IR signal from the samples.[12]

Spectra Images, PA-IR Spectra, and Normalization. The slit images dispersed across the FPA (spectral image) are similar

to those described in earlier papers,[3,4] and the calculation for the absorbance spectra is the same:

$$A = -\log\left[\frac{I_s - I_{db}}{I_0 - I_{db}}\right] \qquad (1)$$

where A represents absorbance. I_s, I_0, and I_{db} represent the uncorrected sample intensity, uncorrected background, and the dark background, respectively.

(12) Tsao, M.-W.; Hoffmann, C. L.; Rabolt, J. F.; Johnson, H. E.; Castner, D. G.; Erdelen, C.; Ringsdorf, H. *Langmuir* **1997**, *13*, 4317−4322.
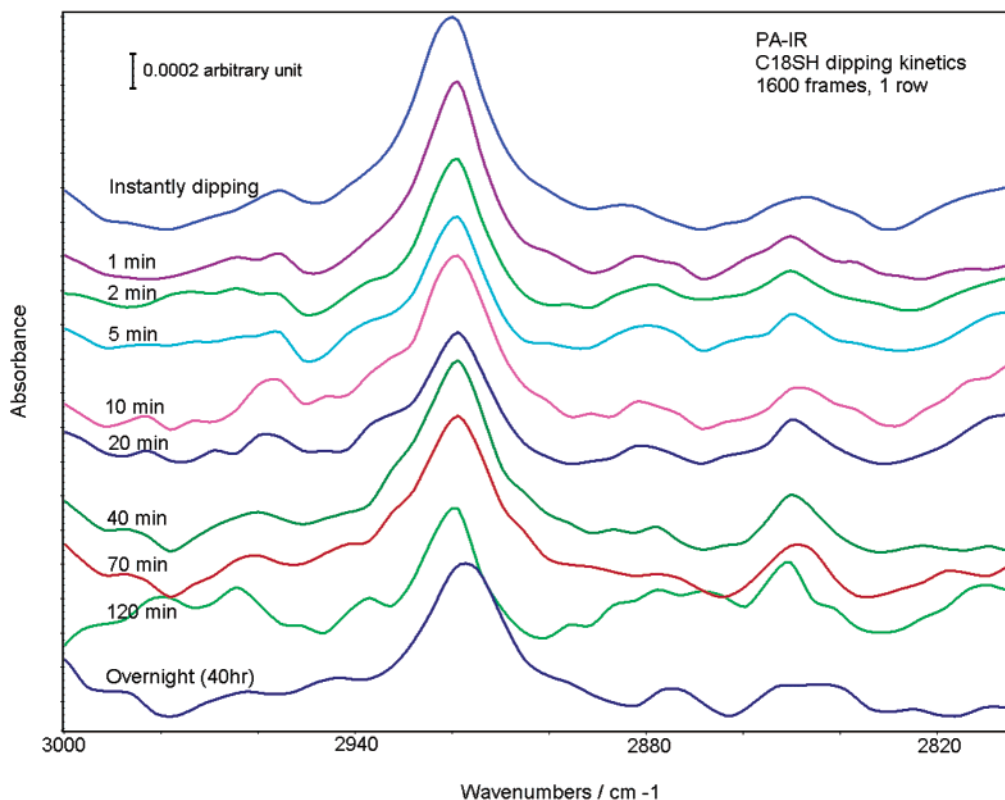
Figure 5. The time-resolved PA-IR spectra of ODT SAMs on the surface of gold.

In all spectra, the same row-dependent frequency shift is used to normalize for the optical slit curvature.

Signal Averaging of Spacially Resolved Spectra. The useful part of the spectral image is about 64 pixel rows high and approximately 200 pixels wide. All spectra corresponding to line images in this paper were obtained by signal averaging four pixel rows. After the initial averaging of four pixel rows, the number of spectra is reduced from 64 to 16. As discussed previously,[4] each original pixel row corresponds to a distance of $300 \ \mu m$ along the sample holder for each line image. Since four rows were signal averaged, a final spatial resolution of 1.2 mm resulted. Thus each line image corresponds to distance of 16×1.2 mm ≈ 1.7 cm. The spectral resolution at ~ 2920 cm^{-1} was about 6 cm^{-1} as determined by comparison of PA-IR and FT-IR spectra of polyethylene naphthalate (PEN). This same PEN film was also used for frequency calibration.

Noise Level Consideration. In Figure 2, when a 100% line is recorded with and without polarizers, a peak-to-peak noise level of $\sim 1 \times 10^{-3}$ absorbance units was obtained from one row of one frame (one coadd) collected with an integration time of 1.5 ms (total acquisition time of 17 ms, integration time plus read time). In comparison with our initial studies,[13] the noise level was lowered from $\sim 2.7 \times 10^{-3}$ absorbance units due to an increase in the amount of light by incorporating a collection mirror close to the infrared light source (Figure 1, torroidal mirror B) in the original optical arrangement.

With a polarizer, the peak-to-peak noise level is $\sim 0.5 \times 10^{-3}$ absorbance units under the same collection conditions as mentioned above due to the diminution of the light intensity caused by the presence of a polarizer. This observation would indicate that we are somewhere between shot noise and source fluctuation noise limited. Hence, in this study, a polarizer with the direction perpendicular to the surface was used in order to reduce the noise level of the final spectra when 1600 frames are averaged. With the polarizer, the peak-to-peak noise level is $\sim 3 \times 10^{-5}$ absorbance units.

FT-IR Measurements. Infrared spectra were collected at 4 cm^{-1} resolution with a Nexus 670 FT-IR Fourier transform infrared spectrometer (Thermo Nicolet Corp., Madison, WI) equipped with a DTGS detector. Each spectrum was collected with the coaddition

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Table 1. Peak Assignments for Bulk and Self-Assembled ODT Monolayer[a]

	peak center (cm^{-1})	description
bulk	2954	CH$_3$ asymmetric stretching polarized perpendicular to the skeletal plane
	2933	CH$_2$ symmetric stretching (Fermi resonance)
	2918	CH$_2$ asymmetric stretching
	2898	CH$_2$ asymmetric stretching
	2890	
	2872	CH$_3$ symmetric stretching
	2850	CH$_2$ symmetric stretching
SAM	2964	CH$_3$ asymmetric stretching polarized paralleled to the skeletal plane
	2937	CH$_2$ symmetric stretching (Fermi resonance)
	2918	CH$_2$ asymmetric stretching
	2902	CH$_2$ asymmetric stretching
	2877	CH$_3$ symmetric stretching
	2850	CH$_2$ symmetric stretching

[a] The latter was collected at p-polarization (ref 5).

of 1000 scans, apodized with a medium Beer-Norton function, and Fourier transformed with one level of zero filling. The same Harrick GIR attachment was used for both the FT-IR and the PA-IR measurements.

Results and Discussions

Comparison of FT-IR and PA-IR. The FT-IR spectrum of a self-assembled ODT monolayer on the gold surface was collected using 1000 scans with a resolution of 4 cm^{-1}. The total acquisition time was approximately 20 min (with another 20 min for background collection). In addition, the total bench purging time is approximately 10 min. The corresponding PA-IR spectrum was obtained from one row of 1600 frames with an integration time of 2.4 s and a total acquisition time of 27.2 s for each of I_d, I_0, and I_{db}. So the final integration for each spectrum is
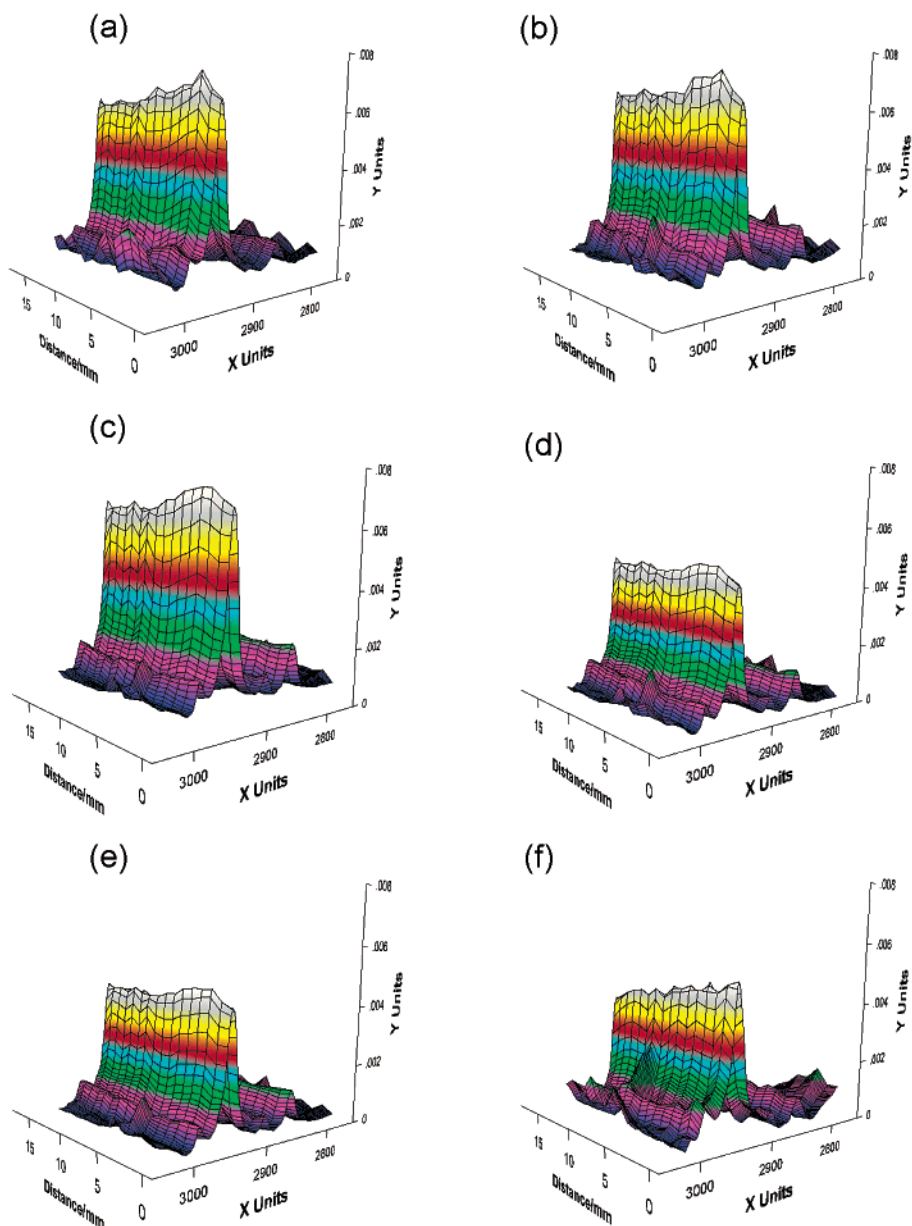
Figure 6. Line images of self-assembled ODT monolayers on gold substrates produced with different dipping times: (a) $1-2$ s; (b) 1 min; (c) 5 min; (d) 10 min; (e) 20 min; (f) 70 min.

7.2 s, and the acquisition time is 81.6 s. The spectra are shown in Figure 3.

The S/N ratio in the spectrum from PA-IR is comparable to that of the FT-IR, but it was obtained in a much shorter time, which makes a time-resolved study of the formation of the oriented self-assembling monolayers possible.

In this study, we concentrated on the $C-H$ stretching modes of the ODT to investigate the chain conformation and the intermolecular environment of the long-chain thiol. Due to the overlapping of peaks, we fit the band profile to separate the different $C-H$ stretching components using GRAMS32. The curve fitting results for both the bulk ODT and the ODT SAM are shown in Figure 4. After peak fitting, the different $C-H$ stretching modes were assigned according to Snyder,[14] and the band assignments are shown in Table 1.

Comparing the spectrum of the bulk sample, which is isotropic, with the spectrum of the SAM (which has only

$E_\perp$ polarization, according to the surface selection rules[7,15]), it is clear that the former shows only the asymmetric $C-H$ stretching component of the CH_3 group at 2954 cm^{-1}, while the latter only has a band at 2963 cm^{-1}. Snyder[14] assigned the two peaks to the CH_3 asymmetric stretching polarized perpendicular and parallel to the backbone skeletal plane, respectively. This PA-IR study recorded spectra at a grazing angle of incidence and gave a field enhancement for the radiation polarized perpendicular to the surface. Only highly ordered planar zigzag alkane chains, which have a component of the CH_3 asymmetric stretch change in dipole moment normal to the surface, will show up in the $E_\perp$ spectrum. This indicates that the ODT monolayer is well organized on the surface of gold.[8,14,16,17]

Organization and Order of ODT SAMs as a Function of "Dipping Time". Since FT-IR collection of a monolayer spectrum normally requires at least 20 min,

(14) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta* **1978**, *34A*, 395–406.

(15) Pearce, H. A.; Sheppard, N. *Surf. Sci.* **1976**, *59*, 205–217.
(16) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437–463.
(17) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96* (2), 927.

with a DTGS detector, it is difficult to collect a series of time-resolved spectra on the time scale needed to investigate the dipping process. On the other hand, due to the ultrahigh sensitivity of the focal plane array, the ultrafast PA-IR instrument can easily record the IR spectrum of a monolayer in 3−6 s.

Since we are confined to the 3400−2000 cm^{-1} region because of the InSb array, comparing to a faster detector for the comparison with FT-IR would involve tradeoffs. Using an MCT detector would be faster, but the bandwidth would also increase 3400−700 cm^{-1} and serial measurement (reference followed by sample) with a concomitant purge would still be required. Polarization modulation theoretically would obviate the purge requirement, but in principle, water vapor is still present and is never totally removed. In a head-to-head comparison, FT-IR measurements can be made faster than shown here but not without adding additional experimental complexity. At this stage of development, PA-IR measurements are, at least, competitive with FT-IR measurements on SAMs but enjoy a slight speed advantage. Future improvements in detector technologies, electronics, grating configurations, and so forth will only improve the performance and speed of the no-moving-parts PA-IR instruments.

Figure 5 shows the line spectra of ODT SAMs reacting with gold for different dipping times. For short dipping times, the integrated intensity of the asymmetric CH_2 stretching band near 2920 cm^{-1} is bigger and its position is found at a higher frequency, compared with the spectra obtained with a longer dipping time. This indicates that the conformation of the CH_2 chains is disordered. This also suggests that the disordered chains lie almost parallel to the gold surface.[2,5,16] In addition, the CH_3 intensities are very weak. Although dense monolayers assemble rather quickly, well-ordered monolayers have been shown to take days to form.[16] With an increase in dipping time, the CH_2 band becomes more symmetrically shaped and moves toward lower frequency, while the relative intensity of the CH_3 band increases. This behavior is indicative of a transition from an amorphous arrangement of chains to one with trans chains with the methyl groups aligned[17] normal to the surface. These observations suggest that a transition from less order to more order occurs, indicating that with an increase in ODT coverage on gold, molecular chains tend to orient more perpendicular to the surface. A highly organized, densely packed monolayer with the CH_2 stretching vibration centered about 4 cm^{-1} lower than that for the film resulting from 1−2 s dipping time was observed after dipping a sample in solution for 40 h.

Many groups have investigated the orientation of ODT SAMs on the surface of gold by both experiment and simulation[16,18−21] and have reported that the tilt angle of an organized ODT chain on gold is ∼30°. The formation of these ordered SAMs involves different stages of organization and is a two-dimensional ordering process. Himmelhaus[22] et al. used sum frequency generation (SFG) to study the kinetics of docosanethiol self-assembly onto gold and found three stages of monolayer formation. The initial stage is very fast and involves the formation of Au−S bonds; the second stage involves the relatively slow transition from a disordered to an all trans conformation.
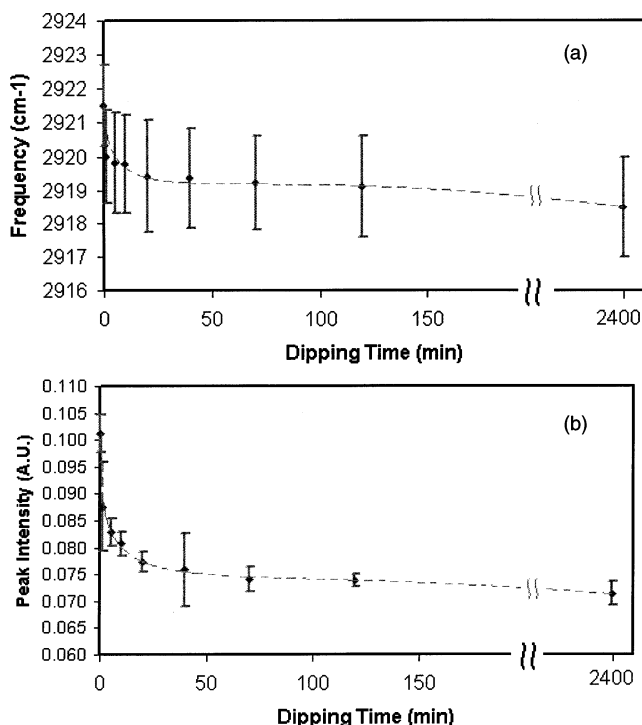
(18) Brunner, H.; Vallant, T.; Mayer, U.; Hoffmann, H. *Surf. Sci.* **1996**, *368*, 279−291.
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Figure 7. (a) The change in frequency of the asymmetric CH_2 stretching band vs dipping time. (b) The change of peak intensity of the asymmetric CH_2 stretching band vs dipping time.

The final stage takes many hours and involves the organization of methyl end groups. Our PA-IR spectra give a detailed picture of the temporal evolution of the formation of ODT SAMs, and the observed kinetics is consistent with this three-step organization process.

Spatially Resolved Spectra. Six sample spectra were selected from those shown in Figure 5, and the corresponding spatially resolved spectra (line images) are presented in Figure 6 for a selected dipping interval. These represent a spatial resolution of 1.2 mm. Each image contains 16 spectra and thus corresponds to a distance of 1.7 cm, which is just the effective width of the gold-coated glass slide in the optical path. Due to the highly ordered gold crystal (111) surface, the ODT SAM deposits macroscopically evenly on the gold surface independent of the dipping time.[5,23] This is easily concluded from the observation of uniform peak intensities along the sample slides. With an increase in dipping time, the area of the observed asymmetric CH_2 vibration decreases from ∼0.007 to ∼0.005 arbitrary units. This can be interpreted as evidence of the formation of more condensed domains with longer dipping time, since with an increase in conformational order there will be more closely packed chains. This will lead to more condensed domains and a concomitant shift of both the CH_2 symmetric and asymmetric stretching vibrations to lower frequencies.[16]

The relationship between dipping time and the average position of the asymmetric CH_2 stretching vibration as well as its corresponding averaged integrated intensity is plotted in panels a and b of Figure 7, respectively. In Figure 7a, the frequency of the peak decreases very quickly from 2921.5 to 2919.8 cm^{-1} when the dipping time changes from 1−2 s to 5 min. However, the change in frequency then reaches a plateau that has a very small slope and the change is only from 2919.76 to 2919.1 cm^{-1} after dipping

(23) Richter, A. G.; Yu, C.-J.; Datta, A.; Kmetko, J.; Dutta, P. *Colloids Surf., A* **2002**, *198−200*, 3−11.

for 120 min. For longer dipping times (40 h), this value reaches 2918.5 cm^{-1} and the SAM is highly organized and oriented. In Figure 7b, the intensity of the asymmetric CH$_2$ stretching vibration changes as a function of dipping time and exhibits a similar behavior as shown in Figure 7a. The averaged, spatially resolved spectra show that for ODT SAMs on gold, a disordered monolayer formed during the initial (1−2 s) dip and up to 5 min exposure to ODT solution. With an increase in dipping time, the monolayer became more ordered with highly organized SAMs observed after several days of immersion in ODT solution.

Conclusion

Infrared spectra with excellent signal-to-noise ratio and IR line images of monolayer films have been collected using a PA-IR spectrograph. IR spectra having a noise level as low as 3×10^{-5} absorbance units could be obtained. The line image spectra are comparable to those obtained by FT-IR spectroscopy, but the PA-IR spectra were collected with a much shorter collection time. By curve fitting, the peaks characterizing both highly ordered and disordered alkane chains can be assigned, and these were used to study the organization process during the self-assembly.

This study shows that macroscopically uniform monolayers form within seconds but that they are disordered. After 5 min dipping in solution, the CH$_2$ asymmetric peak positions are relatively constant, indicating that conformationally ordered chains are present. Finally, highly ordered and orientated SAMs are formed after many hours of submersion in ODT solution.