Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 6. In-Situ FTIR External Reflectance Spectroscopy of Monolayer Adsorption and Reaction Chemistry

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A new in-situ application of FTIR external reflectance spectroscopy (FTIR-ESR), which is useful for real-time evaluation of monolayer and multilayer adsorption and reaction chemistry at the vapor/solid interface at pressures near 1 atm, is described. The utility and versatility of the method is illustrated by two proof-of-concept experiments. The first experiment involves adsorption of $H_2N(CH_2)_9CH_3$ onto a naked Au substrate from the vapor phase. In-situ FTIR-ERS indicates that the amine forms a stable, ordered monolayer on the Au surface; that is, $H_2N(CH_2)_9CH_3$ self-assembles onto the Au surface from the vapor phase. The second experiment involves vapor-phase adsorption of a $HS(C_6H_5)OH$ monolayer onto a naked Au surface, followed by an in-situ coupling reaction with $[CH_3(CH_2)_7](CH_3)_2SiCl$. Real-time FTIR-ERS characterization of the organic bilayer is consistent with previously reported ex-situ FTIR-ERS results; however, kinetic data can be abstracted from the new in-situ data. The rate constant for the surface silane coupling reaction is estimated to be 0.30 min^{-1}.

INTRODUCTION

We have applied a new in-situ method, which is useful for obtaining real-time infrared spectroscopic data, to organic monolayer and multilayer surfaces and chemical reactions that occur thereon. This FTIR external reflection method is only applicable to processes that occur at the vapor/solid interface at pressures near 1 atm, and therefore, it is intended to complement ex-situ analyses and in-situ thin-film analyses of processes that occur in ultrahigh vacuum (UHV) or condensed phases. Preliminary results suggest there are six potential advantages to this approach: (1) spectral interferences due to solvent are eliminated; (2) solvent effects on monolayer structure and reaction chemistry are eliminated; (3) reaction chemistry on high-energy organic surfaces can be carried out in the absence of ambient-phase impurities; (4) sequential reaction chemistry can be performed without the necessity of removing and then repositioning the substrate; (5) certain types of monolayer chemistry occur only in the gas phase; (6) atmospheric-pressure, vapor-phase surface chemistry provides an important link between UHV and condensed-phase studies.

The results presented here are intended to extend our previous reports of monolayer self-assembly and reaction chemistry that occur in vapor-phase ambients.[1-5] We believe that many chemical and physical processes involving ultrathin films adsorbed onto modified or naked metallic substrates that are presently performed in condensed phases could be more profitably studied in the vapor phase since, as shown here, data collection and analysis are greatly simplified.

Monolayer and multilayer self-assembly chemistry is useful for constructing functional organic surfaces.[3,6-8] A particularly popular and versatile version of monolayer self-assembly occurs when a Au substrate contacts a dilute ethanolic solution of a suitable organomercaptan.[7,9] This treatment results in a surface-adsorbed monolayer possessing well-defined chemical and physical properties, which have been characterized by contact angle measurements, electrochemical methods, FTIR external reflection spectroscopy (FTIR-ERS), optical ellipsometry, scanning probe microscopy, UHV surface spectroscopy, and other techniques.[7] Except for a few studies,[1-5,10-12] all monolayer self-assembly chemistry has focused on condensed-phase surface preparation followed by ex-situ analysis. Clearly, in-situ analysis is preferable since the details of monolayer formation and stability can be addressed in real time. However, attempts to study self-assembly chemistry in condensed phases have largely been stymied by spectral interferences or high-vapor-pressure solvents.

We have shown that the differences between the average properties of vapor- and liquid-phase-deposited self-assembling organomercaptan monolayers are minimal,[1-5] and we used mass-sensitive surface acoustic wave (SAW) devices to obtain real-time kinetic measurements of self-assembly adsorption kinetics[1] and subsequent monolayer reaction chemistry.[2-4] Since SAW devices provide very high mass

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sensitivity, they are excellent tools for quantifying vapor-phase processes that involve mass changes; however, they do not provide essential chemical or structural information.[13] In contrast, FTIR-ESR provides a high degree of both chemical and structural information, but it is not analytically quantitative. Thus, we view in-situ SAW and FTIR-ERS methods as complementary tools for studying monolayer chemistry in vapor-phase ambients.

Prior to this report, most in-situ FTIR spectroscopy of organic surfaces has relied upon either a modulation technique, in which the background spectrum is subtracted in real time,[14] or an internal reflection spectroscopic approach, which involves multiple radiation/monolayer encounters.[15] Modulation techniques are exemplified by spectroelectrochemical experiments that involve modulation of electrode potential in ultrathin-layer electrochemical cells.[16] This is a very useful approach for experiments that only address potential-dependent changes in the vibrational spectra of thin films. However, for many analyses, especially those that require complete chemical and structural characterization, in-situ vapor-phase analysis is an attractive alternative. Internal reflection spectroscopy is only useful on nonmetallic substrates and therefore cannot be applied to organomercaptan self-assembly. There has been one elegant example involving sum-frequency spectral analysis of self-assembled monolayers in condensed phase, but this is a difficult and generally inaccessible analytical method.[12] To our knowledge, there have been no prior reports of real-time FTIR–ERS measurements of monolayer adsorption or chemical reaction chemistry.

EXPERIMENTAL SECTION

Chemicals. The following chemicals were used as received: $CH_3(CH_2)_{11}SH$ (98%, Aldrich), $CH_3(CH_2)_9NH_2$ (95%, Aldrich), $CH_3(CH_2)_9CH_3$ (99%, Aldrich), $[CH_3(CH_2)_7](CH_3)_2SiCl$ (Hüls America), CH_3CH_2OH (100%, Midwest Grain Products), H_2SO_4 (98%, J. T. Baker), and H_2O_2 (30%, J. T. Baker). $HS(C_6H_5)OH$ (90%, Aldrich) was purified by sublimation before use. Water was purified with a Milli-Q (Millipore) deionization system.

Substrate Preparation. Polished 10-cm-diameter Si wafers were coated by electron-beam evaporation of 300 Å of Ti and 2000 Å of Au and then diced into 1.0 × 3.0 cm pieces. Immediately prior to monolayer modification the Au substrates were cleaned in a freshly prepared "piranha" solution for 15 s (**Caution**: "piranha" solution, 1:3 concentrated H_2SO_4/30% H_2O_2, reacts violently with many organic materials and should be used with extreme caution; it should not be stored in sealed containers), rinsed with deionized water, and then dried in a flowing stream of N_2.

Flow System and Flow Cell. Schematic diagrams of the flow system and cell are shown in Figure 1. Two manual gas flowmeters (Cole Parmer) control the partial pressure of the vapor-phase reactants (Figure 1A). We recently replaced the manual flowmeters with computer-operated mass flow controllers, which has greatly simplified and expanded the versatility of the dosing system. One N_2 stream (liquid N_2 boil-off) is directed into a vial which contains a solid or liquid reactant with a significant vapor pressure. The flow rate was kept low, typically 250 mL/min, so that the vapor stream exiting the sample vial was nearly saturated with reactant vapor. The exiting vapor stream was mixed with sufficient pure N_2 to achieve the desired analyte partial pressure. In order to directly compare the data discussed in this report with those previously obtained by in-situ SAW analysis, the reactant vapor was mixed in a 1:1 ratio with pure N_2.[1-5]

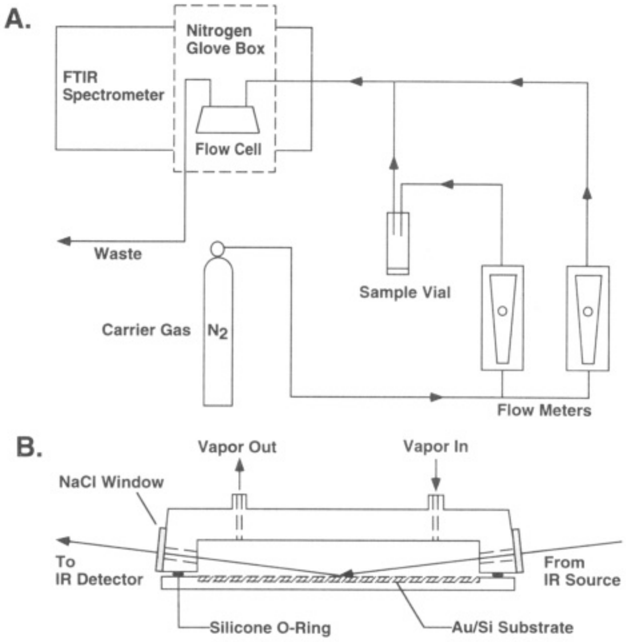

Figure 1. Schematic illustrations of (A) the vapor-phase FTIR-ERS flow system and (B) the flow cell.

The flow cell consists of a cover and a base (Figure 1B). Two 12 × 12 × 2 mm NaCl windows (International Crystal Laboratories) are glued onto the ends of the cell with silicone rubber (Dow Corning). Flanged Teflon nuts ($^1/_4$ in. × 28 mm) of the type used in liquid chromatography connect the cell in series to the Teflon gas flow lines. The cell base contains a recessed region for the Au/Si substrate. A silicone O-ring is compressed by four mounting nuts to seal the cover to the base. The flow cell was designed to fit onto a Seagull variable-angle reflection assessory (Harrick Scientific). The cell volume is about 3 mL. The total internal path length of the cell is about 4.5 cm and the infrared beam is incident on a 1.5 × 0.2 cm area of the substrate.

Real-Time FTIR-ERS Measurements. Measurements were made using a Digilab FTS-40 FTIR spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid N_2-cooled MCT detector. All spectra were obtained using *p*-polarized light incident on the substrate at an angle of 80–85°. The number of scans and spectral resolution were determined by the time scale required for individual experiments: fewer scans and lower resolution were used for fast reactions, while higher resolution and better signal-to-noise ratios were achieved for slower reactions. As presently configured, the upper limit for kinetic measurements is fixed by the speed of the FTIR interferometer. For a Digilab FTS-40 configured to record 16 scans at a resolution of 8 cm^{-1}, the minimum time required to obtain a single spectrum is 5 s. The maximum duration for a single experiment is defined by the onset of spectral fringing, which probably results from mechanical instabilities in the spectrometer or the flow cell. Satisfactory results, however, are routinely obtained for periods of several hours.

RESULTS AND DISCUSSION

We performed two proof-of-concept experiments designed to illustrate the utility of this in-situ spectral approach for analyzing self-assembly chemistry processes in real time. The first experiment involves a study of the interaction between an amine-terminated *n*-alkane and Au. This interaction only occurs in the vapor phase and in low polarity solvents.[6] The second set of experiments involves in-situ spectral analysis of a chemical reaction that occurs at an organic monolayer surface. We previously reported an in-situ SAW analysis of this reaction; the in-situ FTIR-ERS data presented here complement and extend the previous results.

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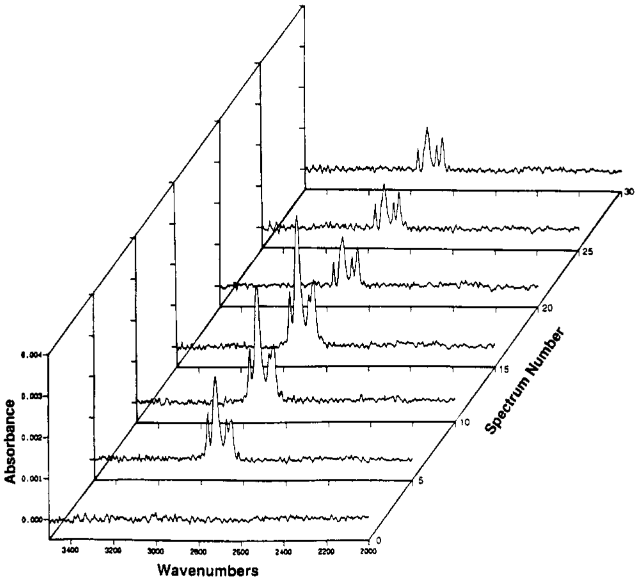

Figure 2. Time-resolved FTIR-ERS spectra obtained by dosing a naked Au substrate with the following: spectrum 0, pure N_2; spectra 5–15, 50%-of-saturation $CH_3(CH_2)_9NH_2$ in N_2; spectra 20–30, pure N_2. Each spectrum was acquired in 5 s and is the sum of 16 individual spectra obtained at 8-cm^{-1} resolution. The spectra shown in the figure are spaced by 2.5 min.

Vapor-Phase Deposition of $CH_3(CH_2)_9NH_2$ onto Au. We recently noticed that amine-terminated *n*-alkanes undergo monolayer self-assembly much like the organomercaptans. In contrast to the organomercaptans, however, amine-terminated *n*-alkanes do not spontaneously adsorb to Au surfaces from high-polarity solvents such as ethanol, because the Au/N interaction energy is insufficient to compete with solvent adsorption.[6] However, $Au/NH_2(CH_2)_nCH_3$ monolayers do form from vapor-phase ambients, and they are stable for periods of at least several hours in a variety of vapor-phase media. In contrast, preformed vapor-phase-deposited $Au/NH_2(CH_2)_nCH_3$ monolayers are not stable in polar condensed phases. In this section we briefly discuss a preliminary in-situ FTIR-ERS kinetic study of $NH_2(CH_2)_9CH_3$ adsorption onto Au substrates. Our intent is to emphasize the spectral method, but in a forthcoming publication we will provide a detailed account of the structure, formation kinetics, and chemistry of amine-terminated *n*-alkane monolayers self-assembled from vapor-phase ambients onto Au substrates.

In-situ, vapor-phase deposition of $CH_3(CH_2)_9NH_2$ was carried out by exposing a nominally clean Au surface to a pure N_2 gas stream for 1 min and then switching to a 50%-of-saturation $CH_3(CH_2)_9NH_2$ vapor stream for 7.0 min. The $CH_3(CH_2)_9NH_2$-containing vapor was then turned off, and the substrate was purged in pure N_2 for an additional 7.0 min. FTIR-ERS spectra, each of which consisted of 16 individual scans at 8-cm^{-1} resolution, were acquired every 30 s during the course of the 15-min experiment. Figure 2 presents seven such spectra, which are spaced in time to reflect the overall results of the experiment. A condensed representation of the complete data set is given in Figure 3. The important features of the spectra obtained during the amine-dosing portion of the experiment (spectra 5, 10, and 15; Figure 2) are the asymmetric and symmetric methyl C–H stretching vibrations at 2966 and 2878 cm^{-1}, respectively, and the asymmetric and symmetric methylene C–H stretching vibrations at 2932 and 2855 cm^{-1}, respectively. Vibrations corresponding to N–H stretching modes are noticeably absent in the high-frequency region, probably as a result of the infrared surface selection rule.[17]

Following the N_2 purge cycle (spectra 20, 25, and 30; Figure 2), both the intensities and positions of these four bands change. The intensity decreases about 3-fold and then stabilizes at a value corresponding to that of a single monolayer of $Au/HS(CH_2)_9CH_3$.[7] Compared to the spectra obtained prior to N_2 purging, the absorptions resulting from the asymmetric and symmetric methylene C–H bands shift down in frequency by 10 and 2 cm^{-1}, respectively, while the positions of the methyl C–H stretching vibrations remain unchanged.

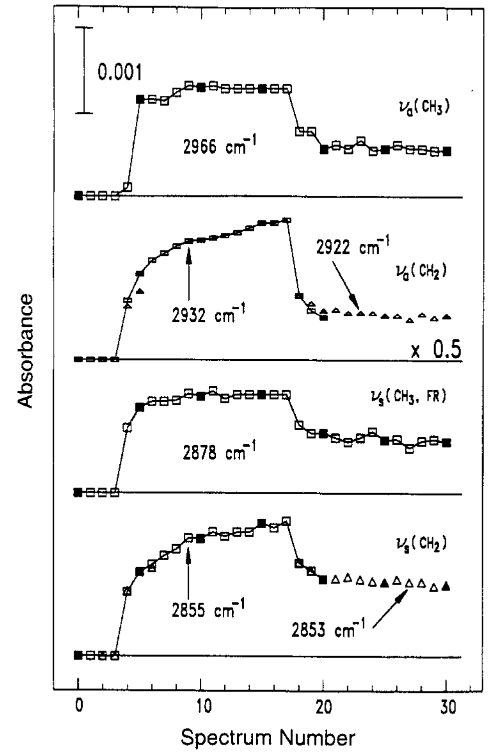

Figure 3. Plots of the peak absorbance for the methyl and methylene C–H stretching modes, which arise from $CH_3(CH_2)_9NH_2$, versus spectrum number. The absorbances corresponding to the filled squares were obtained from the 7 spectra shown in Figure 2, and the data represented by open squares were obtained from 24 additional spectral not shown in Figure 2. Spectra 0–3 were obtained during pure N_2 purging of the Au surface; spectra 4–17 were obtained during 50%-of-saturation $CH_3(CH_2)_9NH_2$ dosing of the surface; spectra 18–30 were obtained during a pure N_2 purge cycle. Time-resolved spectra were obtained within 5 s and were acquired every 30 s.

The differences in spectral intensity and peak positions are consistent with a transition from *n*-alkylamine molecules in the vapor phase and adsorbed to the Au substrate to molecules only in a structured surface phase. That is, we propose that, between 1.0 and 7.0 min, the hydrocarbon spectrum arises from a superposition of peaks arising from gas-phase and surface-confined $CH_3(CH_2)_9NH_2$, but when the amine is switched off and the cell volume is exposed to a pure N_2 purge, only absorptions arising from the surface-confined adsorbate survive.

Several pieces of evidence support this scenario. First, the absorption frequencies before N_2 purging are typical of those found for methylene groups in structureless liquid or vapor-phase environments, but after purging, these peaks shift to lower energies and become narrower; both observations are characteristic of solid-phase-like organomercaptan monolayers.[7,11,18] Second, we observed that the intensity of the peaks in the methyl and methylene stretching region decreases very rapidly when the $CH_3(CH_2)_9NH_2$ vapor is purged with

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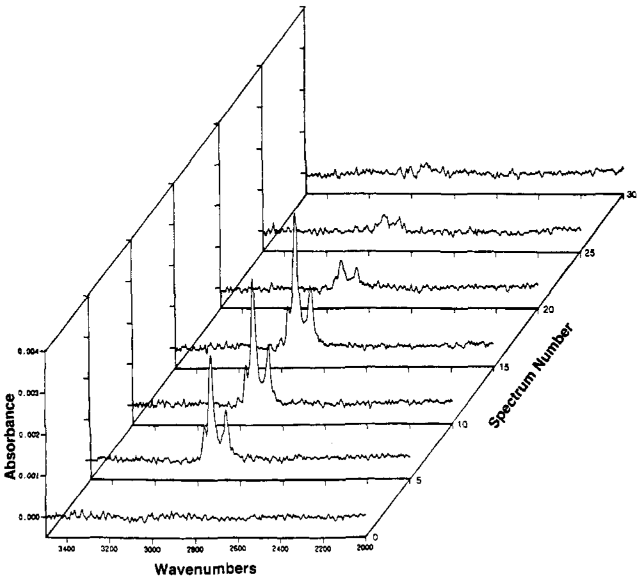


Figure 4. Time-resolved FTIR-ERS spectra obtained by dosing a Au/HS$(CH_2)_{11}CH_3$ monolayer surface with the following: spectrum 0, pure N_2; spectra 5–15, 50%-of-saturation $CH_3(CH_2)_9NH_2$ in N_2; spectra 20–30, pure N_2. Each spectrum was acquired in 5 s and is the sum of 16 individual spectra obtained at 8-cm^{-1} resolution. The spectra shown in the figure are spaced by 2.5 min.

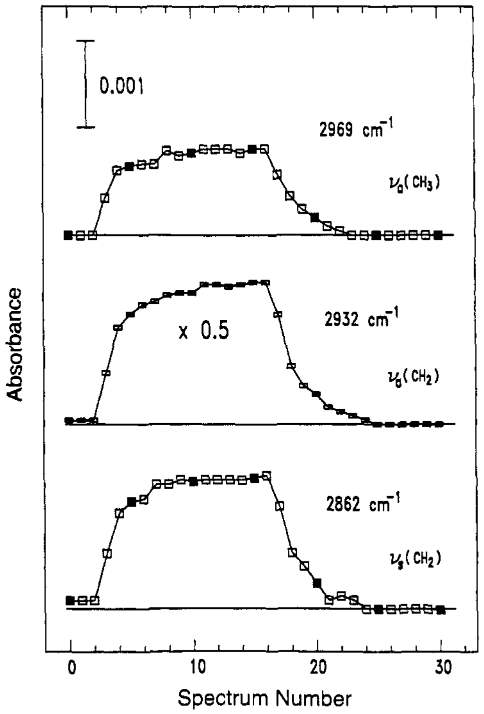


Figure 5. Plots of the peak absorbance for the methyl and methylene C–H stretching modes, which arise from $CH_3(CH_2)_9NH_2$, versus spectrum number. The absorbances corresponding to the filled squares were obtained from the 7 spectra shown in Figure 4, and the data represented by open squares were obtained from 24 additional spectra not shown in Figure 4. Spectra 0–2 were obtained during pure N_2 purging of the Au/HS$(CH_2)_{11}CH_3$ monolayer surface; spectra 4–16 were obtained during 50%-of-saturation $CH_3(CH_2)_9NH_2$ dosing of the surface; spectra 17–30 were also obtained during a pure N_2 purge cycle. Time-resolved spectra were obtained within 5 s and were acquired every 30 s.

pure N_2 (Figure 3). This observation is also consistent with the notion of a vapor-phase ambient that is quickly swept out of the cell by the N_2 purge. The time required to remove the vapor-phase amine is somewhat longer than that calculated on the basis of the cell volume and the N_2 flow rate, probably as a result of slow desorption of $CH_3(CH_2)_9NH_2$ that might condense on the flow system tubing. Third, to ensure that $CH_3(CH_2)_9NH_2$ interacts specifically with the Au surface, we performed an experiment identical to that represented in Figures 2 and 3, except that the Au/amine interaction was eliminated by coating the Au surface with a single monolayer of $CH_3(CH_2)_{11}SH$ prior to dosing with $CH_3(CH_2)_9NH_2$. The results of this experiment are shown in Figures 4 and 5, and they clearly indicate that persistent $CH_3(CH_2)_9NH_2$ binding takes places only on nominally naked Au. Note also that the hydrocarbon peak heights for spectra obtained in the presence of the $CH_3(CH_2)_9NH_2$ ambient are roughly the same regardless of whether the Au surface is initially naked or covered by a monolayer of $CH_3(CH_2)_{11}SH$. Finally, we did a second control experiment that was identical to the first, except the Au surface was naked and the vapor-phase adsorbent was changed to $CH_3(CH_2)_9CH_3$, which can only interact with the Au surface through weak van der Waals forces. The results of this experiment (Figure 6) show that persistent surface adsorption only occurs in the presence of amine groups. In addition, the data indicate that the time required to remove all $CH_3(CH_2)_9CH_3$ from the cell volume is somewhat shorter than the time necessary to purge $CH_3(CH_2)_9NH_2$ (Figures 3 and 5). This might reflect differences in the interactions of the two probes with the Teflon flow system, the presence of a weakly surface-condensed layer of $CH_3(CH_2)_9NH_2$, or slight differences in the vapor pressures.

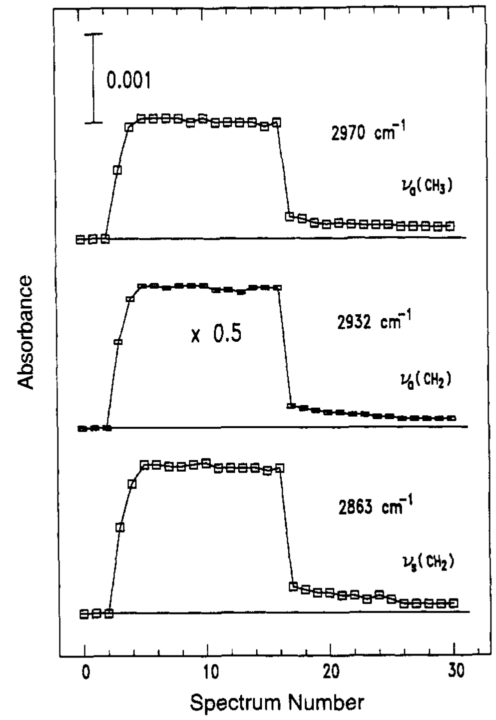
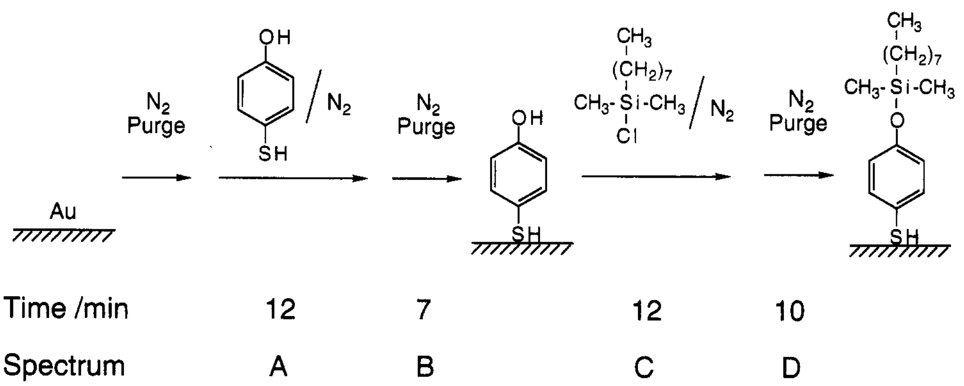


Figure 6. Plots of the peak absorbance for the methyl and methylene C–H stretching modes, which arise from the $CH_3(CH_2)_9CH_3$, versus spectrum number. Spectra 0–2 were obtained during pure N_2 purging of the Au surface; spectra 4–16 were obtained during 50%-of-saturation $CH_3(CH_2)_9CH_3$ dosing of the surface; spectra 17–30 were also obtained during a pure N_2 purge cycle. Time-resolved spectra were obtained within 5 s and were acquired every 30 s.

These results can be summarized as follows. When $CH_3(CH_2)_9NH_2$ is admitted to the flow cell, roughly one monolayer partitions onto the Au surface, while a steady-state concentration remains in the vapor phase. Upon N_2 purging, all of the vapor-phase amine is removed, leaving behind only a persistently bound, structured monolayer that is stabilized by a combination of Au/N and interchain van der Waals interactions. Such monolayers are stable in N_2 for at least several hours, but are readily removed in polar condensed phases.[6]

Scheme I



Coupling of Au/HS(C_6H_5)OH with [$CH_3(CH_2)_7$]$(CH_3)_2$SiCl. It is difficult to extract information about the *n*-alkylamine adsorption kinetics discussed in the previous section, because ambient-phase $CH_3(CH_2)_9NH_2$ interferes with a time-resolved spectral analysis of the adsorption process. We have overcome this difficulty in the past by using in-situ SAW methods, which are unaffected by the presence of gas-phase molecules, to provide kinetic data about such adsorption processes.[1] However, if condensation of a weakly bound multilayer occurs, it is not possible to extract kinetic information about monolayer adsorption processes from SAW data. In contrast, if a new IR-active bond forms or breaks as a result of a molecular encounter with the substrate, it will give rise to a surface-specific band that can be used to unambiguously measure monolayer reaction kinetics even in the presence of interferences from the ambient or surface-confined multilayers.

We previously reported an in-situ SAW and ex-situ FTIR-ERS and ellipsometry analysis of the coupling reaction that occurs between a surface-confined monolayer of 4-hydroxythiophenol, HS(C_6H_5)OH, and the vapor-phase probe molecule dimethyloctylchlorosilane, [$CH_3(CH_2)_7$]$(CH_3)_2$SiCl.[2] The results proved that a stoichiometric surface reaction occurred, which resulted in formation of a covalently linked siloxane: Au/HS(C_6H_5)O–Si$(CH_3)_2$[$CH_3(CH_2)_7$]. Unfortunately, we were not able to follow the reaction kinetics in this prior study, because the experimental conditions utilized resulted in the formation of several physisorbed layers of the silane coupling agent in addition to the chemically bonded monolayer, thereby complicating the SAW response.[2]

Here we show that in-situ FTIR-ERS can provide true surface reaction kinetic information. The sequence of events leading to the spectra shown in Figure 7 is illustrated in Scheme I. First, the naked Au substrate was exposed to a pure N_2 purge until a stable background spectrum was obtained. Next, the Au surface was exposed to a 50%-of-saturation HS(C_6H_5)OH vapor stream for 12 min and the spectrum shown in Figure 7A was obtained. The spectrum shown in Figure 7B resulted after purging with pure N_2 for 7 min to remove condensed multilayers of the adsorbate.[2] Next, the Au surface was exposed to a 50%-of-saturation [$CH_3(CH_2)_7$]$(CH_3)_2$SiCl vapor stream for 12 min (Figure 7C), and finally the flow cell was again purged with pure N_2 for 10 min (Figure 7D).

The peak assignments for the spectra shown in Figure 7B, which correspond to the Au/HS(C_6H_5)OH surface, are as follows: aromatic ring vibrations at 1594, 1579, 1487, and 1428 cm^{-1}; a broad C–O stretching peak at 1264 cm^{-1}; and a broad phenolic O–H stretching peak centered at 3350 cm^{-1}.[2,19]

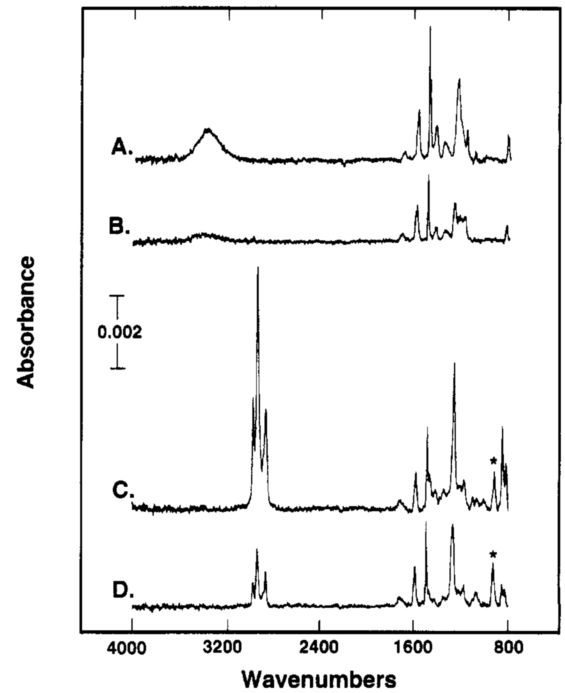


Figure 7. FTIR-ERS spectra arising from the surface-monolayer silane coupling reaction shown in Scheme I. Spectra A–D were obtained after the reaction steps corresponding to those shown in Scheme I. The 918-cm^{-1} peak, which corresponds to the surface reaction product, is marked by an asterisk.

After introduction of the silane coupling agent, and subsequent N_2 purging (Figure 7D), there are important spectral changes. The somewhat enhanced aromatic ring stretches are still present at 1582 and 1485 cm^{-1}, but the phenolic O–H band, originally present at 3350 cm^{-1}, (Figure 7B) has disappeared. There are two overlapping bands at 1277 and 1260 cm^{-1} resulting from the asymmetric Si–phenoxy stretch and the symmetric H_3C–Si–CH_3 bending mode, respectively,[2,20] and there are strong absorptions present between 2880 and 2920 cm^{-1} that result from the C–H stretching modes of the methyl and methylene groups of the hydrocarbon portion of the coupling agent. More importantly, there is a new absorption at 918 cm^{-1}, which arises from the symmetric Si–phenoxy stretching mode of the Au/HS(C_6H_5)O–Si$(CH_3)_2$[$CH_3(CH_2)_7$] reaction product.[2,19,20] Note that the height of this peak is the same in Figure 7C,D, even though the intervening N_2 purge greatly attenuates all other absorptions arising from the vapor-phase reactant.

Since the band at 918 cm^{-1} is unique to the reaction product, we can determine the surface reaction kinetics in the presence

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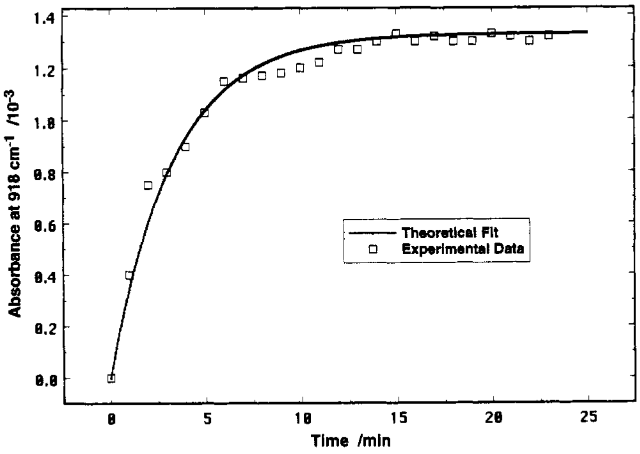

Figure 8. Plot of the peak absorbance at 918 cm^{-1} as a function of reaction time during the sequence shown in Scheme I.

of the ambient-phase reactant. To determine the kinetic rate constant, we acquired a spectrum every minute during the dosing sequence illustrated in Scheme I and plotted the peak intensity at 918 cm^{-1} as a function of reaction time (Figure 8). The data indicate that 95% of the coupling reaction is complete within 10 min and that the peak intensity at 918 cm^{-1} does not change after prolonged exposure to either mixed $[CH_3(CH_2)_7](CH_3)_2SiCl/N_2$ or pure N_2 purge streams. We fit the data shown in Figure 8 by assuming that the coupling reaction obeys simple first-order Langmuirian kinetics.[1] The best-fit exponential is given by the solid line in the figure, which leads to a calculated reaction rate constant of 0.30 min^{-1} for this surface coupling reaction under the conditions used in this experiment.[21]

CONCLUSION

We have used an in-situ FTIR-ERS flow cell to reveal the details of adsorption processes and to follow the course of a surface reaction in real time. The structural and kinetic information that results from the in-situ analysis reported here cannot conveniently be obtained by other means. For example, we were able to extract chemical rate information from the silane surface coupling reaction that was not previously accessible using ex-situ FTIR-ERS or in-situ SAW measurements. Additionally, the signal-to-noise ratios of in-situ spectra are enhanced compared to those obtained in ex-situ experiments, since removal and repositioning of the Au substrate, which leads to noise in the form of spectral fringing and contamination, is avoided.

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[21] It has been suggested that trace amounts of water may catalyze silane coupling reactions of the type discussed here. See for example: (a) Plueddemann, E. P. *Silane Coupling Agents*, 2nd ed.; Plenum: New York, 1991. (b) Dubois, L. H.; Zegarski, B. R. *J. Phys. Chem.* **1993**, *97*, 1665.