FTIR Spectroscopy of an alkanethiol monolayer
Laboratories 11 & 12

Purpose. This experiment has two goals: (1) measuring the extent of order within the alkanethiol monolayers you have made and (2) determining the tilt angle of the aliphatic chains. We will accomplish these two goals by measuring the absorption spectrum of the C-H stretching resonances for the alkanethiol chains. These resonances occur in the 2800 cm^{-1} to 3000 cm^{-1} region and are best accessed using external reflection FTIR spectroscopy.

Background. Measuring the absorption spectrum of a single layer of molecules can be challenging even if the layer constituents are strong absorbers. For the vibrational resonances we will be measuring, the extinction coefficient is on the order of 100 L/mol-cm, making the measurement even more challenging. There are several "tricks" that we employ to obtain the vibrational spectrum of an alkanethiol monolayer.

The simplest means for estimating the absorbance signal is with Beer's law.

$$A = sr$$

$$s \approx 100 L/mol\text{-}cm = 1.66x10^{-20}cm^2/mlc$$

$$r = 10^{15}mlc/cm^2$$

$$\therefore A \approx 1.7x10^{-5}$$

Thus a high quality instrument will be required for the measurement. It is important to remember that we are measuring the reflectance and not the absorbance directly. From the Fresnel equations recall that the reflection coefficient for an interface *increases* with increasing angle of incidence. This means that the transmission coefficient and thus the transmittance, T, *decreases* with increasing incidence angle. Since A = -log$_{10}$T, A for the interface increases with increasing incidence angle. This concept is schematized in Figure 1. The calculated A values are actually an approximation based on the bulk refractive index of alkanethiols. A more complete treatment of this issue is given in the attached paper. The point of this figure is to illustrate that there is a significant benefit in terms of signal size and thus S/N ratio for measuring reflectance at high incidence angles.

Surface Selection Rule: As suggested in Figure 1, there is an advantage to controlling
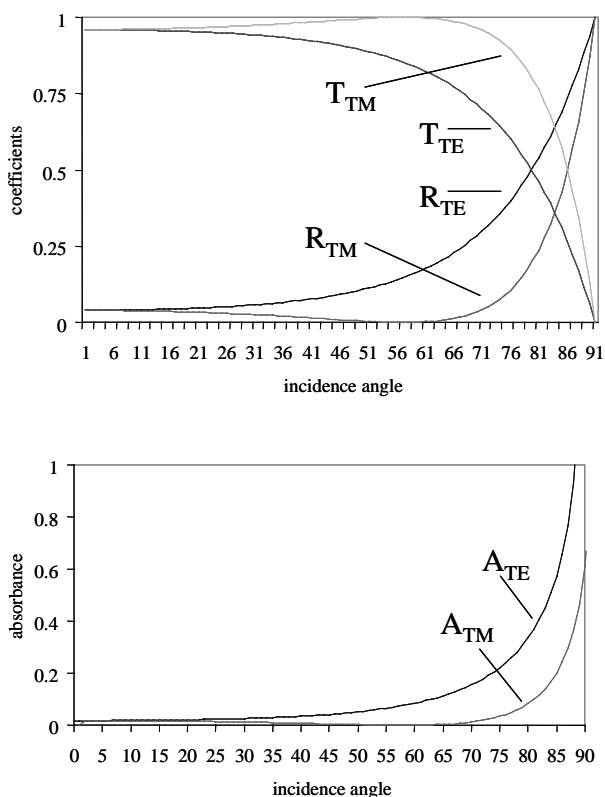

Figure 1. Top: Reflectance and Transmittance curves calculated for TE and TM modes. Bottom: A values calculated from T curves in top panel.

the polarization of the IR light that is incident on the substrate containing the monolayer. This is also true for a different reason. There is a surface selection rule that prevents the incident electric field from coupling to an adsorbate for a certain polarization. This is true for TE polarized light, where the oscillating image dipole generated in the substrate does not contain components that can be mapped onto the Cartesian projection of the alkanethiol absorption transition moments. For the TE mode, the image dipole oscillates in the plane of the substrate and thus couples to the delocalized electrons in the metal. For TM polarization, the E-field at a metal is perpendicular to the surface. Thus the E-field of the light can only interact with a transition moment near the surface of the metal if it has a component perpendicular to the surface. This is only true for the TM polarization. This fact also tells us that the only active infrared modes will be those where the change in dipole moment due to the vibrational motion has a component normal to the substrate.

External Reflection FTIR
Fourier transform infrared spectrometry is a widely used means to measure the vibrational absorption spectrum of many different types of samples. Because this technique is based on instrumental and chemical principles that should be familiar, we do not present an extended discussion of this technique here. The only unique aspect of the measurements that you will perform with the Mattson FTIR is the use of an external reflection attachment.
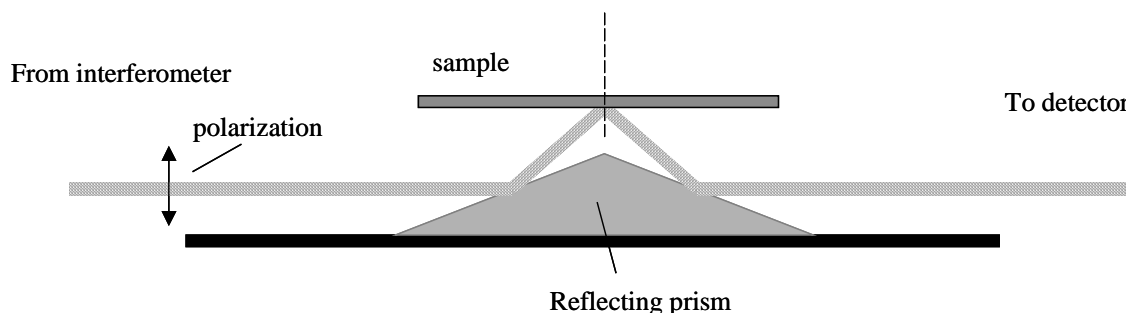

Figure 2. Schematic of external reflection attachment for the Mattson FTIR. The angle of incidence is fixed at 80º with respect to the surface normal.

The external reflection attachment offers enhanced absorption sensitivity for the measurement of monolayer samples. Greenler calculated how absorption factor (in this case defined as $(R_o-R)/R_o$ varies with incident angle and Figure 5 of his paper contains these results, showing that absorption increases dramatically at near-grazing angles. You will demonstrate the origin of this enhancement through your experiments and the sixth homework assignment. For further detailed information on the principles of operation of an FTIR, consult any good instrumental analysis text such as Ingle and Crouch.

Determination of order within the monolayer. The infrared spectrum of alkanes has been studied in excruciating detail and a great deal is understood about the relationship between band position and mesoscopic structure within the sample. For example, there are a family of aliphatic C-H stretching resonances in the 2800 cm^{-1} to 3000 cm^{-1} spectral region.

Sample	Asymmetric CH_2 stretch	Symmetric CH_2 stretch
Liquid alkane	2923 cm^{-1}	2854 cm^{-1}
Solid alkane	2918 cm^{-1}	2849 cm^{-1}
Alkanethiol monolayer	2916 cm^{-1}	2848 cm^{-1}

The band positions for each resonance are related to many factors. From an intuitive perspective, viewing the vibrational resonances as harmonic oscillators, the frequency of the resonance will depend on the shape and width of the potential well. In confined environments or in those characterized by a large potential energy gradient, dE/dq, the band position is expected to appear at a higher frequency compared to cases where there is less physical confinement or a more shallow potential energy gradient for the attractive surface. Among the factors that can influence the relevant potential well shape are the relative amount of *trans* and *gauche* conformers in the alkane chains and the details of interchain packing. Because *trans* conformers are more energetically favorable than *gauche* conformers, the transition for the *trans* form is slightly lower in energy than that for the *gauche* form. In terms of local environment, the closer to a crystalline (lowest energy) environment the alkane chain can establish, the lower the resonance energies will be. Comparison of the values you obtain for your monolayers to those in this table will provide some insight into the extent of ordering within your monolayer. It is also important to consider the width of the resonances. The broader the bands, the larger the conformational distribution associated with it. The typical case is that the monolayer bands will approximate those for a liquid alkane in both band position and width immediately after the layer is formed. After suitable annealing, the bands will exhibit a red-shift and narrowing to produce a spectrum characteristic of a well-ordered alkanethiol SAM.

In addition to -CH_2 bands, you will also observe -CH_3 bands. The position of all of these bands is given in one of the articles we handed out in class (*JACS 109,* 3559-3568*).* We don't consider the -CH_3 stretches as much as the -CH_2 stretches because of their position at the monolayer terminus. There is likely to be more disorder at the top of the layer than in the middle of the layer.

Determination of Tilt Angle

Allara and Nuzzo utilized FTIR extensively to determine the orientation of molecules on a surface. (*Langmuir, 1,* 52-66*).* I will not follow their description, as it is more complex than necessary, but the treatment given below is exactly the same. The main point of the treatment is that the intensity of a mode is proportional to the square of the dot product of the transition dipole moment, M, and the electric field, E, as shown in equation 1. The fact that the E vector is perpendicular to the plane of the surface implies that the intensity will vary with orientation

$$I \propto (M \bullet E)^2 \hspace{8cm} 1$$

according to equation 2, where Z is the unit vector in the direction of the surface normal, and χ is the angle between the transition dipole and the surface normal. Thus the intensity of the

$$(M \bullet Z)^2 \propto Cos^2\chi \hspace{8cm} 2$$

absorption band will vary with the square of the cosine of χ.

An isotropic monolayer will behave as if the angle with the surface normal were 54.7°. You can prove this in your homework. Given this fact, you can easily obtain a relation between an

$$\frac{I}{3 I_{isotropic}} = \cos^2 \chi$$

anisotropic spectrum and an isotropic one as shown in equation 3 where I stands for the intensity of a particular mode. Thus if you can calculate the intensity of an isotropic mode and measure the intensity of an anisotropic mode, you can calculate the orientation of the mode with respect to the surface normal. (Note that I is directly proportional to absorbance.)

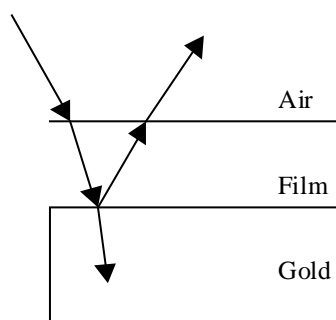## Calculation of the spectrum of the absorbance of an iostropic monolayer

We have already solved this problem in our treatment of ellipsometry. You will remember that we calculated the overall reflection coefficient, Q, for both TE and TM polarization for a system such as that shown in Figure 3. Now you only need the TE polarization. The overall reflection coefficient for this system is given in equation 4 where the variables are defined as they were in

$$Q = \frac{r_{01} + r_{12}e^{-i2\beta}}{1 + r_{01}r_{12}e^{-i2\beta}} \qquad 4$$

Figure 3. Schematic diagram of an IR beam reflecting from a gold-film interfact. Multiple reflections are not shown.

ellipsometry. To calculate the reflectivity, R, we take the square of the overall reflection coefficient, Q. The reflectivity of bare gold, R_o, is simply the square of the Fresnel coefficient. We can then calculate a pseudo-absorbance as log (R_0/R). This will give you the "absorbance" spectrum of an isotropic monolayer, because the optical constants are those for an isotropic film.

Calculation of Molecular Orientation

The first step in determination of orientation is to calculate the ratio of absorbance for the measured spectrum and the calculated spectrum. Using this ratio, you can calculate the orientation for a particular mode using equation 3. In the case of octadecanethiol monolayers, we are most concerned with the -CH$_2$ stretches as these will provide details of the chain orientation. There are two -CH$_2$ modes, the symmetric and asymmetric stretches (2848 and 2916 cm^{-1}, respectively). The symmetric mode is parallel to the plane containing the backbone of the all-*trans* chain and perpendicular to the chain axis, while the asymmetric mode is perpendicular to the plane containing the backbone of the chain. By determining the angle between the two stretches and the surface normal, we can calculate the tilt and rotation of the all-trans chain.

To determine the orientation, we start with the plane of the CCC backbone as the XZ plane. This will give the direction vector of the symmetric stretch as (1**i** + 0**j** + 0**k**). The direction vector of the asymmetric stretch will be (0**i** + 1**j** + 0**k**). In order to change the angle with respect to the surface normal, we can tilt the molecule by angle θ or rotate the molecule about the chain axis by the angle φ. These angles are shown in Figure 4. One can also cause the molecule to

precess about the Z axis, but this will not change the angle of the dipoles with respect to the surface normal. We need to know how these rotations will affect the orientations of direction vectors. First consider tilt in the XZ plane. If we put the direction vectors at the origin, we will get the results in equations 5 where x, y, and z are the di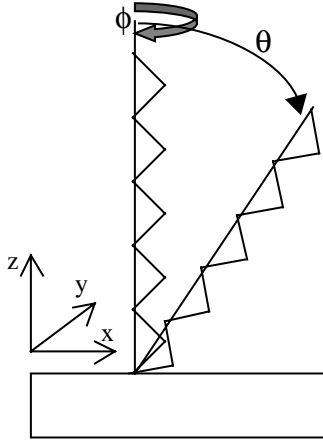rection vectors after tilt and x_o, y_o, and z_o are the direction vectors before tilt. Next consider rotation about the chain axis by the angle ϕ. If we do this before tilting, the molecular axis is the z-axis. For the rotation about the molecular axis, we get the equations listed in 6. By sequentially applying equations 6 and equations 5, we can transform the initial direction vectors into the rotated ones given in equations 7. (Note you must do the rotation first and then the tilt.) Then we simply need to determine the angle between the direction vectors of the transition dipoles and the surface normal. We will vary the angle of rotation and tilt until the calculated angles match those determined by equation 3. Our only remaining task is thus to determine angles between the direction vectors for transition dipoles and the surface normal. The angle between any two direction vectors, χ, can be calculated using equation 8, where **d** and **D** are any two direction vectors. Of course the vector for the surface normal will be $(0\mathbf{i}+0\mathbf{j}+1\mathbf{k})$.

Figure 4. Tilt and rotation angles for an alkanethiol.

$$x = z_o \sin\theta + x_o \cos\theta$$
$$y = y_o$$
$$z = z_o \cos\theta - x_o \sin\theta$$

5

$$x = x_o \cos\phi + y_o \sin\phi$$
$$y = y_o \cos\phi + x_o \sin\phi$$
$$z = z_o$$

6

$$x = z_o \sin\theta + x_o \cos\phi \cos\theta + y_o \sin\phi \cos\theta$$
$$y = y_o \cos\phi + x_o \sin\phi$$
$$z = z_o \cos\theta - x_o \cos\phi \sin\theta - y_o \sin\phi \sin\theta$$

7

$$\cos\chi = \frac{|\mathbf{d} \bullet \mathbf{D}|}{\|\mathbf{d}\| \ \|\mathbf{D}\|}$$

8

FTIR Measurements

   Only the Mattson Research (black) and Infinity FTIR instruments will be used for this experiment. Both have MCT detectors and the Research instrument has a water-cooled source. When you enter the lab, the FTIR's will be on. Log onto the computer and select the WinFirst software. If the **Control Panel** is not visible, it can be selected from the **Tools** menu.

To Load the Correct Procedure:

In the **Control Panel** choose **Load Method…** and select "reflecta.ini" and then Okay.
Then choose **Spectrometer Set-up…** and make sure that:
   Number of scans for both the background and the sample = 1024
   Resolution = 4 cm $^{-1}$
   Gain = 1 (Research) or Gain = 4 (Infinity)

To Collect and Save a background of your clean gold substrates:

Place the substrate over the opening on the top of the reflectance attachment, close the sample compartment, and wait a couple of minutes to allow the compartment to purge (~5 minutes).

From the **Control Panel** select **Background** and then hit **Scan**.

Save the background to your Z: drive directory (**File** > **SaveAs** > Z:\filename). The file will automatically be given a **.bkg** extension.

To Load a previously saved Background:

Go to the **Tools** menu and select **Background Viewer.** Type in the name of your background. This backgound will be shown and automatically be used for all subsequent sample scans.

To Collect and Save a Sample Scan:

Place your sample over the opening in the reflectance attachment, close the sample compartment, and wait for the compartment to purge (~5 minutes).

Load the background. (Note: the background used must have been collected using the same parameters.)

From the **Control Panel**, select **Sample** and then press **Scan**.

Save the spectrum with an appropriate name to your Z: drive (**File** > **SaveAs** > Z:\filename).

Log off the computer when you are done but do not turn off the FTIR unless you are the last group to use it for the day.

Procedure

Week 1:

1.   Clean 2 gold-coated substrates using the plasma cleaner and determine the complex refractive index of one of them.

2.   Immerse the slide for which you determined *n* and *k* in 1×10^{-3} $\underline{M}$ octadecanethiol in ethanol for 30 minutes. Remove it from solution and rinse copiously with ethanol.

3.   While waiting for the monolayer to form, place the other clean gold slide on the FTIR external reflectance sample holder. We use the holder because it provides a reproducible mounting surface and angle of incidence. Measure the response of the clean, bare substrate and save those data as the background spectrum. Think carefully about the spectral range over which you want to acquire the data. Once you have completed this measurement, place this substrate in a sealed vial and leave it for next week's experiment.

4.   Measure ellipsometric thickness of the monolayer formed from the 30 minute immersion. Place the sample on the FTIR external reflectance mount and record its spectrum. To ensure reproducibility, record three different spectra. Put monolayer back in the deposition solution to anneal for a week.

5.   Based on the signal intensities of the absorbance spectra and the literature given to you, calculate the chain tilt angle for this monolayer.

Week 2:

1.   Determine the complex refractive index of the substrate. Record the background spectrum of the bare substrate that you stored for a week in a vial. Once those data are recorded, clean this substrate in the plasma cleaner and acquire a second background spectrum. Determine the complex refractive index of the substrate after cleaning.

2.   Take the slide that has been immersed in 10^{-3} $\underline{M}$ octadecanethiol in ethanol for one week. Remove it from solution and rinse copiously with ethanol.

3.   Measure ellipsometric thickness of the monolayer formed from the one week immersion. Place the sample on the FTIR external reflectance mount and record its spectrum. To ensure reproducibility, record three different spectra. Make sure you use the same spectral range and resolution as you did in the first week.

4.   Based on the signal intensities of the absorbance spectra and the literature given to you, calculate the chain tilt angle for this monolayer. Compare the values for tilt angle you obtain for the two different experiments.