

## SUPPORTING INFORMATION

### Interfacial Structure in Thin Water Layers Formed by Forced Dewetting on Self-Assembled Monolayers of $\omega$ -Terminated Alkanethiols on Ag

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IRRAS data can be used to determine the average alkyl chain tilt from the surface normal for a self-assembled monolayer (SAM) film. This was done here as a means of quantifying sample-to-sample variability in the SAMs produced to eliminate concerns about such variance as a major contribution to observed spectral differences. Application of this treatment to SAMs formed from undecanethiol (UDT) are described that substantiate the high degree of control of the Ag surface and SAM preparation procedures used here.

Treatment of IRRAS data for elucidation of average tilt angle proceeds as follows. The experimental reflection spectrum must be compared to a calculated spectrum for an isotropically-oriented film of comparable thickness in order to determine average molecular orientation in the SAM. This calculation requires knowledge of the optical constants at the relevant frequencies for the molecule of interest. In the case of self-assembled monolayers, information in the  $\nu(\text{CH})$  region is used. A transmission IR experiment at normal incidence on the bulk thiol monomer from which the SAM is made provides a simple means of approximating the imaginary part of the refractive index,  $k(\nu)$ , at relevant frequencies. The transmission is approximately related to  $k(\nu)$  through

$$\frac{I}{I_0} = e^{-4\pi k(\nu)d\nu} \quad (1)$$

where  $I/I_0$  is the fraction of power transmitted through the sample,  $d$  is the path length,  $\nu$  is the frequency in wavenumbers, and  $k(\nu)$  is the extinction coefficient.<sup>S1,S2,S3</sup> From estimates of  $k(\nu)$  determined in this way, the corresponding  $n(\nu)$  values can be calculated from a Kramers-Kronig (KK) transformation using Maclaurin's formula<sup>S4</sup>

$$n(\nu_i) = n_\infty + \frac{2}{\pi} \int_{\nu_1}^{\nu_2} \frac{\nu k(\nu)}{(\nu^2 - \nu_i^2)} d\nu \quad (2)$$

where  $\nu_i$  represents the  $i^{\text{th}}$  point in the frequency set over the range from  $\nu_1$  to  $\nu_2$ . The term  $n_\infty$  has been taken to mean the value of  $n(\nu)$  far below the electronic absorption and far above the infrared absorption. This initial set of  $n(\nu)$  values is then used in a more rigorous calculation of a theoretical transmission spectrum providing significantly improved  $k(\nu)$  values. More accurate values of  $n(\nu)$  are then obtained by a similar KK calculation. With these values of  $n(\nu)$  and  $k(\nu)$  in hand, calculation of a theoretical reflectance spectrum is then performed using a three-phase model as reported previously.<sup>S1,S2</sup>

The orientation of the alkyl chain can be calculated from reflection spectrum because of the anisotropy of the surface electric field. In general, the intensity of a given mode is proportional to the square of the scalar product of electric field and the dipole moment derivative,  $M$ , with respect to the normal coordinate,

$$I \propto |M \cdot E|^2 \quad (3)$$

It follows that the mode intensity will vary with orientation at the surface according to

$$|M \cdot z|^2 \propto \cos^2 \theta \quad (4)$$

where  $\theta$  is defined as the angle between  $M = (d\mu/dq)$  and surface normal,  $z$ . For an ideally flat surface, with known optical constants and for a known thickness, the real infrared spectrum can be calculated as described in the above section. The calculated isotropic adsorbate spectrum will differ from the observed spectrum by the intensity of each mode scaled according to equation 4 with the condition that alignment of a transition dipole moment along the  $z$  axis gives an intensity three times that of the intensity for a randomly oriented transition dipole moment. This relationship is shown in equation 5:<sup>S1,S2</sup>

$$\cos^2 \theta = \frac{A_{\text{obs}}}{3(A_{\text{cal}})} \quad (5)$$

where  $\theta$  is the angle of average tilt of a vibrational mode with respect to the surface normal,  $A_{\text{obs}}$  is the observed absorbance, and  $A_{\text{cal}}$  is the calculated absorbance for an isotropic layer with comparable packing density.

The thickness of the UDT layer was measured to be 2.0 nm using ellipsometry; this value is similar to the reported value.<sup>S4</sup>  $n_{\infty}$  is taken to be 1.45.<sup>S5,S6,S7</sup> Figure S1 shows the observed and calculated spectra of UDT monolayer at Ag and Table 1 shows the calculated tilt angle and calculated and observed frequencies ( $\text{cm}^{-1}$ ) of the  $\nu_{\text{a}}(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2)$  modes for UDT on Ag. The tilt angle was calculated based on the integrated absorbance of the  $\nu_{\text{a}}(\text{CH}_2)$  mode and the uncertainties were determined from the sample-to-sample variance of the difference in observed absorbance for the  $\nu_{\text{a}}(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2)$  modes.<sup>S8</sup>

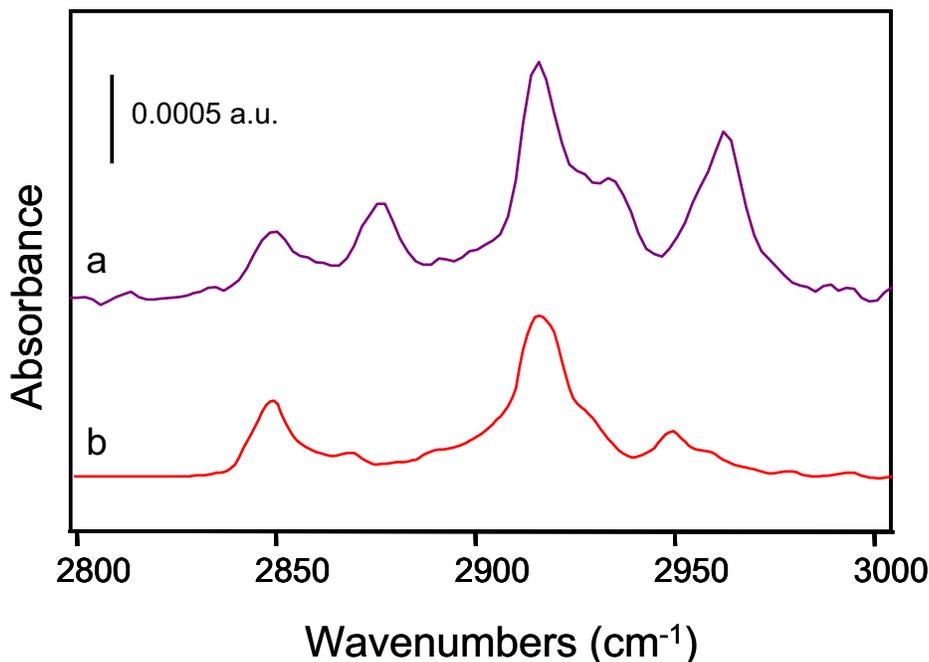


Figure S1. (a) Infrared reflection-absorption spectrum for UDT SAM on Ag. (b) Calculated spectrum for a 2.0 nm isotropic film of UDT.

Table S1. Observed and calculated peak frequencies ( $\text{cm}^{-1}$ ) for the  $\nu_a(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  modes and the calculated tilt angle for UDT SAMs on Ag.

$\nu_a(\text{CH}_2)$		$\nu_s(\text{CH}_2)$		Tilt angle (deg)
obs	calc	obs	calc	
2918	2919	2850	2850	$13 \pm 3$

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