Supporting Information

Errors in the PMIRRAS relative method for the angle determination

The following text describes a fragment of work which is in preparation for an independent publication. It is used to support arguments and conclusions above but should not be published elsewhere until the paper is complete and published by Vlad Zamlynny.

During the relative method of the tilt angle determination[1] one takes the ratio of the integrated intensities of the CH_2 and CH_3 stretching vibrations, determined during Reflection Absorption (RAS) experiment, A_{CH2}^R and A_{CH3}^R and determined during an independent Transmittance experiment, A_{CH2}^T and A_{CH2}^T.. Because the orientation of CH_3 groups remains random at all times ($\cos^2 \Theta_{CH3}^R = 1/3$) following equation (1), this ratio yields:

$$\frac{A_{CH2}^R}{A_{CH3}^R} = \frac{A_{CH2}^T}{A_{CH3}^T} \cdot \frac{\cos^2 \Theta_{CH2}^R}{1/3} \quad (1).$$

The tilt angle is determined after rearrangement of Equation (1) as

$$\cos^2 \Theta = \frac{1}{3} \frac{A_{CH2}^R}{A_{CH3}^R} \frac{A_{CH3}^T}{A_{CH2}^T} \quad (2) \text{ or}$$

$$\cos \Theta = \left(\frac{1}{3} \frac{A_{CH2}^R}{A_{CH3}^R} \frac{A_{CH3}^T}{A_{CH2}^T} \right)^{\frac{1}{2}} \quad (3) \text{ or further}$$

$$\Theta = \cos^{-1}\left[\left(\frac{1}{3}\frac{A^{R}_{CH2}}{A^{R}_{CH3}}\frac{A^{T}_{CH3}}{A^{T}_{CH2}}\right)^{\frac{1}{2}}\right] \quad (4).$$

Error Analysis.

For a function $y = x^{a}$ where a is a positive constant, the error analysis yields:

$$\frac{\sigma y}{y} = a\frac{\sigma x}{x} \quad (5),$$

Where $\frac{\sigma x}{x}$ and $\frac{\sigma y}{y}$ are the relative standard deviations of x and y, respectively. Applying

dependence (5) to equation (3), we can obtain

$$\frac{\sigma(\cos\Theta)}{\cos\Theta} = \frac{1}{2}\frac{\sigma(A^{R}_{CH2}\cdot A^{T}_{CH3}/3\cdot A^{R}_{CH3}\cdot A^{T}_{CH2})}{(A^{R}_{CH2}\cdot A^{T}_{CH3}/3\cdot A^{R}_{CH3}\cdot A^{T}_{CH2})} \quad (6)$$

For angles between 0 and 90 degrees, analysis of propagation of errors yields

$$\sigma(\cos\Theta) = \sin\Theta\sigma\Theta \quad (7).$$

Using equation (7) and following the propagation of errors rules for multiplication and division, we can obtain:

$$\sigma\Theta = \frac{1}{2}\left[\left(\frac{\sigma A^{R}_{CH2}}{A^{R}_{CH2}}\right)^{2} + \left(\frac{\sigma A^{R}_{CH3}}{A^{R}_{CH3}}\right)^{2} + \left(\frac{\sigma A^{T}_{CH2}}{A^{T}_{CH2}}\right)^{2} + \left(\frac{\sigma A^{T}_{CH3}}{A^{T}_{CH3}}\right)^{2}\right]^{\frac{1}{2}}\cot\Theta \quad (8).$$

Here $\left(\dfrac{\sigma A^{R}_{CH2}}{A^{R}_{CH2}}\right)$, $\left(\dfrac{\sigma A^{R}_{CH3}}{A^{R}_{CH3}}\right)$, $\left(\dfrac{\sigma A^{T}_{CH2}}{A^{T}_{CH2}}\right)$ and $\left(\dfrac{\sigma A^{T}_{CH3}}{A^{T}_{CH3}}\right)$ are the relative standard deviations of

the integrated intensities of corresponding bands.

Simplifications and Assumptions:

Typically the relative standard deviations of transmittance measurements are significantly (at least an order of magnitude) smaller than the values associated with reflectance (RAS) measurements. Hence $\left(\dfrac{\sigma A^{T}_{CH2}}{A^{T}_{CH2}}\right)^{2}$ and $\left(\dfrac{\sigma A^{T}_{CH3}}{A^{T}_{CH3}}\right)^{2}$ are generally at least

two orders of magnitude smaller than $\left(\dfrac{\sigma A^{R}_{CH2}}{A^{R}_{CH2}}\right)^{2}$ and $\left(\dfrac{\sigma A^{R}_{CH3}}{A^{R}_{CH3}}\right)^{2}$. Thus it is reasonable to

ignore these terms in equation (8). It is obvious from the above formulae that the relative standard deviations of the integrated intensities are inversely proportional to the areas of corresponding bands. While area of CH_3 peak is not affected by the orientation of the molecules at the surface, following Equation (1) the area of CH_2 peak is proportional to square cosine of the tilt angle of the corresponding transition dipole. It is reasonable to assume that the Relative Standard Deviations RSD_{RAS} for transition dipoles associated with CH_3 and vertically oriented CH_2 vibrations are comparable (since both are determined from the same spectra)

$$RSD_{RAS} = \left(\dfrac{\sigma A^{R}_{CH2}}{A^{R}_{CH2}}\right) \approx \left(\dfrac{\sigma A^{R}_{CH3}}{A^{R}_{CH3}}\right) >> \left(\dfrac{\sigma A^{T}_{CH3}}{A^{T}_{CH3}}\right) > \left(\dfrac{\sigma A^{T}_{CH2}}{A^{T}_{CH2}}\right) (9).$$

The RSD for CH_2 vibrations should vary with tilt angle as

$$\left(\frac{\sigma A^R_{CH2}}{A^R_{CH2}}\right) = \frac{RSD_{RAS}}{\cos^2\Theta} \ (10).$$

Combining equations (9) and (10) with equation (8) one obtains the simplified final relationship

$$\sigma\Theta = \frac{1}{2}\left[\left(\frac{RSD_{RAS}}{\cos^2\Theta}\right)^2 + \left(RSD_{RAS}\right)^2\right]^{\frac{1}{2}} \cot\Theta \ \ (2)$$

In summary, if the RSD_{RAS} =5% (error in the area determination) the relative method is expected to yield reasonable errors ($\pm10^0$) within variations of the tilt angle between10 and 80 degrees.

Above derivations and conclusions agree with previously published results concerning error analysis of the application of PM IRRAS in the absolute method in the angle determination[2].

STM Imaging

In Figures SI1 and SI2 we show STM images corresponding to ordered domains of C6 where molecular resolution is observed- Note that in both images molecular disorder is clearly observed at step edges in agreement with previous observation[3].
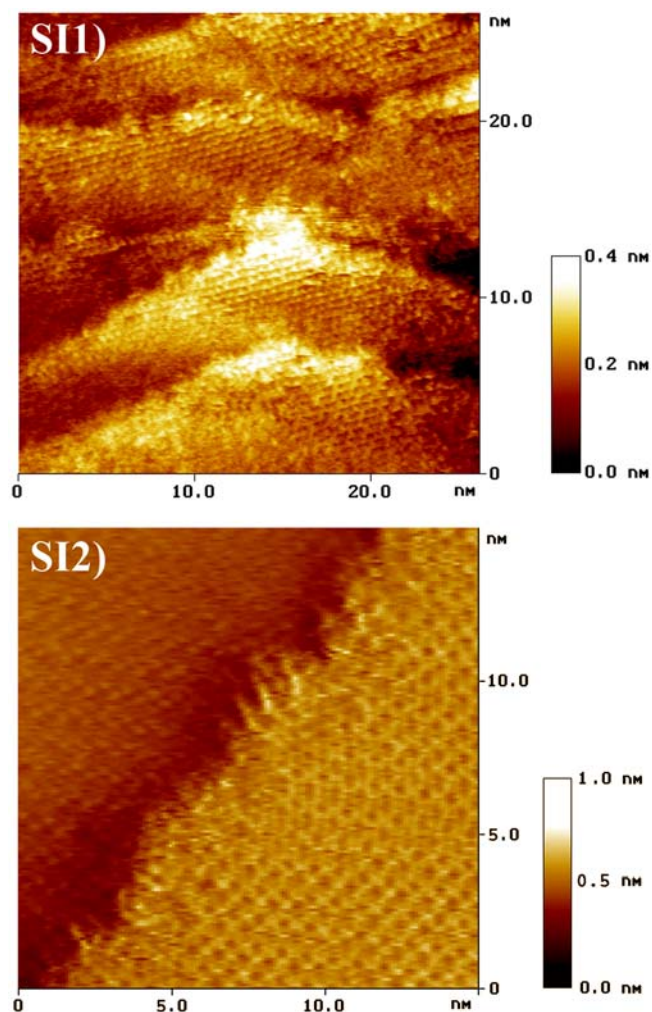
SI1) 25 X 25 nm STM image of hexanethiol (C6) on Au(111). This image shows ordered small terraces covered by ordered C6 domains where the molecules are resolved.

SI2) 15 X 15 nm STM image of hexanethiol (C6) on Au(111). The disorder in the steps edges is more noticeable.

1.   Arnold, R.; Terfort, A.; Woll, C., *Langmuir* **2001,** 17, (16), 4980-4989.
2.   Bin, X.; Lipkowski, J., *Journal of Physical Chemistry B* **2006,** 110, 26430-26441.
3.   Stranick, S. J.; Kamna, M. M.; Krom, K. R.; Parikh, A. N.; Allara, D. L.; Weiss, P. S., *Journal of Vacuum Science & Technology B* **1994,** 12, (3), 2004-2007.