

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231672246>

Helium diffraction from overlayers physisorbed on a self-assembled organic monolayer

ARTICLE *in* LANGMUIR · DECEMBER 1990

Impact Factor: 4.46 · DOI: 10.1021/la00102a017

CITATIONS

30

READS

7

4 AUTHORS, INCLUDING:



Jia Wang

Brookhaven National Laboratory

106 PUBLICATIONS 4,805 CITATIONS

SEE PROFILE

Helium Diffraction from Overlayers Physisorbed on a Self-Assembled Organic Monolayer

Christopher E. D. Chidsey

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Gang-yu Liu, Giacinto Scoles,* and Jia Wang

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received March 12, 1990. In Final Form: May 18, 1990

Low-energy helium diffraction has been used to study the structure of overlayers of Xe, Kr, H₂O, CH₃OH, and *n*-C₆H₁₄ physisorbed on a monolayer of CH₃(CH₂)₂₁SH self-assembled on a Au(111) film supported by mica. Xe and Kr have a close-packed structure with lattice constants 4.45 ± 0.05 and 4.07 ± 0.03 Å, respectively, which are slightly larger than the interatomic distances in the corresponding bulk phases. No surface order is detected with H₂O and CH₃OH overlayers, which is consistent with the fact that these adsorbates do not wet this organic surface. Although *n*-C₆H₁₄ is known to wet the surface of CH₃(CH₂)₂₁SH/Au(111)/mica, it may not form an ordered overlayer, as we were not yet able to detect any diffraction in this case.

The interfacial properties of organic materials, such as wetting, adhesion, lubrication, and corrosion inhibition, are of great importance in many areas of technology and material science.¹ However, the relationship between such macroscopic physical and chemical properties and the underlying structures of the organic substrate and the contacting material is poorly understood. Monolayers of *n*-alkanethiols self-assembled on Au(111) provide model systems with well-defined organic surface structures.²⁻⁴ In addition, the interfacial properties of these model systems are relatively well-known.²⁻⁵ The wettability, quantified by the measurement of the contact angle, θ , between the tangent to a drop of liquid where it meets the organic substrate and the substrate surface itself, has been shown to depend sensitively on the surface composition.² There have also been attempts at understanding the microscopic basis of wetting using temperature-programmed desorption (TPD) measurements, which provide qualitative information about the interactions between the adsorbates and the organic substrate.⁵ It is still difficult, however, to make direct connections between the wetting behavior and the microscopic structures of the substrate surface and the adsorbates, mostly because of the lack of the structural information. There have been no reports, to our knowledge, on the structures of adsorbed layers on these organic substrates. Because it is highly surface sensitive and non-destructive, low-energy atom diffraction is the ideal tool for probing the structures of adsorbed layers.⁶ Low-energy helium diffraction has already been used in our laboratory to detect the molecular order at the surface of

monolayers of *n*-alkanethiols chemisorbed on a Au(111) film on mica.³ The results clearly show that the surfaces of these alkanethiol monolayers consist of domains of hexagonally arrayed CH₃ groups with a lattice constant of 5.01 ± 0.02 Å. In this paper, we report the first use of low-energy helium diffraction to study the structures of physisorbed overlayers on top of an alkanethiol monolayer in the hope of furthering our understanding of interfacial phenomena on organic substrates at the molecular level.

The substrate used in our experiment, CH₃(CH₂)₂₁SH/Au(111)/mica, was prepared in two steps. First, epitaxial films of Au(111) about 1500 Å thick were grown by vapor deposition on mica.^{7a} Second, the thiol was adsorbed from a 1 mM solution in ethanol onto the Au(111) film.^{7b} The substrate sample was attached to the sample manipulator with a silver paste and kept at about 35 K during the diffraction measurements.

The low-energy helium diffraction apparatus has been described previously.⁸ The low-energy helium beam was generated by expanding 40 psig of UHP helium through a 0.020-mm nozzle cooled to ~55 K. The velocity dispersion ($\Delta v/v$) was less than 2%, and the beam energy was ~12 meV. The wave vector of the helium beam was calibrated via diffraction from a NaCl(001) surface. The organic substrate was prepared for gas deposition by heating to ~200 K, which is above the condensation temperature of the adsorbates. The clean surface was then exposed to an effusive flux of the desired compound and the surface heater turned off. The deposition was monitored by detecting the intensity of the specular beam.^{8b} When the adsorbate molecules first begin to accumulate on the surface, they are highly mobile, which results in a rapid decrease of the specular intensity. After the first layer was formed,^{8b} the dosing gas flux was interrupted by an electromechanical flag. The adsorbates used in the experiment include Xe, Kr, H₂O, CH₃OH, and *n*-C₆H₁₄. For H₂O, CH₃OH, and *n*-C₆H₁₄, we bubbled

(1) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* 1987, 3, 932.

(2) (a) Bain, C. D.; Troughton, E. B.; Tai, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321. (b) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7155. (c) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7164.

(3) Chidsey, C. E. D.; Liu, G. Y.; Rowntree, P. A.; Scoles, G. *J. Chem. Phys.* 1989, 91 (7), 4421.

(4) (a) Strong, L.; Whitesides, G. M. *Langmuir* 1988, 4, 546. (b) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* 1987, 109, 3559.

(5) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1990, 112, 570.

(6) (a) Toennies, J. P. *J. Vac. Sci. Technol.* 1987, A5, 440. (b) Kern, K.; Comsa, G. In *Advanced Chemical Physics*; Lawley, K. R., Eds.; Wiley: London, 1989. (c) Kern, K.; Comsa, G. In *Chemistry and Physics of Solid Surfaces VII*; Vanselow, R.; Howe, R., Eds.; Springer: Heidelberg, 1988, p 65. (d) Barker, J. A.; Auerbach, D. *J. Surf. Sci. Rep.* 1983, 4, 59.

(7) (a) Chidsey, C. E. D.; Loiacono, D. N.; Sleator, T.; Nakahara, S. *Surf. Sci.* 1988, 200, 45. (b) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* In press.

(8) (a) Danielson, L.; Ruiz, J. C.; Schwartz, C.; Scoles, G.; Hutson, J. M. *Faraday Discuss. Chem. Soc.* 1985, 80, 47. (b) Aziz, R. A.; Buck, U.; Jönsson, H.; Ruiz-suárez, J. C.; Schmidt, B.; Scoles, G.; Slaman, M. J.; Xu, J. *J. Chem. Phys.* 1989, 91 (10), 6477.

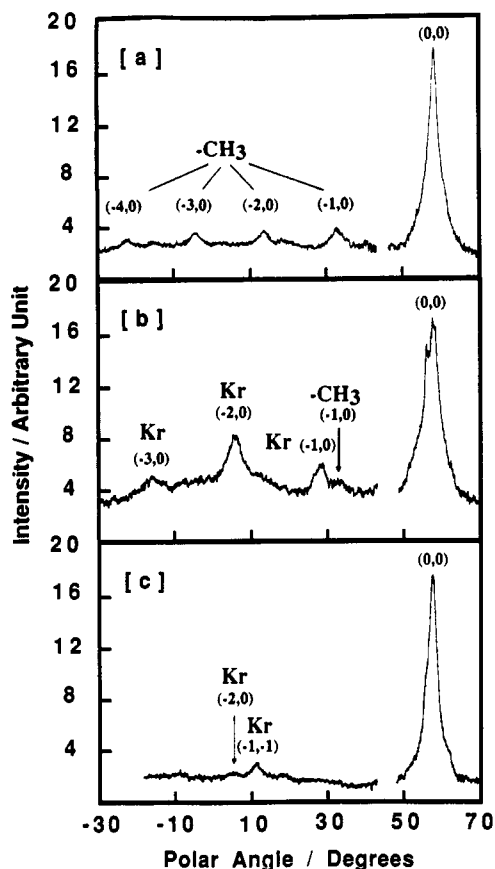


Figure 1. (a) Helium diffraction from $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$. The azimuthal angle is 0° and the incident angle is 57.3° . The incident beam energy is 12.1 meV and the crystal temperature is 35 K. (b) Helium diffraction from $\text{Kr}/\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ under the same condition as part a. (c) Same as part b except the azimuthal angle is 30° .

helium gas through the liquids and used the resulting gas mixture for the deposition.

Parts b and c of Figure 1 show the diffraction spectra of Kr physisorbed on $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ for two different azimuthal angles chosen from many spectra taken at different azimuths.⁹ Only a very weak $(-1,0)$ substrate peak (Figure 1b) remains, indicating that the surface is almost completely covered by Kr. The difference between the azimuths of maximum intensity for the $(-1,-1)$ and the $(n,-0)$ peaks is 30° , and the azimuthal angle at which the maximum $(-n,0)$ peak intensities for the Kr overlayer occurs is the same as for the $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ surface, indicating that the CH_3 and Kr lattices share the same orientation to within 3° . The lattice constant for the Kr overlayer calculated from the diffraction peak positions is $4.07 \pm 0.03 \text{ \AA}$, significantly smaller than the substrate ($5.01 \pm 0.02 \text{ \AA}$), so the Kr overlayer must be incommensurate with the substrate, as shown in Figure 2.

Our previous experiments³ have already demonstrated that the CH_3 groups at the surface of $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ do not form a perfect two-dimensional single crystal. Indeed, this surface consists of domains of hexagonally arrayed molecules whose average size is of the order of 100 \AA . Most of these domains share a common orientation. However, some azimuthal disorder is present on the surface. One would expect that these imperfections will appear in the Kr overlayer as well, and indeed they

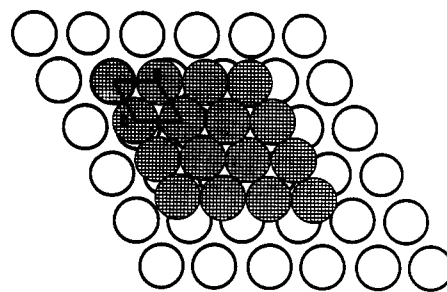


Figure 2. Top view of the $\text{Kr}/\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ unit cell structure, showing the incommensurate nature of the Kr overlayer. The open circles represent the CH_3 -groups of the substrate and the shaded circles represent Kr atoms.

do. As can be seen in Figure 1b, the diffraction peaks for the Kr overlayer are also very broad, even slightly broader than the substrate peaks, and the $(-2,0)$ peak of the Kr overlayer which belongs to the 0° azimuth also appears, although very weakly, at the 30° azimuth.

The structure of the Xe overlayer is the same as that for Kr except that it has a larger lattice constant ($4.45 \pm 0.05 \text{ \AA}$). In principle, the structures of the rare gas overlayers can be predicted on the basis of the adatom-adatom and adatom-substrate interaction energies.¹⁰ In fact, much theoretical work has been done to understand the known structures of rare gas overlayers on other substrates.¹⁰ For Kr and Xe molecules adsorbed on this organic substrate, theory predicts that the triangular lattices of Kr and Xe layers will rotate about 4° and 7° , respectively, relative to the substrate triangular lattice.^{10a,b} However, our experiments show that the rotations are less than 3° . One possible explanation is that the small size of the domains of ordered Kr or Xe interrupts the periodicity which is needed to produce enough free energy gain to allow the rotation of the overlayer lattice.^{10c} Accepting that the rotational angle is zero, the lattice constants of Kr and Xe overlayers calculated from Shiba's formula^{10a} are 4.08 and 4.46 \AA , respectively, which are in good agreement with our measured values.

Molecules, such as water, methanol, and *n*-hexane have also been deposited on $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$. No diffraction was observed for either H_2O or CH_3OH , indicating that these molecules do not form ordered overlayers on this organic surface. It is not possible to exclude that our nonequilibrium procedure for overlayer deposition is responsible for the lack of order of the polar molecule overlayers. However, we have successfully grown overlayers of polar molecules on various substrates by using this technique.¹¹ Moreover, TPD measurements under similar experimental conditions suggest that H_2O molecules form clusters on the surface.⁵ As has been pointed out,⁵ clustering is consistent with the observation that this surface is extremely hydrophobic, as evidenced by the fact that the advancing contact angles (θ_a) are $110\text{--}115^\circ$ for H_2O on $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ and 22° for CH_3OH .^{2a,5} In principle, we should be able to calculate the average size of H_2O or CH_3OH clusters from an analysis of the shape of the specular peak.¹² However, such a calculation

(9) For the definition of the azimuthal angle and a schematic diagram, see: Engel, T.; Rieder, K.-H. In *Structural Studies of Surfaces*; Höhler, G., Eds.; Springer: Berlin, Heidelberg, New York, 1982; Vol. 91.

(10) (a) Shiba, H. *J. Phys. Soc. Jpn.* 1979, 46 (6), 1852. (b) McTague, J. P.; Novaco, A. D. *Phys. Rev. B* 1979, 19 (10), 5299. (c) Bruch, L. W.; Phillips, J. M. *Surf. Sci.* 1980, 91, 1.

(11) (a) Ruiz-Suarez, J. C.; Klein, M. L.; Moller, M. A.; Rowntree, P. A.; Scoles, G.; Xu, J. *Phys. Rev. Lett.* 1988, 61, 710. (b) Liu, G. Y.; Rowntree, P. A.; Scoles, G.; Xu, J. *Surf. Sci.* 1989, 224, 43. (c) Rowntree, P. A.; Scoles, G.; Xu, J. *J. Chem. Phys.* 1990, 92 (6), 3853.

(12) (a) Kruger, D. W.; Savage, D. E.; Laggally, M. G. *Phys. Rev. Lett.* 1989, 63 (4), 402. (b) Dekieviet, M.; Liu, G. Y.; Rowntree, P. A.; Scoles, G. Unpublished results.

would be complicated by the imperfection of the substrate, which may be the major contribution to the broadening of the (0,0) peak. As in the case of H_2O and CH_3OH , we are unable to observe diffraction from the adsorbed $n\text{-C}_6\text{H}_{14}$ layer. However, since the substrate is known to be wetted by $n\text{-C}_6\text{H}_{14}$,⁵ and helium scattering from a layer of non-spherical molecules is likely to be inelastic, we have to issue a word of caution and invite the reader to consider this result as an indication, instead of a proof, of the lack of order in the physisorbed hydrocarbon layers.

In summary, the structure of physisorbed overlayers on $\text{CH}_3(\text{CH}_2)_{21}\text{SH}/\text{Au}(111)/\text{mica}$ has been characterized by low-energy helium diffraction. Accurate lattice constants for adsorbed layers of Kr and Xe have been extracted directly from the data. These results indicate the possibility of probing the surface structure of ordered Langmuir-Blodgett or self-assembled multilayers.¹³ The question of whether or not the order present in the first

monolayer propagates to the second one is an interesting issue with clear implications for our understanding of the physical chemistry of membranes. For nonwetting overlayers, a substrate with fewer defects would make it possible to correlate the diffraction peak widths with the contact angles and to obtain quantitative information about the average island size of the adsorbates.

Acknowledgment. It is a pleasure to thank Nick Camillone III for his help during the measurements and G. Robinson for his help in drafting the manuscript. Helpful discussions with R. Nuzzo and L. Dubois are gratefully acknowledged. G.S. thanks S. Fain for a useful conversation about incommensurate overlayers. We also thank Princeton University for financial support.

(13) (a) Ulman, A.; Tillman, N. *Langmuir* 1989, 5, 1418. (b) Lee, H.; Kepley, L. J.; Hong, H.-G.; Alzhler, S.; Mallouk, T. E. *J. Phys. Chem.* 1988, 92, 2597.