

New Optical Absorption Band Resulting from the Organization of Self-Assembled Monolayers of Organic Thiols on Gold

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Experimental evidences are presented supporting the existence of a new optical absorption band observed when monolayers of alkylthiol are self-assembled on gold substrate. This new absorption is centered at about 800 nm and has a very broad absorption peak. The intensity of the new band correlates with the density of molecules and the quality of the organization of the monolayer.

Introduction

Adsorption of molecules or atoms on a metal surface can affect the surface's electronic properties in several ways. When one material is adsorbed on top of the other, the electrochemical potential of the adsorbate and the substrate has to equalize. This must be done by charge transfer at the interface to reach thermodynamical equilibrium, namely the electronic states of the two materials are mixed at the interface. When a chemical bond is formed between the adsorbate and the substrate, an additional charge may be transferred in order to form the bond. All these considerations are valid independent of the organization or the special properties of the adsorbates.¹ However, enhanced charge transfer may occur if an organized closely packed monolayer is formed from organic molecules having a dipole moment.² In this case, the need to reduce the electrostatic energy within the layer induces an additional charge transfer between the metal substrate and the layer. Some recent experiments seem to provide direct evidence for this effect.³ In other studies, it was found that, due to the organization of the organic monolayer, the charge density of the adsorbed molecule is modified.⁴ It was also suggested that the new magnetic properties observed upon the formation of organic monolayers on gold are related to the organizationally induced charge transfer.^{5,6}

Since typically the amount of charge transferred per adsorbed molecule is relatively low, in the case of large molecules, it does not usually result in any recognizable structural effect. Nevertheless, spectroscopy should be able to provide evidence supporting the existence of these new hybrid adsorbate–substrate states. Recent experimental^{7,8} and theoretical studies indicate that indeed the electronic structure at the interface between the self-assembled organized organic layer and the solid substrate can reveal new states that have new properties not found either in the solid substrate itself or in the organic molecules. Some of these new states can be found using electron spectroscopy methods, where the sensitivity to the electronic structure of the interface is very high.^{9–12} Furthermore, new optical absorption bands were found at Au/S interfaces due to

the modification of the near-surface gold electronic structure upon thiol chemisorption.¹³ Recent calculations¹⁴ also indicate that the electronic structure at the interface of a self-assembled monolayer of S–C₆H₅ on either Cu or Au does not even resemble the electronic structure of either the metal or the molecules.

Here we present empirical evidence supporting the existence of a new optical absorption band observed when monolayers of alkylthiols are self-assembled on a gold substrate. The intensity of the new band correlates with the density of molecules and the quality of the organization of the monolayer.

Experimental Method

The molecules, 1-octadecanethiol (C₁₈H₃₇–SH) or 1-hexadecanethiol (C₁₆H₃₃–SH), were adsorbed on a 200-nm thick gold film, which was deposited on a 4-nm chromium adhesion layer formed on a borosilicate 11 × 11 mm glass slide (from Metallhan del Schröer GmbH). The slides were inserted into a 1 mM solution of the specific compound in ethanol for a given time, up to 12 h, and then washed with ethanol. The gold slides were cleaned, prior to the adsorption, by an ultraviolet ozone cleaning system (UVOC model T10/OES/E) for 27 min; afterward, they were immersed in pure ethanol for 20 min to remove the oxides.

The absorption spectrum of a monolayer of octadecanethiol adsorbed on gold was taken using reflective spectroscopy (Spekol V-570 spectrophotometer). The reflectance was measured as a function of wavelength, using a clean gold slide as a reference. The spectrum of clean gold was subtracted from that of the gold coated with the monolayer.

A WVASE32 spectroscopic ellipsometer was used to obtain the ellipsometric data at an incident angle of 70°. The measurements were performed at wavelengths between 250 and 1100 nm, with sampling steps of 5 nm. The ellipsometry data were fitted by commercial software, WVASE32, from J. A. Woollam Co., Inc.¹⁵ The contact angle with water was measured using an automated goniometer (Rame-Hart, model-100).

Results and Discussion

Figure 1 shows the absorption of a monolayer of 1-octadecanethiol adsorbed on gold. The spectrum was obtained using

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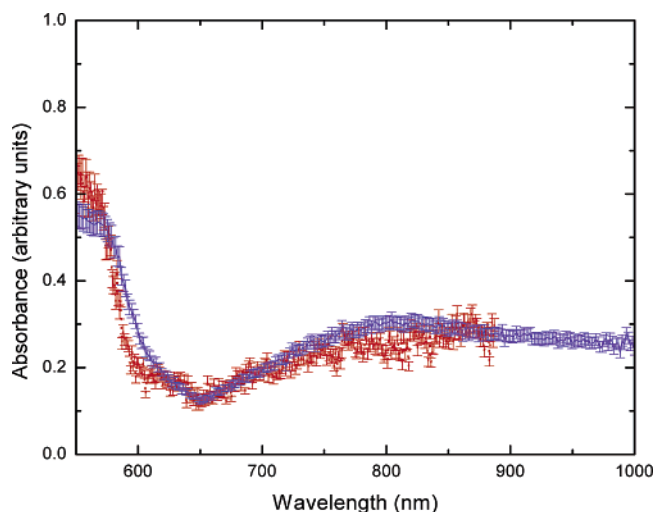


Figure 1. The absorption spectrum of a monolayer of 1-octadecanethiol adsorbed on gold. The monolayer had a contact angle of 115° . The spectrum was taken either using ellipsometer (blue- solid) or by measuring the reflectance (red-dotted). The widths of the lines indicate the error in the measurements.

two different methods: reflection spectroscopy and ellipsometry. Clearly, there is an excellent agreement between the results obtained by the two methods. The organic molecules themselves absorb only in the near UV; however, when the monolayer is formed on gold, one also observes the absorption of the gold at about 550 nm, which is modified by the adsorbed layer. This absorption is similar to the one reported in ref 13. In addition, a weaker new absorption band is observed at about 800 nm. This band cannot be related simply to small modifications of the absorption of the gold metal, since it is red shifted too much.

Figure 2A presents the absorption spectrum of 1-octadecanethiol adsorbed on gold for various contact angle measured with water. By varying the adsorption time, the quality of the monolayer can be modified, as indicated by the contact angle. In Figure 2B a clear correlation can be observed between the intensity of the band at 800 nm and the absolute value of the cosine of the contact angle, when the contact angle is in the range of 80° – 115° . Full coverage corresponds to a contact angle of $115 \pm 1^\circ$.

To understand this correlation, we can assume that the surface of the substrate is covered with patches of monolayer and between these patches there are voids. The part of the surface covered with patches is f_1 , whereas the voids expand the f_2 portion of the surface area. Hence we can use the following expression¹⁶

$$\gamma_L(1 + \cos \vartheta) = f_1 W_1 + f_2 W_2 \quad (1)$$

where W_1 and W_2 represent the work of cohesion of the water with either the monolayer patches or with the voids, respectively, γ_L is the surface energy of the liquid water, and θ is the contact angle measured. Equation 1 can be rearranged so that

$$\cos \vartheta = \frac{f_1 W_1}{\gamma_L} + \frac{f_2 W_2}{\gamma_L} - 1 \quad (2)$$

Since $f_2 = 1 - f_1$,

$$\cos \vartheta = \frac{f_1 W_1}{\gamma_L} + \frac{(1 - f_1) W_2}{\gamma_L} - 1 = f_1 \left[\frac{W_1 - W_2}{\gamma_L} \right] + \frac{W_2}{\gamma_L} - 1 \quad (3)$$

Therefore, $\cos \theta$ is proportional to the fraction of the surface

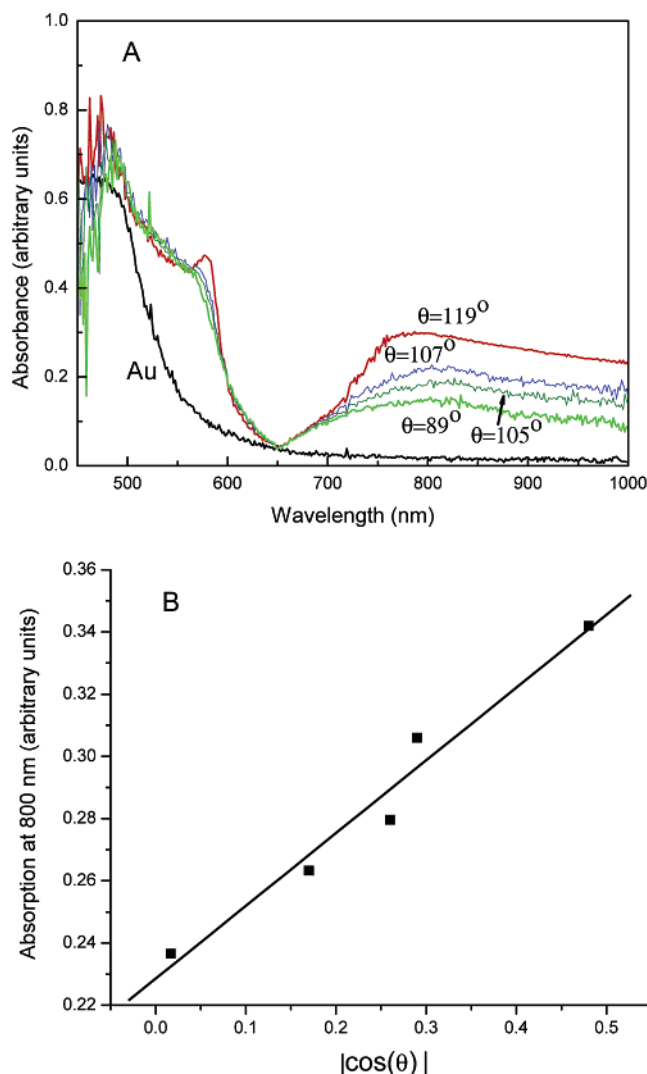


Figure 2. (A) The absorption spectrum of 1-octadecanethiol adsorbed on gold for different qualities of the monolayers, characterized by their contact angle with water. (B) The peak intensity at 800 nm measured as a function of the monolayer quality, as indicated by the absolute value of the cosine of its contact angle with water.

coated with the monolayer or, in other words, to the density of molecules on the surface.

The correlation observed between the intensity of the band at 800 nm and the cosine of the contact angle indicates that indeed the new band is related to the density of molecules adsorbed on the gold substrate. The band intensity and shape seem to depend only weakly on the type of thiols adsorbed on the gold substrate. This was observed for several alkylthiols as well as monolayers made from glutathione.

A detailed calculation is required to learn about the exact nature of the observed absorption. This type of calculation is in the forefront of today's abilities. However, a general conclusion can be made based on the fact that the absorption is at such a low energy and is so broad; these two facts indicate that the states involved in the absorption are delocalized. This conclusion is consistent with recent calculations whereby delocalized states were found in monolayers of organic thiols adsorbed on gold or copper.¹⁴ These delocalized states result from a fraction of an electron transferred from the substrates to the organic layer. These types of states were also observed in two-photon photoelectron spectroscopy performed on self-assembled monolayers adsorbed on Ag(111).¹⁷

The present results provide additional evidence that indeed new electronic properties emerge when molecules are self-assembled as an organized organic layer.¹⁸ These new properties can manifest themselves in various ways¹⁹ and must be taken into account when hybrid inorganic–organic devices are built.

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References and Notes

- (1) Seki, K.; Hayashi, N.; Oji, H.; Ito, E.; Ouchi, Y.; Ishi, H. *Thin Solid Films* **2001**, *393*, 298.
- (2) (a) Vager, Z.; Naaman, R. *Chem. Phys.* **2002**, *281*, 305. (b) Lvov, V. S.; Naaman, R.; Tiberkevich, V.; Vager, Z. *Chem. Phys. Lett.* **2003**, *381*, 650.
- (3) Alloway, D. M.; Hofmann, M.; Smith, D. L.; Gruhn, N. E.; Graham, A. L.; Colorado, R., Jr.; Wysocki, V. H.; Lee, T. R.; Lee, P. A.; Armstrong, N. R. *J. Phys. Chem. B* **2003**, *107*, 11690.
- (4) Ray, S. G.; Cohen, H.; Naaman, R.; Liu, H.; Waldeck, D. H. *J. Phys. Chem. B* **2005**, *109*, 14064.
- (5) Carmeli, I.; Leituss, G.; Naaman, R.; Reich, S.; Vager, Z. *J. Chem. Phys.* **2003**, *118*, 10372.
- (6) Ray, S. G.; Daube, S. S.; Leituss, G.; Vager, Z.; Naaman, R. *Phys. Rev. Lett.* **2006**, *96*, 036101.
- (7) Umbach, E. *Prog. Surf. Sci.* **1991**, *35*, 113.
- (8) Gao, W.; Kahn, A. *J. Phys.: Condens. Matter* **2003**, *15*, S2757.
- (9) Hufner, S. *Photoelectron Spectroscopy: Principles and Applications*, Springer-Verlag: Berlin, 1995.
- (10) Horn, K.; Scheffler, M. in *Handbook of Surface Science, Vol. 2: Electronic Structure*; Richardson, N. V., Holloway, S., Eds.; Elsevier: Amsterdam, 2000.
- (11) Harris, C. B.; Ge, N.-H.; Lingle, R. L., Jr.; McNeil, J. D.; Wong, C. M. *Annu. Rev. Phys. Chem.* **1997**, *48*, 711.
- (12) Zhu, X.-Y. *Surf. Sci. Rep.* **2004**, *56*, 1.
- (13) Shi, J.; Hong, B.; Parikh, A. N.; Collins, R. W.; Allara, D. L. *Chem. Phys. Lett.* **1995**, *246*, 90.
- (14) Perebeinos, V.; Newton, M. *Chem. Phys.* **2005**, *319*, 159.
- (15) The values of n and k , obtained from the ellipsometric studies, form the complex refractive index: $N(\gamma) = n(\gamma) + ik(\gamma)$. The conversion reflectivity R is given by: $R = (n - 1)^2 + k^2 / (n - 1)^2 + k$ when $R + T = 1$; and $A = -\log(1/T)$ when T is the transmission and A is the absorption.
- (16) Israelachvili, J. N.; Michelle, L. G. *Langmuir* **1989**, *5*, 288.
- (17) Miller, A. D.; Gaffney, K. J.; Liu, S. H.; Szymanski, P.; Garrett-Roe, S.; Wong, C. M.; Harris, C. B. *J. Phys. Chem. A* **2002**, *106*, 7636.
- (18) Naaman, R.; Vager, Z. *Acc. Chem. Res.* **2003**, *36*, 291.
- (19) Cahen, D.; Naaman, R.; Vager, Z. *Adv. Funct. Mater.* **2005**, *15*, 1571.