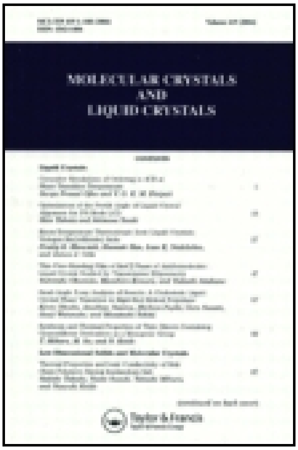

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Penning Ionization Electron Spectroscopy on Self-Assembled Monolayer of 1-Mercapto-8-Bromooctane on Au(111)

ABDUAINI ABDUREYIM[a], SATOSHI KERA[a], HIROYUKI SETOYAMA[a], RYOCHI SUZUKI[b], MASARU AOKI[b], SHIGERU MASUDA[b], KOJI K.OKUDAIRA[a], MAKOTO YAMAMOTO[a], NOBUO UENO[a,c], and YOSHIYA HARADA[a]
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Penning ionization electron spectroscopy (PIES) and ultraviolet photoelectron spectroscopy (UPS) were used to characterize self-assembled monolayers (SAMs) of 1-mercapto-8-bromooctane adsorbed on Au(111) from aqueous solution. The analysis of the relative band intensity of Penning spectrum indicates that the molecule stand up right to the substrate surface at room temperature. Upon heating, the molecule becomes tilted in the layer.

Keywords: Penning ionization electron spectroscopy; ultraviolet photoelectron spectroscopy; 1-mercapto-8-bromooctane; self-assembled monolayers; Au(111)

INTRODUCTION

Organosulfur compounds form well-ordered, self-assembled monolayers (SAMs) on metal or semi-conducter surfaces[1]. The characterization of surfaces of SAMs is important in understanding properties of such technologically useful organic thin films. Recently we have used Penning ionization electron spectroscopy (PIES) to study the electronic structure and molecular orientation of the SAM of thiophenol[2]. In PIES, the kinetic energy of electrons ejected by collisions between a target T (gas or solid) and metastable atoms A* is analyzed;

$T + A^* \rightarrow T^+ + A + e^-$, e^- for energy analysis. This method is selectively sensitive to the outermost surface layer because metastable atoms do not penetrate into inner layers. Furthermore, an orbital of a target molecule extending outside the molecular surface interacts more easily with the metastable atom than with an inner orbital and gives a stronger band in the Penning spectrum[3]. Thus, the analysis of the relative intensity of Penning spectrum provides information on the geometrical orientation of molecules in the outermost layer.

In the present study we extended our work to characterization of the SAM of 1-mercapto-8-bromooctane (BrC8) adsorbed on Au (111) from aqueous solution. We also measured the PIES and ultraviolet photoelectron spectrum (UPS) of gas phase BrC8 as a reference for the assignment of the SAM bands (the abbreviation PIES and UPS are used to stand for the electron spectra as well as for electron spectroscopies).

EXPERIMENTAL

The Au(111) substrate was prepared by thermal evaporation of gold onto a mica surface at a substrate temperature of 570 K and in a vacuum of $\sim 10^{-7}$ torr. The film thickness was about 100-200 nm. The (111) orientation of the evaporated Au film was confirmed by X-ray diffraction. The molecule BrC8 was synthesized by the reaction of 1-8-dibromooctane and sodium hydrogen sulfide[4]. The monolayer was prepared by soaking the substrate in 1 mM hexane solution for 2 days. It was rinsed in hexane for 10 min and then dried in air.

The PIES and UPS were measured under an ultrahigh vacuum (base pressure, ~ 10^{-9} Torr). The details of the experimental apparatus have been described elsewhere[5].

RESULTS AND DISCUSSION

Fig. 1 shows the He*(2^3S, 19.82 eV) PIES and He I (21.22 eV) UPS of gaseous BrC8. The electron energy scale for UPS is shifted relative to that for the PIES by 1.4 eV, the difference of their excitation energies (21.22 eV-19.82 eV=1.4 eV). In the figure the peak shift and band broadening of the PIES compared to those of the UPS are due to the presence of the interaction potential in the colliding system.

In Fig.1, the spectra have eleven bands denoted by 1-11. These bands can be assigned on the basis of MO calculation (ab *initio* method with a STO-6G basis set and the Koopmans' theorem) and the previous assignment of UPS bands of n-butyl chloride and n-propyl thioalkahol[6]. Band 1 is related to the nonbonding MO's of the S atom, $n_{\perp}$(S), which is distributed perpendicular to the carbon skeleton plane. Bands 2 and 3 are assigned to the nonbonding MO's of the Br atom, $n_{\parallel}$(Br) and $n_{\perp}$(Br), which are distributed parallel and perpendicular to the carbon skeleton plane. Bands 4, 7 and 10 are related to the pseudo-π (pπ) MO's, distributed perpendicular to the carbon skeleton plane. Band 5 and 6 are related to the σ_{CS} and σ_{CBr} MO's, respectively. Band 8 is related to the MO's such as the $\sigma_{C\ 2p}$ and pπ. Band 9 is assigned to the σ_{CH} MO's of the -CH_2Br end. Finally, band 11 can be ascribed to the $\sigma_{C\ 2s}$ MO's, being located in the high ionization energy region. In the gas-phase PIES, bands 1-3 are very much enhanced in comparison with the other bands (4-11). This is because, bands 1-3 contain the contributions of the S_{3p}

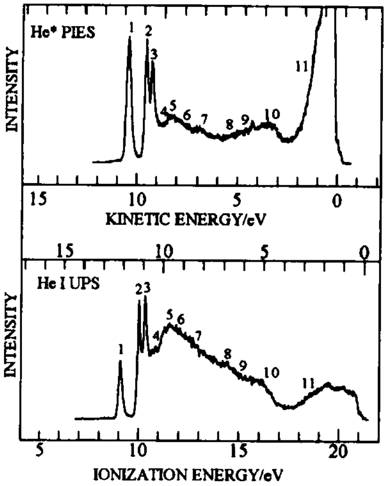

FIGURE 1 He*(2^3S) PIES and He I UPS of gaseous BrC8

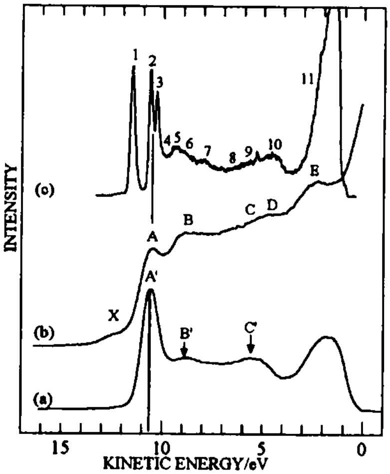

FIGURE 2 (a) He*(2^3S) PIES of the BrC8 SAM, (b) He I UPS of the BrC8 SAM, and (c) He*(2^3S) PIES of the gaseous BrC8

and Br_{5p} AO's that are distributed outside the molecular surface and effectively interact with metastable atoms.

Fig. 2 shows the He*(2^3S) PIES and the He I UPS of BrC8 SAM at room temperature, together with the He*(2^3S) PIES of gaseous BrC8. In Fig. 2, the electron energy scale for the solid UPS [curve (b)] is shifted relative to that for the solid PIES [curves (a)] by 1.4 eV as in the case of Fig. 1. Compared to the solid PIES, the energy scale for the gas-phase PIES [curve (c)] is also shifted to higher energy by 1.1 eV (see below). In Fig. 2, the band positions of the gaseous PIES [curve (c)] agree with those of the SAM spectra [curves (a) and (b)] with the energy shift of 1.1 eV. This energy shift is mainly due to the relaxation of metal electrons and the electrons of neighboring adsorbed BrC8 moieties upon ionization.

In the UPS of the SAM, we can see bands A-E and X. These bands correspond to gaseous bands, except for band X. Band X is considered to be due to an orbital originated from the interaction of the Au_{5d} and S_{3p} AO's.

The UPS is strongly affected by the electron emission from the substrate, because photons penetrate through the SAM and interact with the substrate. Thus, we can not derive useful information on the molecular orientation by the UPS.

In the PIES of the SAM, band A' related to bands 2 and 3 |$n_{\parallel}$(Br) and $n_{\perp}$ (Br) bands| in the gaseous spectrum are much enhanced relative to the other bands. Further, bands B' and C' corresponding to bands 6 (σ_{CBr}) and 9 (σ_{CH} of the -CH_2Br end) are relatively strong. On the other hand, the $n_{\perp}$(S) (band 1 in the gaseous spectrum) and pπ (band 10) are missing in the SAM PIES. These findings indicate that molecules stand upright to the substrate plane exposing the bromine atom outside the surface. In this orientation metastable atoms effectively interact with the $n_{\parallel}$(Br), $n_{\perp}$(Br) and σ_{CBr} orbitals distributed further outside the surface.

Fig. 3 shows the temperature dependence of the He* (2^3S) PIES of the SAM. Upon heating up to 353 K, band A' related to the $n_{\parallel}$(Br) and $n_{\perp}$(Br) orbitals becomes weak, while the bands 4' and 10' due to pπ MO's become strong. Also band 5' due to the σ_{CS} MO and band X appear. These changes are considered to be caused by the desorption of physisorbed molecules, which makes some space among chemisorbed molecules and leads to tilted orientation. In fact, in the tilted molecular arrangement, pπ MO's

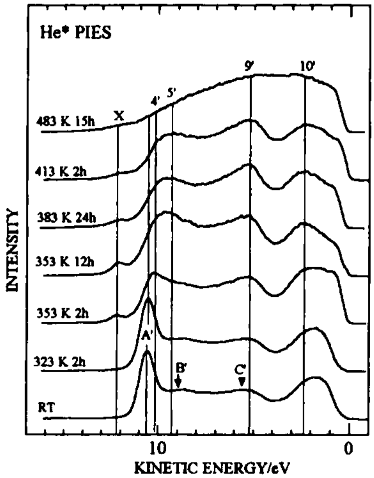

FIGURE 3 The temperature dependence of the He*(2^3S) PIES of the BrC8 SAM

distributed on the side of the molecule are exposed outside the surface and interact effectively with metastable atoms to give strong pπ bands (4' and 10'), and thereby $n_{\parallel}$(Br) and $n_{\perp}$(Br) bands (A') become weak. In particular, the appearance of bands X and 5' indicates that the number of desorbed molecules (physisorbed molecules) are fairly large, because the orbitals corresponding to these bands are distributed around the roots of the chemisorbed molecules. The presence of physisorbed molecules in the SAM was confirmed by XPS experiment[7]. It was observed that the PIES of the SAM little changes on prolonged heating at 353 K. Therefore, only the chemisorbed molecules remain on the substrate at this temperature after desorption of the physorbed species. As shown in Fig. 3, the spectrum gradually changes upon further raise of the temperature and the SAM features are missing after heating at 483 K for 15 h, showing that most of the chemisorbed molecules are desorbed. The PIES shows a broad structureless feature in this case, because Penning process does not occur at the metal surface and metastable atoms de-excite *via* resonance ionization followed by Auger neutralization[8].

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