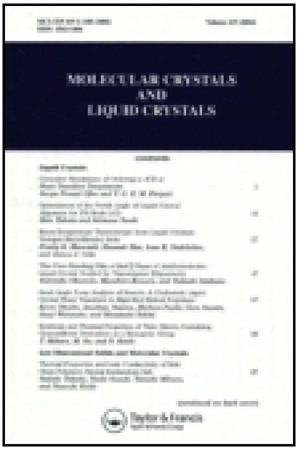

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Calculation of Photoelectron Angular Distributions from ω-(n-pyrrolyl)alkanethiol Self-assembled Monolayers for Different Molecular Orbitals of Pyrrole Group

Shinji Hasegawa [a] , Kyuya Yakushi [a] , Hiroo Inokuchi [a] , Koji Kamiya-okudaira [b] , Nobuo Ueno [b] , Kazuhiko Seki [c] & Eizi Morikawa [d]

[a] Institute for Molecular Science

[b] Department of Materials Science, Faculty of Engineering, Chiba University

[c] Research Center for Material Science and Department of Chemistry, Nagoya University

[d] Center for Advanced Microstructures and Devices, Louisiana State University

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Calculation of Photoelectron Angular Distributions from ω-(n-pyrrolyl)alkanethiol Self-assembled Monolayers for Different Molecular Orbitals of Pyrrole Group

SHINJI HASEGAWA, KYUYA YAKUSHI, HIROO INOKUCHI, KOJI KAMIYA-OKUDAIRA[a], NOBUO UENO[a], KAZUHIKO SEKI[b] and EIZI MORIKAWA[c]

Institute for Molecular Science, [a]Department of Materials Science, Faculty of Engineering, Chiba University, [b]Research Center for Material Science and Department of Chemistry, Nagoya University and [c]Center for Advanced Microstructures and Devices, Louisiana State University

We calculated photoelectron angular distributions from ω-(n-pyrrolyl)alkanethiol self-assembled monolayers (pyrrolyl-SAMs) for different π molecular orbitals, π_N and π_C, originating from the pyrrole group. The calculations were carried out within a single-scattering approximation of photoemission process. In the approximation, the photoelectron intensity is caused by not only the self-scattering waves from a pyrrole group but also the single-scattering waves scattered in the vicinity of the pyrrole group. Therefore, the angular patterns involve information on the surface arrangement of the pyrrole groups as well as the character of the molecular orbitals.

Keywords: photoelectron angular distributions; ω-(n-pyrrolyl)alkanethiol; self-assembled monolayers; single-scattering approximation

INTRODUCTION

It is usually difficult to determine quantitative molecular orientations in thin films of large organic molecules. Some experimental techniques damage their fragile surfaces during probing them, and some are not sensitive enough. As we have confirmed for several organic molecules, measurement of angle-resolved ultraviolet photoemission spectra (ARUPS) and succeeding comparison with calculated photoelectron angular distributions (takeoff and azimuthal angles dependences of photoelectron intensity) can provide quantitative information on such surfaces with less damage [1-8]. For the ARUPS technique, the reliable calculations of the photoelectron intensity are indispensable.

In our previous paper, we reported on the calculated photoelectron angular distributions from ω-(n-pyrrolyl)alkanethiol (Fig. 1) self-assembled monolayers (pyrrolyl-SAMs) for two different surface structures, face-stacked and herring-bone arrangements of pyrrole groups [9]. The calculated results of π_N state originating from the pyrrole group are significantly different between these arrangements, which suggests that the ARUPS technique can be used as a clue for studying the surface structures of the substituent groups. In this report, we focus on the photoelectron angular distributions of another molecular orbital (MO) of π_C state. It is shown that the calculated angular patterns of these π states well signify each MO character.

EXPERIMENTAL

Details of ARUPS measurement were described in elsewhere [10]. *Ab-initio* MO calculations and molecular dynamics (MD) calculations were carried out using Gaussian 98 program (Gaussian, Inc.) and HyperChem R5.1 (Hypercube, Inc.), respectively. The photoelectron intensity calculations were carried out on IBM SP2 computer at Computer Center of Institute for Molecular Science (IMS). We used the program (IAC31) written by one of authors (S. H.) which have been developed especially for organic thin films [11]. Details of these calculations were described in our previous papaer [9].

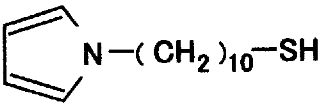


FIGURE 1 Molecular structure of ω-(n-pyrrolyl)alkanethiol.

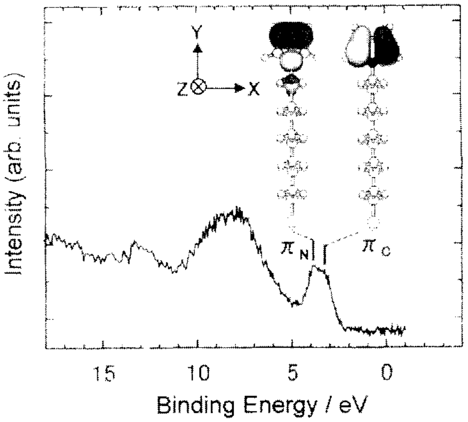


FIGURE 2 Measured ARUPS of pyrrolyl-SAMs on polycrystalline Ag substrate at $\alpha = 0°$ and $\theta = 80°$ (defined in Fig. 4). The incident photon energy was $h\nu = 37$ eV and the spectrum was measured at $T = -110°C$. Two π MOs, π_N and π_C, are illustrated in the insert.

RESULTS AND DISCUSSION

Figure 2 shows a measured ARUPS of the pyrrolyl-SAMs on a polycrystalline Ag substrate. The band assignments of the spectrum were performed by comparing with the density of states obtained by the STO-6G *ab-initio* MO calculation of a thiolate (C_4H_4N-$(CH_2)_{10}$-S-Ag) [10]. The broad band at the lowest binding energy originates from the two π states of π_N and π_C which are the MOs used in the present calculation. As graphically illustrated in the Figure, the π_N state mainly consists of both N_{2p} and C_{2p} atomic orbitals, and the π_C state consists of only C_{2p} orbitals. Note that the MO phases described by white and black lobes. The π_N state exhibits symmetrical phase for the Z-Y plane (perpendicular with respect to the pyrrole plane), whereas the phase of the π_C state is different for the plane and a node exists in the plane.

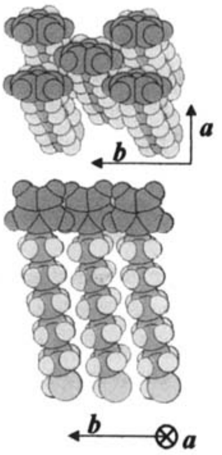
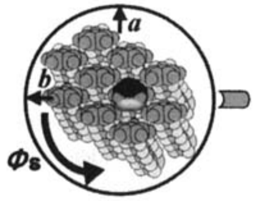
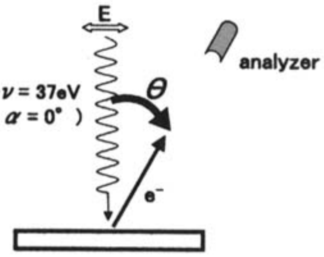


FIGURE 3 An example of surface structures in pyrrolyl-SAMs calculated by simulated annealing method.



(a) top view



(b) side view

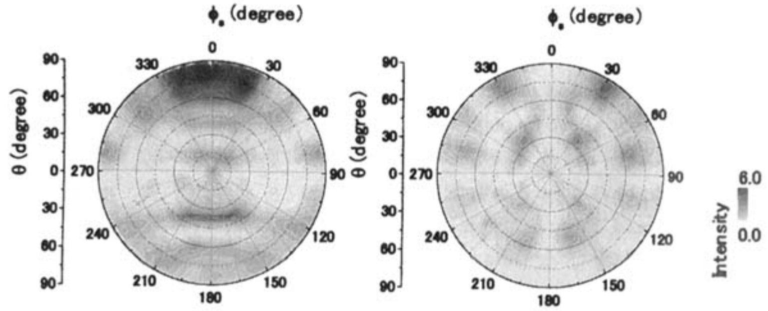
FIGURE 4 Calculation setup and definition of angular parameters. The analyzer is situated in the electric field plane of polarized light.

The surface structure of the pyrrolyl-SAMs used in the present calculations is the face-stacked arrangement of the pyrrole groups shown in Fig. 3. This was deduced by the MD calculations as an example of probable surface structures. Although the pyrrole groups in the SAMs prepared on Au films were suggested to form an open packing structure [12], we carried out the calculations with a hypothesis that the pyrrole groups are closely packed by attractive interaction of alkyl chains. This may be the case that expected for the SAMs with longer alkyl chains or on other metal substrates anchoring its sulfur headgroup.

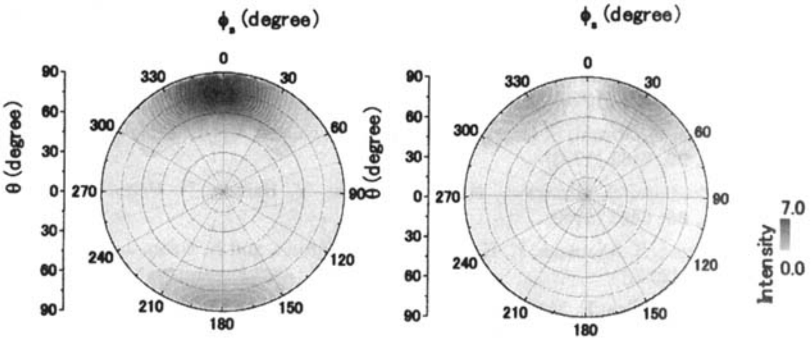
The experimental setup for the present calculations is shown in Fig. 4. In a single-scattering approximation for differential photoionization cross section, the self-scattering and single-scattering waves contribute to the photoelectron intensity [13, 14]. The self-scattering waves are the photoelectron waves which emanate from each atomic orbital constituting a MO state (for example, the π_N state is illustrated in Fig. 4 (a)) and come to an analyzer directly. The emanating waves are scattered at neighboring atoms, then come to the analyzer as the single-scattering waves. In the present calculations, the single-scattering waves were considered only for the atoms in the nearest neighboring six molecules. The analyzer is positioned within the electric field ($\boldsymbol{E}$) plane of the polarized synchrotron light (the incidence angle is $\alpha = 0°$). The takeoff angle of photoelectrons θ, which is the polar angle of the analyzer, is defined from surface normal. $\phi_S = 0°$ is defined when the lattice vector a (almost same direction with the Z axis in Fig. 2) is in the $\boldsymbol{E}$ plane.

The calculated results of the photoelectron angular distributions are shown in Fig.s 5 and 6, where the photoelectron intensity is displayed as a map with the variables of θ and ϕ_S. We first explaine the contribution of the self-scattering waves which exhibit dominant feature of the angular patterns. For the π_N state (Fig. 5 (a)), strong intensity is noticed along azimuthal direction of $\phi_S \simeq 0°$ at polar angles of $\theta = 60° \sim 90°$. This reflects that the pyrrole groups orient with their planes almost perpendicular to the substrate and face to the azimuthal direction giving the strong intensity [9]. On the other hand, no intensity along the azimuthal direction is seen for the π_C state (Fig. 5 (b)). This is due to the MO character of the initial state, that is, the π_C state has a node with respect to the Y-Z plane (see Fig. 2). Under the present calculation setup in Fig. 4, the photoelectron intensity becomes zero when the node plane coincides with the $\boldsymbol{E}$ and the analyzer plane. These calculated angular patterns well signify the characters of the π_N and the π_C state.

In addition to the self-scattering waves, we consider the contribution of the single-scattering waves. Fig.s 6 (a) and (b) show the photoelectron angular distributions calculated by using the both waves. The main angular pattern of each (a) and (b) is the almost same as that in Fig. 5, and additionally the weak pattern is seen at $\theta \leq 60°$. The angular pattern is symmetrical with respect to the direction of $\phi_S \simeq 0°$. This signifies that the neighboring pyrrole groups are arranged symmetrically along the direction to which the pyrrole groups face.



(a) π_N (b) π_C



(a) π_N (b) π_C

FIGURE 6 Calculated photoelectron angular distribution with the single-scattering approximation for (a) π_N and (b) π_C state.

Acknowledgments

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