

# Evolution of a Two-Dimensional Band Structure at a Self-Assembling Interface<sup>†</sup>

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Received: January 24, 2002; In Final Form: April 11, 2002

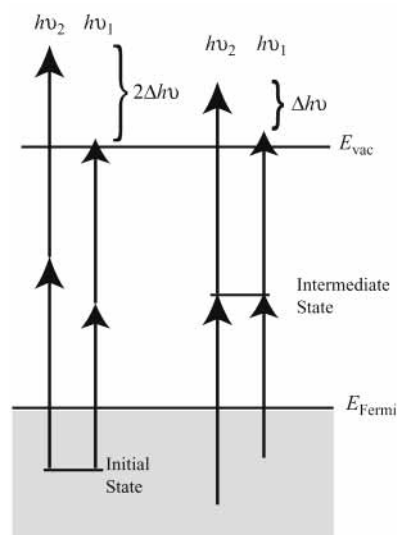
Two-photon photoemission is used to investigate the interfacial band structure of the methanethiolate/Ag(111) interface. Two adsorbate-induced electronic states are observed: one occupied, the other an unoccupied excited state. The initially occupied and unoccupied electronic states have effective masses of  $-2m_e$  and  $0.5m_e$ , respectively. At a low coverage of thiolate molecules, the unoccupied state is measured to be nondispersive. At intermediate coverages both nondispersive and dispersive unoccupied electronic states are observed. This coverage dependent evolution can be interpreted as a phase transition from a less dense to a more dense layer configuration.

## Introduction

Charge injection from a metal electrode into a molecular layer is an essential step in the operation of molecular electronic devices. A detailed understanding of the electronic structure at the metal/molecule interface is important to the investigation of molecular electronic events. Individual molecular electronic states such as HOMOs (highest occupied molecular orbitals) and LUMOs (lowest unoccupied molecular orbitals) combine to form the valence and conduction bands in molecular crystals. Electronic structure in the direction parallel to the interface can also influence charge injection and conduction perpendicular to the interface.<sup>1</sup>

Many experimental and theoretical investigations of molecular electronic devices have focused on thiolate self-assembling monolayers (SAMs).<sup>2–7</sup> Thiolate SAMs provide an excellent system for several reasons: the layer structure and assembly dynamics are well documented, chemisorption ensures a strong bond between the molecule and the substrate, self-assembly ensures structurally consistent overlayers, and current synthesis techniques can be applied to create a variety of systems to study.<sup>2,3</sup> Experiments have measured conduction through single molecules,<sup>4</sup> as well as rectification by an assembled monolayer.<sup>5</sup> Thiolate monolayer tail groups have been used to tune the Schottky energy barrier, and control charge injection into organic diode device structures.<sup>6,7</sup> The structure of the thiolate SAMs adsorbed on Ag(111) has been extensively studied.<sup>8–10</sup> Poirier and Pylant studied the adsorption of a wide variety of thiolate molecules onto a Au(111) surface using scanning tunneling microscopy (STM).<sup>11</sup>

The band structure parallel to the surface of both occupied and unoccupied states can be determined by measuring the kinetic energy of the photoemitted electron as a function of parallel momentum ( $k_{||}$ ). This is accomplished by changing the angle of the sample with respect to the detector. A dispersive electronic state is characterized by a parabolic increase in kinetic energy as a function of  $k_{||}$ . These electronic bands are fit with the equation  $E_{\text{kin}} = E_0 + \hbar^2 k_{||}^2 / 2m^*$ , where  $E_{\text{kin}}$  is the measured



**Figure 1.** Schematic picture of the TPPE process. Electron kinetic energy measurements at multiple wavelengths will distinguish initially occupied from initially unoccupied states. The kinetic energy of electrons photoemitted from initially occupied states (left) changes by twice the amount of the change in photon energy ( $2\Delta h\nu$ ). The kinetic energy of electrons photoemitted from initially unoccupied intermediate states (right) will change by the same amount as the change in photon energy ( $\Delta h\nu$ ).

kinetic energy of the electron,  $E_0$  is the electron energy at  $k_{||} = 0$ , and  $m^*$  is the effective electron mass used as a fitting parameter.<sup>12</sup> An  $m^* = m_e$  indicates a free electron dispersion. A flat band indicates a nondispersive electronic state. When single molecule properties dominate, electronic states will be nondispersive, while an electron in a dispersive band is delocalized over many molecular units. All interfacial states are localized perpendicular to the interface.

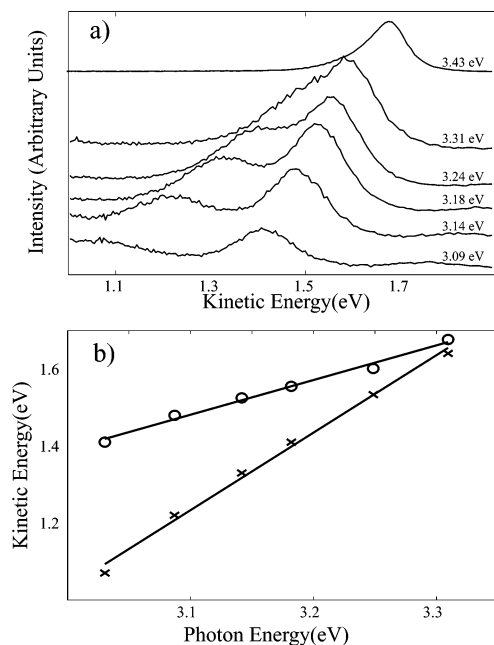
## Experimental Section

The results of an angle-resolved monochromatic two-photon photoemission (TPPE) study of the interfacial electronic structure of methanethiolate SAMs are presented as a function of coverage. This technique allows determination of the interfacial electronic band structure parallel to the surface.<sup>12–14</sup> Figure 1

<sup>†</sup> Part of the special issue "G. Wilse Robinson Festschrift".

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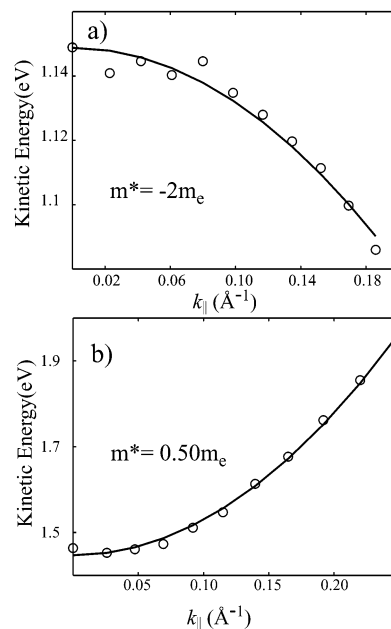
**Figure 2.** (a) Kinetic energy spectra at several wavelengths. The signal of the spectra at 3.43 eV photon energy is reduced by a factor of 4. This high signal intensity demonstrates the resonant population of the LUMO from the HOMO. (b) Kinetic energy peak maxima from (a) plotted as a function of photon energy. The slopes of the two fit lines are  $0.91 \pm 0.11$  and  $2.01 \pm 0.11$ , or 1 and 2 within error, and clearly indicate that one state is initially occupied and that the other is initially unoccupied.

depicts the TPPE process for electrons photoemitted from both occupied and unoccupied states.

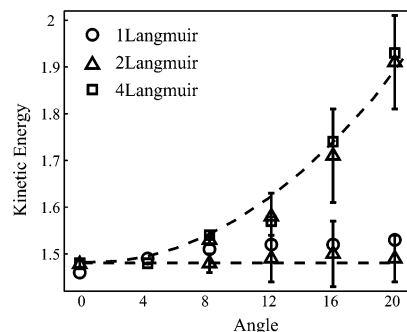
Dimethyl disulfide ( $\text{CH}_3\text{SSCH}_3$ ) dissociates and forms methanethiolate ( $\text{CH}_3\text{S}^-$ ) upon exposure to noble metal surfaces.<sup>2,3,15,16</sup> A leak valve was used to introduce dimethyl disulfide into an ultrahigh vacuum chamber containing the Ag(111) surface. The sample was exposed at 297 K, and the temperature was then decreased to 120 K to improve signal quality. The data reported here were taken at exposures of 1, 2.5, and 4 langmuir. At 4 langmuir, low-energy electron diffraction spots are observed, indicating an ordered overlayer, and the TPPE signal does not continue to evolve with increased exposure. The electron diffraction pattern is consistent with the results previously observed for thiulates on Ag(111).<sup>17</sup> For these reasons, the 4 langmuir exposure will be referred to as the saturated monolayer. The work function was determined to be 3.2 eV by fitting an image state progression in the saturated monolayer to a quantum defect. The electronic energies of the adsorbate induced states are the same at all three coverages.

## Results

Two adsorbate-induced electronic states are observed in the TPPE spectrum for a saturated monolayer of methanethiolate/Ag(111). Figure 2a shows the kinetic energy spectra for several wavelengths. The slopes fit in Figure 2b indicate that one of the thiolate electronic states is initially occupied and the other is an initially unoccupied intermediate state. The occupied state, or HOMO, is located 1.8 eV below the Fermi level. The unoccupied state, or LUMO, is located 1.6 eV above the Fermi level.<sup>18</sup> Resonant enhancement of the photoemission signal is observed as the photon energy approaches the energy difference between the two states, indicating that a direct HOMO to LUMO transition occurs. The interfacial thiolate electronic states are assigned as such because no silver peaks are located at the observed energies prior to thiolate absorption. The unoccupied



**Figure 3.** Dispersions of the HOMO and LUMO for the saturated monolayer and the fits (solid lines). (a) The occupied band has an effective mass of  $-2m_e$ . (b) The unoccupied band has an effective mass of  $0.5m_e$ .

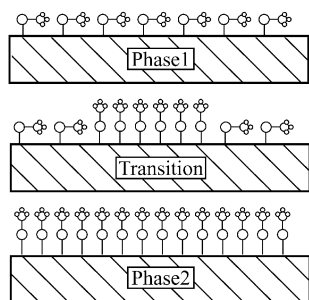


**Figure 4.** Dispersion measurements of the unoccupied state at three coverages. The open circles show the nondispersive behavior at 1 langmuir. The triangles show both dispersive and nondispersive behavior observed at 2.5 langmuir. Finally, the squares show the 4 langmuir saturated monolayer dispersion. Error bars are shown for worst case, the 2.5 langmuir coverage.

state is in the band gap of the Ag(111) surface where other surface states are not observed. The occupied state is located at an energy where silver has a constant density of states.

For the saturated monolayer, both of the observed adsorbate states are dispersive, as seen in Figure 3. The unoccupied band has an effective mass of  $0.50m_e \pm 0.05$ . The kinetic energy of electrons from the occupied band decreases with increased  $k_{\parallel}$ , fitting an effective mass of  $-2m_e \pm 0.5$ . At lower coverages, the LUMO is observed to be nondispersive. Figure 4 shows dispersion measurements for the unoccupied state at three different exposures.

At a 1 langmuir exposure, the state is nondispersive. By the 2.5 langmuir exposure, both dispersive and nondispersive states are observed. The effective mass of the dispersive signal at the 2.5 langmuir coverage is the same as for the complete monolayer. At complete saturation (4 langmuir) the nondispersive feature has mostly disappeared. At intermediate coverages other than the 2.5 langmuir data in Figure 4, both dispersive and nondispersive signals are seen. The intensity of the dispersive (nondispersive) signal increases (decreases) as a function of increased exposure. The coverage dependent disper-



**Figure 5.** (a) Methanethiolate adsorbed laying flat against the surface. (b) Both flat and upright geometries. (c) All of the molecules upright corresponding to the saturated monolayer.

sion measurements clearly show an abrupt transition from a non-dispersive molecular state into a dispersive, delocalized electronic state. No gradual shift of the effective mass as a function of coverage was observed. Dispersion measurements for the occupied state at submonolayer coverage have an effective mass that is too large and a signal-to-noise ratio that is too small to distinguish between dispersive and nondispersive behavior.

### Discussion

Thiolate interfacial electronic states have been seen recently for several molecules on a Cu(111) surface. Nondispersive HOMO and LUMO states,<sup>19</sup> as well as dispersive LUMO and LUMO+1 states, have been observed.<sup>20</sup> Dispersion measurements for these states were mentioned but not published due to poor detector resolution. The angle-resolved measurements reported here for adsorption on a Ag(111) surface show that both states are dispersive. The small effective mass of the unoccupied band ( $0.5m_e$ ) is indicative of a dispersive electronic state with large overlap between neighboring thiolate molecular orbitals. While still dispersive, the larger magnitude of the unoccupied band's effective mass ( $-2m_e$ ) indicates less overlap between the molecular orbitals. Within the tight binding approximation, the negative effective mass of the occupied band is consistent with  $\pi$ -type orbitals possessing nodal planes perpendicular to the surface. This is in agreement with calculations of copper thiolate molecules, whose HOMO is primarily composed of sulfur 3p orbitals with a nodal plane parallel to the S—Cu bond axis.<sup>20</sup>

The simultaneous observation of the dispersive and nondispersive unoccupied states, with no gradual transition between the two, is strongly indicative of a phase transition. Though the chemisorption and data collection occurred at different temperatures, the phase transition was not observed with the temperature change, but rather with the change in coverage. This is consistent with the coverage dependent STM studies of Poirier and Pylant.<sup>11</sup> Their observations show that as the coverage is increased, a lattice gas condenses into a more solidlike phase, with the assembly chains parallel to the surface. A further increase in coverage results in a phase transition to a more dense layer with the chains standing up from the surface and the sulfur atoms from neighboring molecules packed closer together. This process is depicted in Figure 5 and is consistent with the energetics of a methanethiolate molecule adsorbed on a Ag(111) surface. The adsorbed molecule is slightly more stable with the sulfur—carbon bond parallel to the surface than with the S—C bond normal to the surface.<sup>8</sup> With greater coverages, the attractive interaction between carbon chains on neighboring molecules and the increased energy of chemisorption should result in more dense layers with upright chains.

The data are consistent with the following picture. At a coverage of 1 langmuir, the thiolate layer resides mostly in the

low-density phase with the chains parallel to the surface (Figure 5a). This places the sulfur atoms further apart, influences the molecular orbital orientation with respect to the other molecules, and prevents significant overlap of molecular orbitals. By the 2.5 langmuir coverage range, significant area corresponding to islands of upright chains have appeared (Figure 5b). The sulfur atoms are closer together and the molecular orbitals at the linkage between the thiolate and the surface overlap, creating a dispersive electronic state. As the coverage is increased, the islands grow to dominate the spectra (Figure 5c) and the dispersive signal increases in strength while the nondispersive signal disappears. This phase transition is shown by the abrupt nature of the change in band structure.

### Conclusion

This study presents the first quantitative measurement of the two-dimensional band structure of the methanethiolate/Ag(111) interface. The nondispersive to dispersive transition, effective masses of the adsorbate bands, and the HOMO to LUMO excitation are the major results of this study. The observed coverage dependence demonstrates the interdependence of the crystal structure and the electronic structure. Control of interfacial electronic structure is crucial for device fabrication, where a dispersive electronic state can enhance electron transport. In this work the electronic structure was varied by changing the coverage, but other methods of structural control may also be used to influence the interfacial electronic structure.

**Acknowledgment.** This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under ContractNo.~DE-AC03-76SF00098. We acknowledge NSF support for specialized equipment used in the experiments described herein.

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