

Metal Work-Function Changes Induced by Organic Adsorbates: A Combined Experimental and Theoretical Study

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(Received 2 February 2005; published 22 July 2005)

The role of molecular dipole moment, charge transfer, and Pauli repulsion in determining the work-function change ($\Delta\Phi$) at organic-metal interfaces has been elucidated by a combined experimental and theoretical study of $(\text{CH}_3\text{S})_2/\text{Au}(111)$ and $\text{CH}_3\text{S}/\text{Au}(111)$. Comparison between experiment and theory allows us to determine the origin of the interface dipole layer for both phases. For $\text{CH}_3\text{S}/\text{Au}(111)$, $\Delta\Phi$ can be ascribed almost entirely to the dipole moment of the CH_3S layer. For $(\text{CH}_3\text{S})_2/\text{Au}(111)$, a Pauli repulsion mechanism occurs. The implications of these results on the interpretation of $\Delta\Phi$ in the presence of strongly and weakly adsorbed molecules is discussed.

DOI: [10.1103/PhysRevLett.95.046804](https://doi.org/10.1103/PhysRevLett.95.046804)

PACS numbers: 73.30.+y, 79.60.Dp

The mechanism determining work-function changes, $\Delta\Phi$, and electronic level alignment in molecular adsorbates on metal surfaces is an open issue with important implications for the design of electronic devices [1,2]. Weakly interacting adsorbates, such as alkane molecules, are known to decrease the metal work function as much as 1.0 eV [3]. In the case of Xe adsorption on metal surfaces, it has been demonstrated that the dominant origin of the interface dipole responsible for $\Delta\Phi$ is Pauli repulsion [4,5]. However, the extension of this finding to more complex molecular systems is still a matter of debate.

For chemisorbed systems, the picture is even more complex, due to the possible interface charge rearrangement determined by bond formation. Of particular interest, are self-assembled monolayers (SAMs) of sulfur containing organic molecules on gold [6,7]. For these materials, there are at least two, mutually exclusive, concepts currently in the literature describing the nature of the interfacial charge distribution. Theoretical studies suggest that a metal \rightarrow molecule charge transfer occurs [8,9], an observation that plays a central role in the recent interpretation of giant magnetic phenomena [10,11]. On the contrary, photoemission studies of a series of thiolate/Au SAMs [12,13], and theoretical calculations [14] suggest that charge transfer in these materials is small and plays a negligible role in the interfacial electrostatics.

To address these issues, we have undertaken a detailed ultraviolet and x-ray photoemission (UPS, XPS) and high-resolution electron energy loss spectroscopy (HREELS) study combined with first principles electronic structure calculations to probe the interfacial electrostatics of adsorbed dimethyldisulfide, $(\text{CH}_3\text{S})_2$ (DMDS), and methylthiolate, CH_3S (MT), on the Au(111) surface. DMDS is known to adsorb dissociatively on Au(111) at $T > 200$ K, by rupturing the central S-S bond, forming a stable ordered

MT monolayer [15]. Here, we provide the first experimental evidence that a metastable phase of weakly adsorbed DMDS exists at $T < 150$ K. This phase, referred to as a DMDS layer, evolves into the strongly adsorbed MT by simply increasing the temperature above 200 K. This provides us with a unique route for investigating the evolution of the interface electronic properties upon switching from weak adsorption to chemisorption.

All measurements were performed in an ultrahigh vacuum chamber with base pressure 7×10^{-11} mbar. The Au sample was cleaned through sputtering-annealing cycles to 730 K, while DMDS was dosed in the chamber through a leak valve, after pump-freeze-thaw purification cycles. The energy resolution in XPS measurements and in the determination of work-function change was of 2.0 and 0.1 eV, respectively. HREELS measurements were performed with a Leybold ELS 22 spectrometer, with energy resolution better than 6 meV. If not otherwise stated, all measurements reported in the following refer to a $T = 100$ K exposure of 3 langmuir DMDS [1 langmuir (1 L) $\equiv 1 \times 10^{-6}$ torr s], which corresponds to a coverage of about 0.6 monolayer, as determined by XPS [16].

Electronic structure calculations were performed within the gradient corrected density functional approximation [17], periodic boundary conditions, and norm-conserving pseudopotentials using a plane-wave basis set with energy cutoff of 45 Ry. Calculations were carried out with the implementation of the free energy functional [18] within the CPMD code [19]. Binding geometries and energetics of MT and DMDS on Au(111) have been extensively studied by similar methodologies [8,20,21]; thus we focus on the previously reported lowest energy binding configurations of both species. For MT, we employ a single molecule in a $(\sqrt{3} \times \sqrt{3})R30^\circ$, whereas for DMDS, a $c(3 \times \sqrt{3})$ cell is employed providing an identical 1:3 S: Au ratio. Calculations

lations for a S:Au ratio of 1:6 are performed by doubling the unit cells along the shortest cell vector and removing the second adsorbate. All structures were calculated using a six Au atom thick slab which is periodic in the (x, y) plane with an 8–10 Å vacuum layer, with fully optimized geometries and converged with respect to Brillouin zone integration: an $8 \times 8 \times 1$ and $4 \times 6 \times 1$ Monkhorst-Pack k mesh for MT and DMDS, respectively. The work function, Φ , is calculated from the difference in energy between the value of the electrostatic potential, V_{ES} , in the vacuum region and E_{Fermi} . The dipole layer arising in the vacuum region as a result of the periodic boundary conditions was subtracted. Reported molecular electronegativities are obtained by half the difference between the calculated first ionization potential and electron affinity.

The formation of the DMDS layer at 100 K has been studied by both HREELS and XPS. In Fig. 1, the evolution of its vibrational spectrum as a function of annealing temperature is reported. The HREELS spectrum of the MT monolayer (obtained by dosing DMDS at room temperature) is also shown for comparison (upper curve). The most intense feature of the MT spectrum is located at 30 meV, and corresponds to the S-Au stretching mode [21,22]. Weaker features, observed above 100 meV, have been assigned to modes involving C and H [21,22]. In the $T = 100$ K DMDS spectrum the energy position of the main peak is redshifted to 16 meV. Upon annealing to 250 K, this feature disappears, transforming into the 30 meV thiolate S-Au peak. We thus associate the 16 meV feature with the S-Au stretching mode of the DMDS layer. The observed energetic redshift of this mode indicates that the S-Au interaction in the DMDS layer is sensibly weaker than in the dissociatively chemisorbed MT. A smaller but similar redshift, from 30 to 25 meV, has been recently reported for dioctadecyl sulfide adsorption on Au(111) [23].

This assignment is confirmed by the evolution of the binding energy of the S $2p$ core level, as measured by XPS.

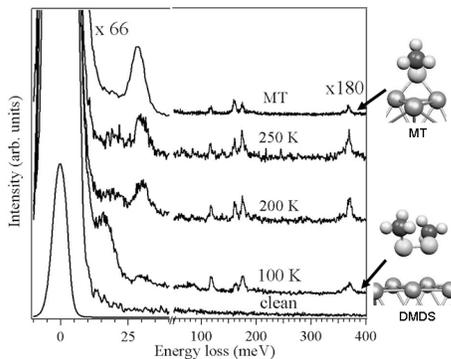


FIG. 1. HREELS spectra of DMDS as a function of annealing temperature. MT spectrum is also shown (upper curve). Spectra were taken in specular geometry ($\theta_{in} = \theta_{out} = 60^\circ$), with primary beam energy of 4.2 eV and energy resolution better than 6 meV.

The S $2p_{1/2}$ core level peak of the $T = 100$ K DMDS layer is found at 163.8 eV, a value typical of weakly adsorbed thiol and disulfide [24]. Upon annealing, and in concomitance with the appearance of the HREELS peak at 30 meV, the S $2p$ core level shifts to a binding energy of 162.0 eV, a value typical of chemisorbed thiolate layers [24]. The combination of HREELS and XPS data therefore demonstrates unambiguously the existence of a weakly adsorbed phase of DMDS at low temperature, which evolves into MT upon annealing above 150 K.

We study the influence of the nature of molecule-metal interaction on Φ by UPS measurements of the electron secondary edge. Relative to the clean Au surface, Φ decreases by -1.2 eV upon deposition of a full MT monolayer at room temperature (corresponding to 5 L exposure; see Fig. 2). For DMDS deposition, the $\Delta\Phi$ variation with exposure reaches a plateau around -1.5 eV and then saturates at -1.9 eV. The first plateau corresponds to a coverage region between 0.6 and 1 monolayer (ML) (as estimated by XPS), while the saturation is reached with the formation of a physisorbed multilayer (as indicated by UPS valence band measurements). In Fig. 3 we show the evolution of $\Delta\Phi$ for the 0.6 ML DMDS layer upon annealing. The $\Delta\Phi$ initial value is -1.5 eV at 100 K, which progressively reduces to -1.0 eV around 250 K. Such a reduction cannot be attributed to desorption processes, which are ruled out by the constant value of the S $2p$ peak intensity. We therefore attribute the change in $\Delta\Phi$ to the modification in the chemical nature of the interface induced by the dissociation of DMDS into chemisorbed MT.

To understand these observations, we performed DFT simulation on DMDS and MT layers at ratios of S:Au of 1:3 and 1:6 corresponding to full and half coverage, respectively. Simulations of full-coverage MT/Au(111) place the lowest energy configuration of the thiolate at a bridge site with a binding energy of 0.6 eV relative to gas phase DMDS, in agreement with the experimentally measured 0.65 eV [25] and previous theoretical studies [20,21].

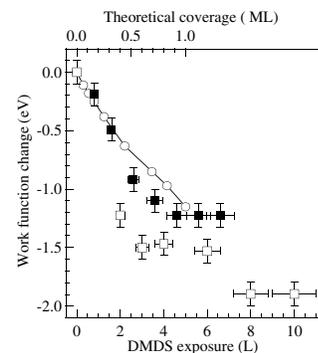


FIG. 2. Comparison of $\Delta\Phi$ as a function of dosage for DMDS deposition at $T = 100$ K (open squares) and at room temperature, to form a MT phase (filled square). A comparison based solely upon the calculated MT molecular dipole layer as a function of coverage (open circle) is also given.

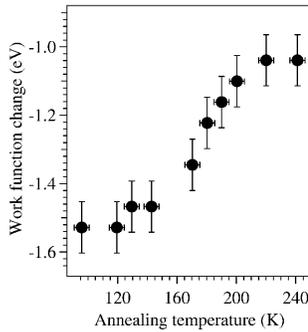


FIG. 3. Change of $\Delta\Phi$ upon annealing of 0.6 ML DMDS.

The structure is characterized by the S atom residing ≈ 2.0 Å above the Au surface with a S-C bond that is tilted by an angle $\theta_{\text{tilt}} = 54^\circ$ relative to the surface normal. For DMDS, we find a stable minimum with binding energy ≈ 0.1 eV, $\theta_{\text{tilt}} = 56^\circ$, and S atoms ≈ 3.0 Å above the surface. The DMDS results may be affected by uncertainties due to the lack of dispersion forces within DFT; however, they clearly indicate a weaker Au-S interaction in accord with the HREELS results.

We consider the calculated V_{ES} for Au(111) with, and without, the molecular adsorbates; see Fig. 4. The clean Au(111) surface reproduces the experimental value of $\Phi_{\text{Au}} = 5.35$ eV. For the MT phase, $\Delta\Phi = -0.8$ and -1.2 eV for half and full coverage in agreement with the experimental values in Fig. 2. For DMDS at half coverage, $\Delta\Phi = -1.0$ eV, which is lower than the MT phase by 0.2 eV, matching the experimental trend but underestimating the magnitude by about 0.2 eV [26]. Experimentally, at low temperature it is not possible to obtain a complete

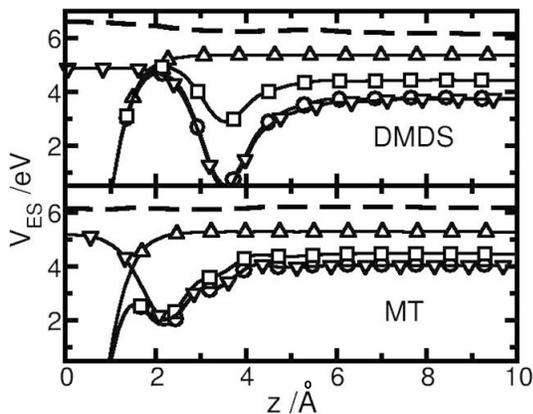


FIG. 4. V_{ES} for DMDS/Au(111) (upper panel) and MT/Au(111) (lower panel) at full (circles) and half (squares) coverage. The zero of the energy is set to the Au Fermi level. The difference (dashed line) between the full-coverage data and a neutral bulk Au slab (upward triangle) plus molecular layer (downward triangle) shows the resulting potential induced by interfacial charge rearrangement. Note that molecular layer and difference curves are shifted by a constant.

DMDS monolayer before starting to grow successive physisorbed layers. We therefore cannot directly compare the theoretical value of $\Delta\Phi$ of the full DMDS monolayer with the corresponding experimental value. Nevertheless, an extrapolation for the full monolayer can be obtained from the coverage dependence of $\Delta\Phi$ (see Fig. 2), leading to a value between -1.5 and -1.7 eV, which matches the theoretical $\Delta\Phi = -1.6$ eV.

The good agreement between experiment and theory indicates that the necessary components to understand the origin of the observed $\Delta\Phi$ are captured by our simulations. To this end, we have considered separately the subsystems containing the Au surface slab and molecular layer and compared the sum of their V_{ES} to that of the total system. For MT/Au(111), V_{ES} is almost exactly the sum of that for a neutral MT layer and a Au(111) surface with no additional contribution from a charge transfer (see Fig. 4 where the difference potential is constant across the interface). Considering the calculated chemical potentials [or electronegativity (EN)], it is straightforward to understand the lack of charge transfer in the MT layers as EN for gas phase MT (EN = 5.4 eV) is almost equal to that of Au(111) (EN = 5.3 eV). Thus, $\Delta\Phi$ can be ascribed almost entirely to the dipole moment of the MT molecular layer. Noting that $\Delta\Phi = 4\pi\rho\mu\cos(\theta_{\text{tilt}})$, where μ is the molecular dipole and ρ the density of molecules at the surface, it is found that the experimental values of $\Delta\Phi$ imply $\mu = 1.4$ and 1.2 D, at half and full coverage. This is significantly lower than the 1.9 D value calculated from the gas phase molecule, a discrepancy that we attribute to the depolarization field generated on a molecule by its neighbors. In order to confirm this idea, we calculated the molecular dipole of an isolated thiolate layer as a function of layer density (i.e., coverage). We model the layer density by gradually increasing the distances between the MT molecules and calculating the estimated $\Delta\Phi$ from the drop in V_{ES} . The obtained values are compared in Fig. 2 with the room temperature experimental data, showing a remarkably good agreement. The underestimation of theoretical values relative to the experiment at intermediate coverage can be rationalized by the formation of full-coverage islands, as indicated by the presence of $(\sqrt{3} \times \sqrt{3})$ spots in the low-energy electron diffraction images at 0.7 ML [27].

Our analysis also provides an explanation as to *why* the weakly bound DMDS lowers Φ more than the chemisorbed MT. The decomposition of V_{ES} into molecular and surface components shows the molecular dipole layer to induce a 1.1 eV drop, almost the same as MT; see Fig. 4. However, the difference curve reveals a jump across the interface that accounts for the remaining component of $\Delta\Phi$ as resulting from a shift in density *from* the molecule *toward* the interface at both coverages. We note that the EN = 5.3 eV of DMDS is the same as Au(111), and hence there is no charge transfer between the molecule and the Au substrate. Thus, we interpret the observed charge displacement as

arising from the shift of the diffuse tail of the Au surface electron density back toward the metal slab via Pauli repulsion with the electrons of DMDS, similar to the case of the Xe [4,5].

The combination of the first experimental observation of a weakly adsorbed DMDS phase with $\Delta\Phi$ measurements and DFT calculations has allowed us to obtain a very complete yet simple picture of the interfacial electrostatic in this system. The quantitative agreement between calculated and experimental values of $\Delta\Phi$ in the MT/Au(111) system clearly demonstrates that no significant charge transfer occurs at this interface, in agreement with more indirect experimental indications. Our analysis underscores the crucial role in determining charge rearrangement played by electronic chemical potential alignment of the molecule and the metal [2]. Given that the EN values fall in the range of 5.3–5.4 eV for alkane thiolates [14], these conclusions may be extended to SAMs of these molecules. As a corollary, modification of the alkyl chain can be used to systematically alter this balance and change $\Delta\Phi$ as demonstrated by the fact that biphenyl-dithiol (EN = 5.7 eV) is found to exhibit a metal-to-molecule charge transfer on Au(111) [28]. Similar arguments may also be extended to finite sized nanoparticles where the EN values of the metal may be tuned by modifying the number of atoms within the cluster. The lack of a charge transfer from gold to alkane thiolates also raises questions as to the interpretation of the magnetic phenomena observed in these films [10,11]. For DMDS the observed larger $\Delta\Phi$ values provide evidence for the role played by Pauli repulsion in complex weakly adsorbed molecules. However, it is important to note that the dominant electrostatic component for both strongly and weakly adsorbed species is the net molecular dipole. Future work will extend this understanding to encompass molecular level alignment in this class of materials.

We acknowledge partial support from INFN through “Parallel Computing Initiative,” and from MIUR through PRIN 2003 and FIRB NOMADE. We thank L. Casalis, A. Morgante, G. Scoles, and E. Tosatti for discussions.

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