An experimental and theoretical investigation of the thiophene/aluminum interface

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The adsorption of thiophene and 2, 2'-bithiophene on Al(111) has been studied using thermal desorption spectroscopy (TDS), angle-resolved UV photoemission (ARUPS), and work function measurements. Ab initio density functional theory calculations have been performed for thiophene on Al(111). Both thiophene and bithiophene bond very weakly to Al(111), as indicated by TDS and calculations of the thiophene absorption energy, which is found to be only 0.54 eV. There is no indication of π-bonding in either the ARUPS data or the calculations. The calculated S–Al distance, 3.7 Å, is much greater than either measured or calculated S–metal distances for covalent bonding. The bonding is shown to be almost entirely electrostatic, with a small contribution from the sulfur lone pair. This is in direct contrast to calculations for Al–thiophene complexes which show covalent bonds between the Al atoms and the thiophene α carbons. The calculations show the molecule to be essentially flat, with a tilt angle of only 2° of the molecular plane relative to the surface. There is some indication of self-assembly of bithiophene on Al(111). © 2001 American Institute of Physics. [DOI: 10.1063/1.1332080]

I. INTRODUCTION

The nature of the interface of large organic molecules with metal surfaces is of growing technological interest, since these interfaces play a leading role in the determination of many important operational parameters in devices based on electroactive organic materials.1 One of the most promising families of organic materials for device applications is that of oligo- and polythiophenes.2 Thiophene (Fig. 1) is a five-membered sulfur containing aromatic compound, and the bonding of adjacent thiophene units to form oligomers or polymers is usually via the α carbons, i.e., the carbons neighboring the sulfur atom, as also occurs in 2,2'-bithiophene (Fig. 1), hereafter referred to as bithiophene for simplicity. As can be seen from Fig. 1, thiophene and bithiophene represent good models for the larger molecules and understanding their interfaces with Al is relevant to devices based around the latter. In addition both molecules are available commercially with high purity, and can be readily dosed in the gas phase into ultra high vacuum for controlled surface science studies of the organic–metal interface.

In oil refineries, organosulfur compounds such as thiophenes are catalytically removed from the oil by the so-called hydrodesulfurization process,3 using metal-based catalysts. This has led to an interest in the fundamental interactions of thiophene with metal surfaces, and largely as a result the literature contains surface science studies of thiophene on several different catalytically active metals: Fe(100),4 Ni(100),5,6 Cu(100),5,7 Cu(111),8,9 Mo(110),10,11 Ru(0001),12 Rh(111),13 Pd(111),14 Pd(100),14 Ag(111),15 Pt(111),16 and Pt(100).16 In most cases reasonably strong bonds to the surface were indicated, as thiophene was found not to desorb molecularly from the surface, but rather break up upon heating. In some cases breakup begins at temperatures as low as 100 K, e.g., Ni(100) (Ref. 6) and Fe(100).4 Only on Cu(100),7 Cu(111),9 Ag(111),15 and Ru(0001) (Ref. 12) was intact molecular desorption observed from the monolayer, although in the case of Ru(0001) this was attributed to the passivation of the surface by decomposition products.12 Where orientation of the molecule has been determined, it has almost invariably been found to lie with the ring parallel to the surface, the exception being Fe(100) (Ref. 4) where partial breakup is already indicated, although in some cases high coverage phases have been found, e.g., on Mo(110) (Ref. 11) and Pt(111),16 where the ring is inclined.

Bithiophene has been studied on a rather smaller range of metal surfaces: Al(111),17,18 Ni(110),16,18-22 Cu(110),18 and Ag(111),15,23 Where orientation has been determined—for Al(111),17 Ni(110),20,21 and Ag(111) (Refs. 15,23)—the molecule has again been found to lie with the ring planes parallel to the surface.

Parallel geometry is often taken as an indication of bonding via the ring π-electrons. This type of bonding is visible in angle-resolved UV photoemission (ARUPS) as a shift towards higher binding energy of the π-orbitals with

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charge transfer, with no emission, also adopts a flat-lying geometry. Thus the absence of geometry, the reverse is not true. Benzene on Al is a general feature of thiophene, with again covalent bonds indicated, except for the interactions of atoms of V, Cr, Cu, and Au with polythiophene molecule. Similar calculations have been performed though for the interactions of atoms of V, Cr, Cu, and Au with thio-muirs and thiophene. This so-called $\pi$-stabilization is a general feature of $\pi$-bonding of aromatics to surfaces, and has been observed in a wide range of benzene studies. Although $\pi$-bonding is invariably accompanied by a parallel geometry, the reverse is not true. Benzene on Al(111), which bonds via a purely electrostatic mechanism involving no charge transfer, with no $\pi$-stabilization observed in photoemission, also adopts a flat-lying geometry. Thus the absence of $\pi$-stabilization cannot be taken as an indication of a nonparallel geometry.

The most commonly used metal for the electron injecting contact in prototype devices is aluminum. There have been a number of theoretical studies of the interaction of Al with thiophenes. However these studies have been of isolated Al atoms with individual thiophene molecules, which is perhaps better described as a complex than as an interface. These studies indicated the formation of covalent bonds between the Al atoms and the $\pi$ carbons of the thiophene molecule. Similar calculations have been performed for the interactions of atoms of V, Cr, Cu, and Au with thiophene, with again covalent bonds indicated, except for Au, where no interaction was found.

It is by no means clear that these calculations can be regarded as representative of a true thiophene–metal interface. It is usual for the electron injecting metal contact in devices to be evaporated onto the organic, and thus the initial stages of interface formation are likely to involve the interaction of isolated metal atoms with an organic. However, the final interface is of a metallic solid with the organic, which is a very different situation. Where experimental studies have been performed of Al deposited on thiophenes, the results have been ambiguous. While x-ray photoemission (XPS) data from the S and C core levels indicate the formation of new species, paradoxically the valence band spectra remain essentially unchanged. In particular the description of the valence band spectra of sexithiophene as undergoing ‘dramatic changes’ upon Al adsorption is rather overstating the case. What is seen in both cases is some smearing out of the existing features, with no indication of any change in the vibrational structure; while some evidence for Al–C vibrations is suggested, surprisingly no change in the vibrational spectrum of sexithiophene has been observed.

In this article we report studies of the interfaces of thiophene and bithiophene with Al(111), an unambiguously metallic form of aluminum, using angle-resolved UV photoemission (ARUPS), thermal desorption spectroscopy (TDS), and $ab$ initio calculations.

II. EXPERIMENT

The experiments were performed in an ultra high vacuum chamber, with a base pressure of $10^{-10}$ mbar equipped with optics for low energy electron diffraction (LEED), and a mass spectrometer for thermal desorption studies. Sample temperature was measured by a thermocouple in direct contact with the sample, for which an ice reference was used during thermal desorption. The sample manipulator permitted cooling to 90 K. The ARUPS data were taken using unpolarized He I radiation ($h\nu=21.2$ eV), and a Vacuum Generators ADES 400 angle-resolving spectrometer, with an overall energy resolution of 100 meV, determined from measurements of the Al(111) Fermi level. The Al(111) sample was cleaned using cycles of Ar$^+$ sputtering, and annealing (675 K). Surface cleanliness was checked using UV photoemission, as the valence band line shape of Al(111) is extremely sensitive to contamination. After sample cleaning was complete, LEED showed an excellent 1×1 pattern. Thiophene and bithiophene (Fluka AG, >98% pure) were further purified using freeze–thaw cycles. Thiophene was dosed via the background, while bithiophene was dosed either from the background or via a pinhole doser from a volume at 380 K to maintain a suitable partial pressure (see Ref. 19 for details). Dosages quoted here, in langmuirs (L), where 1 L = $10^{-6}$ mbar.s, are based on uncorrected ion gauge readings.
III. THEORY

The calculations were performed using the Vienna \textit{ab initio} simulations package (VASP).\textsuperscript{34–36} VASP performs an iterative solution of the Kohn–Sham equations of local density functional (LDF) theory, using residuum minimization techniques. It is based on a plane wave basis set which facilitates the calculation of the Hellmann–Feynman forces. The electron–ion interactions are described using projector-augmented wave (PAW) potentials\textsuperscript{37,38} with a cutoff energy of 400 eV. The calculations were performed using the Perdew–Wang-91 functional\textsuperscript{39} derived from the generalized gradient approximation (GGA) for the exchange-correlation energy.

The surface was modeled using a periodically repeated slab. In the surface plane the thiophene molecules were assumed to form a (\sqrt{7} \times \sqrt{7}) R19.1° superstructure resulting is seven Al atoms per layer. This coverage allows the description of the adsorption of molecular thiophene. Higher coverages, although maybe interesting for the aspect of self-organization of the molecules, were not taken into account. The slab consisted of five layers of Al where the uppermost layer of the substrate was allowed to relax. As even the adsorption on a four-layer slab led to similar results the thickness of the slab was not increased further. For the determination of the adsorption geometry all degrees of freedom of the thiophene molecule were allowed to relax according to Hellmann–Feynman forces. Several high symmetry sites of the surface were chosen for the starting configuration: the on-top, the bridge, and the hollow site were probed with the symmetry plane of the molecule parallel (orientation A) or perpendicular (orientation B) to the surface rows. All calculations have been performed using the theoretical equilibrium constant of 4.052 Å for the Al substrate. The Brillouin zone integration has been performed using a $6 \times 6 \times 1$ Monkhorst–Pack grid.

IV. RESULTS AND DISCUSSION

A. Thermal desorption

Thermal desorption spectra for the parent molecules, for increasing exposures of thiophene and bithiophene on Al(111) at 90 K, are shown in Fig. 2. Possible cracking products, notably molecular hydrogen, were also monitored, but only molecular desorption of the parent was observed after which the surface appeared clean. Desorption of the condensed multilayer occurs at 144 K (thiophene) and 218 K (bithiophene). These temperatures are consistent with those of thiophene\textsuperscript{12,15} and bithiophene\textsuperscript{11} on other metals. The multilayer desorption temperature of bithiophene on Ag(111) was found to be 162 K,\textsuperscript{15} i.e., almost 50 K lower, but the authors were unable to calibrate their temperature scale, so this difference cannot be regarded as significant.

Desorption from the saturated monolayer, reached at exposures of 6 L and 1 L for thiophene and bithiophene, respectively, occurs at 156 K (thiophene) and 255 K (bithiophene). In both cases the monolayer desorption temperature is only slightly higher than that of the multilayer, indicating surface bonds only slightly stronger than the van der Waals interactions between molecules within the multilayer. This was also observed for benzene/Al(111),\textsuperscript{25} but in that case monolayer desorption occurred only 6 K higher than that of the multilayer, suggesting that for the thiophenes the bonding is slightly stronger than the purely electrostatic bond of benzene/Al(111). In comparison, the monolayer desorption temperatures of thiophene from Ag(111),\textsuperscript{15} Ru(0001),\textsuperscript{12} and Cu(100) (Ref. 7) are 148, 170, and 240 K, respectively, although the Ag(111) figure may again be underestimated due to temperature calibration problems.\textsuperscript{15} This suggests that the bonding strength on Al(111) is comparable to that on a noble metal and a passivated surface, and significantly weaker than that on Cu(100). Note that for all the other surfaces on which thiophene has been studied, molecular desorption does not occur; rather the molecule breaks up, further evidence that the bond on Al(111) is relatively weak. For bithiophene, the monolayer desorption temperature on Al(111) is only $\sim$35 K higher than that of the multilayer, suggesting that the bond to the surface is weaker than on compared to Ag(111),\textsuperscript{15} where
the monolayer desorbs at a temperature ~70 K higher than the multilayer.

B. Work function changes

Figure 3 shows the work function changes upon thiophene and bithiophene adsorption. In both cases adsorption causes a lowering of the work function. This is often taken to imply charge transfer, but this is not necessarily the case. For benzene/Al\(^{~111}\), where no charge transfer is indicated, the molecule induces a dipole within the Al\(^{~111}\) surface, which results in a lowering of the work function by ~0.2 eV.\(^{25}\) Taking the values of the exposures required to obtain saturated monolayers, as determined from the thermal desorption results of Fig. 2, the thiophene and bithiophene monolayers were found to lower the work function by 0.2 eV, giving monolayer work function values of 4.1 eV and 4.2 eV, respectively.

C. Angle resolved UV photoemission

Figures 4 and 5 show normal emission ARUPS spectra of thiophene and bithiophene on Al\((111)\), respectively. From the thermal desorption data of Fig. 2 and the work function data of Fig. 3 it is clear that doses of 25 L (thiophene) and 10 L (bithiophene) correspond to condensed multilayers. For thiophene, Fig. 4, the orbital band with the lowest binding energy consists of two nearly degenerate ring \(\pi\)-orbitals, the \(1a_2\) highest occupied molecular orbital (HOMO) and the \(3b_1\), using the notation of Derrick et al., for the gas phase symmetry of thiophene.\(^{40}\) Also marked on Fig. 4 is the \(7a_1\) \(\sigma\)-orbital,\(^{40}\) which would not be expected to take part in any bonding to the surface, and whose energy can therefore be used as a reference. (The band of orbitals between those marked consists of a number of unresolved \(\sigma\)-orbitals, a further ring \(\pi\)-orbital, and the sulfur lone pair.\(^{40}\) The binding energy relative to the vacuum level \((E_{\text{vac}})\) of the \(7a_1\) orbital in the gas phase is 16.6 eV.\(^{40}\) In the multilayer its binding energy is 11.6 eV relative to the Fermi level \((E_F)\), which when combined with the multilayer layer work function of 3.75 eV (Fig. 3) gives a binding energy relative to \(E_{\text{vac}}\) of 15.35 eV. Thus the intermolecular relaxation shift from the gas phase to the condensed multilayer is 1.25 eV, a typical
value for organic molecules. For the monolayer a similar calculation yields a binding energy of 15.3 eV relative to $E_{\text{vac}}$, giving a total relaxation shift of 1.55 eV from the gas phase to the monolayer, i.e., essentially the same as the multilayer.

The photoemission spectrum of the bithiophene multilayer, Fig. 5, is similar to that of thiophene. The main difference is that the two highest occupied $\pi$-orbitals in thiophene have become four in bithiophene.\(^{41}\) By analogy with thiophene, the orbital at $\sim 12$ eV in the multilayer spectrum is most likely a C–H $\sigma$-bond. Although a photoemission spectrum of bithiophene in the base phase has been published,\(^{41}\) the spectrum at binding energies higher than 15 eV relative to $E_{\text{vac}}$ is not shown, thus the gas phase binding energy of the $\sigma$ orbital marked on Fig. 5 is unknown. However, as the dashed lines in Fig. 5 indicate, there are no energy shifts of the $\pi$-orbitals relative to the other valence band orbitals in going from the condensed phase to the monolayer. Therefore it does not seem unreasonable to use the $\pi$-orbitals to determine the relaxation shift. In the gas phase, the highest occupied $\pi$-orbital has a binding energy of 8.0 eV relative to $E_{\text{vac}}$.\(^{41}\) In the condensed multilayer of Fig. 5 its binding energy relative to $E_F$ is 2.8 eV, which, combined with the multilayer work function (Fig. 3) of 3.9 eV, gives a binding energy relative to $E_{\text{vac}}$ of 6.7 eV, i.e., a relaxation shift of 1.3 eV from the gas phase to the multilayer. A similar calculation leads to a value of 1.3 eV from the gas phase to the monolayer, the same relaxation shift as for the multilayer.

The data of Figs. 4 and 5 are referenced to the Fermi level, the natural reference level in photoemission from a metallic substrate. The dominant contribution to the binding energy shifts seen in Figs. 4 and 5, in going from the multilayer to the monolayer, is therefore the shift in the vacuum level, i.e., the change in work function, since the orbital binding energies relative to $E_{\text{vac}}$ remain essentially constant. For both thiophene and bithiophene the relaxation shifts in going from gas phase to condensed multilayer are, within experimental error, extremely close to those in going from the multilayer to the monolayer. This suggests that the screening efficiency in the monolayer, in contact with a metallic surface, is no better than in the multilayer, which again indicates extremely weak bonding.

In both Fig. 4 and Fig. 5 there is no relative shift of the $\pi$- and $\sigma$-orbitals going from the condensed multilayer to the monolayer. Thus there are no obvious orbitals involved in the surface bond, and specifically there is no $\pi$-stabilization evident in the bonding of either thiophene or bithiophene on Al(111), as would be seen if the molecules were bonding to the surface via the $\pi$-electrons. This is unlike the case in, for example, thiophene on Rh(111) (Ref. 13) or bithiophene on Ni(110),\(^{21}\) where $\pi$-stabilization is clearly observed, and is also unlike the bonding of other aromatics to transition metals.\(^{24}\) However this is the same behavior as observed for benzene on Al(111).\(^{25}\) In the latter case symmetry selection rules, combined with photoemission measurements at both normal and off-normal emission, were used to identify the symmetry of the molecule on the surface, and thereby determine that the benzene molecular plane was indeed parallel to the surface.\(^{25}\)

Photoemission spectra as a function of emission angle, for monolayers of thiophene and bithiophene on Al(111) are shown in Figs. 6 and 7, respectively. The thiophene data of Fig. 6 show very little changes with emission angle. In particular the $\pi$-band, containing the $1a_2$ and $3b_1$ HOMO and HOMO-1 orbitals, has the same line shape at all angles, a line shape unchanged from that of the multilayer in Fig. 4. The only significant change with angle observed is for the sulfur lone pair orbital, marked as ‘‘n’’ in Fig. 6. For

![FIG. 6. ARUPS spectra ($h\nu=21.2$ eV) at different emission angles for a monolayer of thiophene on Al(111).](image)

![FIG. 7. ARUPS spectra ($h\nu=21.2$ eV) at different emission angles for a monolayer of bithiophene on Al(111).](image)
thiophene the highest possible surface symmetries are $C_5$ if flat or tilted, or $C_{2v}$ if standing perpendicular to the surface. Symmetry tables relevant to thiophene and bithiophene can be found in Ref. 21. In $C_{2v}$ symmetry, orbitals with $a_1$ symmetry are forbidden in normal emission. 21 The HOMO, which retains its gas phase symmetry of $a_1$, is clearly present in normal emission, and thus $C_{2v}$ symmetry, and hence a perpendicular geometry can be ruled out. For the $C_5$ point group, the symmetries of all the valence band orbitals reduce to either $a'$ or $a''$. For these symmetries selection rules are not particularly exclusive, 21 and so no orbital emissions are forbidden, irrespective of the experimental geometry. Figure 6 shows the lack of angular dependence of the photoemission features, consistent with $C_5$ symmetry. The enhancement of the sulfur lone pair orbital at higher emission angles is not due to a simple selection rule effect, since it has the same symmetry ($a_1$) as the (gas phase) $7a_1$ orbital, which shows no angular effects.

In contrast to thiophene, the bithiophene data of Fig. 7 show considerable variation with angle. In particular, the relative intensities of the four components of the $\pi$-orbital band are clearly a function of angle—the dashed lines serve to show that the angular effects allow each of the four orbitals to be distinguished. There appear to be angular variations in the intensities of all other orbitals, except, paradoxically given its behavior in the thiophene data of Fig. 6, the lone pair.

The orientation of bithiophene on Al(111) is already known from high resolution electron energy loss spectroscopy, 25 which clearly indicates a flat-lying molecule. The orientation of bithiophene on Al(111) is already known from high resolution electron energy loss spectroscopy, 25 which clearly indicates a flat-lying molecule. The question is then whether it adsorbs in the trans configuration, i.e., with the two sulfur atoms on opposite sides of the molecule, as shown in Fig. 1, or a sys configuration, with both sulfurs on the same side. Although in the gas phase the trans form predominates, the energy difference between the two configurations is very small. 42 Unfortunately the symmetries of the flat lying species—$C_2$ for trans and $C_5$ for sys—21 are both very low. For a $C_2$ geometry the symmetries of the four leading $\pi$-orbitals reduce to either $a$ or $b$, while for $C_5$ they are $a'$ or $a''$. 21 In the absence of azimuthal ordering, as would be expected on an fcc (111) surface, the selection rules for $a$, $b$, $a'$, and $a''$ are not exclusive. 21 Therefore symmetry selection rules cannot be used to determine whether bithiophene adsors as sys or trans, and cannot explain the angular variations seen in the data of Fig. 7. These data, however, show similar behavior to those of bithiophene on Ni(110)–p(4×1)–S, 21 an adsorption system where one-dimensional molecular strings form in the [001] azimuth, i.e., where long-range order is present. In that system, significant angular variation of the relative intensities of the four HOMO $\pi$-orbitals was seen along the [001] azimuth, where order is present, but not along [110], where it is absent. The Ni(110)–p(4×1)–S reconstruction acts as a template to force the assembly of bithiophene molecules into an ordered structure. 21 This will clearly not be the case on the close packed Al(111) surface. However, bithiophene has been observed to self-assemble at low temperature on Ag(111), 23 forming relatively large domains, of the order ~100 Å. As already discussed, thermal desorption data from bithiophene on Ag(111) suggest a weakly bound monolayer with a bond strength very similar to that on Al(111). Therefore it seems reasonable that self-assembly may also occur on Al(111). The angular width of the primary beam in high-resolution electron-energy-loss spectroscopy (HREELS) of a monolayer of bithiophene on Al(111) was found to be only 3.7°. 43 Such a relatively sharp (0,0) diffraction reflex is consistent with large domains of an ordered adsorbate. LEED should, in principle be able to identify the presence of long-range order in the bithiophene monolayer. However, the electron beam of a standard LEED apparatus destroys such weakly bound molecules, and therefore cannot be used in this case.

### Table I: Adsorption energies ($E_{ad}$) and geometrical properties of thiophene adsorbed on Al(111): distance to surface, $z$, and sulfur–aluminum and carbon–aluminum distances, $d_{S-Al}$ and $d_{C-Al}$, respectively.

<table>
<thead>
<tr>
<th>Site</th>
<th>$E_{ad}$ (eV)</th>
<th>$z$ (Å)</th>
<th>$d_{S-Al}$ (Å)</th>
<th>$d_{C-Al}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow (A)</td>
<td>0.53</td>
<td>3.9</td>
<td>4.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Hollow (B)</td>
<td>0.54</td>
<td>3.7</td>
<td>3.7</td>
<td>3.8</td>
</tr>
<tr>
<td>Bridge</td>
<td>0.52</td>
<td>4.0</td>
<td>4.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Top (A)</td>
<td>0.53</td>
<td>3.9</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Top (B)</td>
<td>0.53</td>
<td>3.9</td>
<td>4.3</td>
<td>4.1</td>
</tr>
</tbody>
</table>

![Fig. 8](image-url)  
**Fig. 8.** Calculated optimal geometry for thiophene on Al(111).
Although the adsorption energy for thiophene, 0.54 eV, is higher than that calculated for benzene on Al(111), 0.35 eV, it is nevertheless low, and a similar adsorption mechanism is therefore indicated. In all the investigated positions the molecule adsorbs essentially parallel to the surface, although in the case of adsorption in the hollow (B) site the molecular plane is slightly tilted (2°) away from the surface. The structural parameters of the molecule remain unperturbed in all cases. The molecule–surface distance is at least 3.7 Å for all adsorption sites, which is not indicative of chemisorption. In comparison, similar calculations for thiophene on MoS2 (Ref. 44) showed covalent bonding via the α carbons, an S–metal distance of 2.72 Å, and an adsorption energy of 2.0 eV. Calculations of thiophene–Al complexes, where covalent bonding was found to occur, yielded S–Al distances in the range 2.1–2.3 Å, depending on the exact bonding geometry. Similar calculations for other thiophene–metal complexes29 gave S–metal distances of 2.28 Å (V), 2.36 Å (Cr), and 2.24 Å (Cu). Recent studies using surface extended x-ray absorption fine structure (SEX-AFS) and normal incidence x-ray standing waves (NIXSW) have enabled the experimental determination of S–metal distances for several thiophene–metal adsorption systems: 2.31 Å on Pd(111), 2.3 Å on Pd(100), 2.4 Å on Cu(100), 2.6 Å on Cu(111), and 2.2 Å on Ni(100).5 These are all surfaces on which π-bonding occurs. Thus, both experimental and theoretical results are consistent, in that covalent bonding leads to S–metal distances of around 2.5 Å, significantly lower than that calculated for thiophene/Al(111).

The similarity between the bonding mechanisms for benzene and thiophene on Al(111) is evident from the charge redistribution on adsorption. Figure 9 shows isosurfaces of differential charge density, calculated as the difference of the electron densities of the adsorbate–surface complex, and of the clean surface and the free molecule. The adsorption of thiophene, as was also the case for benzene,25 induces a polarization of the Al surface, resulting in a charge depletion of the surface area close to the molecule. Thus the bonding is primarily electrostatic. Further, the π-orbitals of the aromatic ring and the H–σ states are depleted, whereas a charge increase is found in the C–H bonds and along the S–Al axis. It is this S–Al bond which causes the increase in adsorption energy compared to benzene/Al(111).

Inspection of the local density of states of this system, Fig. 10, confirms the similarity between the adsorption of benzene and thiophene on Al(111). Although the charge distribution changes are greatest around the S atom, the local density of states on the sulfur atom of the thiophene molecule is largely unperturbed on adsorption, in agreement with the lack of structural changes. Such changes as are seen are limited to a broadening of the occupied and unoccupied π-states, with no relative energy shifts, in agreement with the photoemission results.

V. CONCLUSIONS

Both thiophene and bithiophene bond only very weakly to Al(111), as indicated by thermal desorption and calculations of the absorption energy. The bond is, however, slightly stronger than that of benzene/Al(111), due to the additional bond formed between the sulfur and the surface. The calculated S–Al distance is comparable to the benzene–Al distance on Al(111),25 and much greater than either measured or calculated S–metal distances for covalent bonding. This conclusion is supported by the relaxation shifts in the photoemission data, where the screening in the monolayer, due to the metallic substrate, appears to be comparable to the intermolecular screening in the physisorbed
multilayer. This suggests that the molecule is too far from the surface for an effective metallic screening response. The bonding is shown to be almost entirely electrostatic, as indicated by the calculated differential charge distributions, and by the photoemission results, where no significant \( \pi \)-stabilization is indicated. The calculated densities of states are in excellent agreement with this latter observation, showing no differential energy shifts, merely a slight broadening of the \( \pi \)-orbitals which would be unobservable in photoemission, where additional broadening mechanisms are already in effect. The calculations show the molecule to be essentially flat, with the calculated tilt angle too small to be discerned experimentally. This is consistent with HREELS results for bithiophene on Al(111), and with a symmetry analysis of the photoemission data. However, symmetry selection rules do not permit the differentiation between flat or tilted thiophene, or between flat lying \emph{sys} or \emph{trans} bithiophene.

There is some indication of self-assembly of bithiophene on Al(111), as has also been observed for bithiophene on Ag(111). Molecular self-assembly occurs when the molecule–molecule interaction is stronger than the molecule–substrate interaction. Since this latter interaction appears very weak on Al(111), indeed possibly weaker even than on Ag(111), it does not seem unreasonable that self-assembly might occur on Al(111). Low current LEED, or low temperature scanning tunneling microscopy studies would be useful to determine whether this is in fact the case.

In summary, the experimental and theoretical results presented in this work show clearly that the interface between metallic aluminum and thiophene does not contain a covalent bond. The bonding is almost entirely electrostatic, with a small contribution from the sulfur. This is in direct contrast to calculations for the Al–thiophene complex, which show covalent bonds between the Al and the thiophene \( \alpha \) carbons. This demonstrates that the Al–thiophene complex, and the Al–thiophene interface represent very different situations.

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