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# Indirect Coupling of an Organic Semiconductor to a *d*-Orbital Surface State

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Adsorption of the organic semiconductor perylene tetracarboxylic acid dianhydride onto Cr(001) decreases the metal *d*-derived surface state lifetime without causing a shift in its energy. This suggests an indirect electronic interaction that contrasts sharply with expectations of *p-d* electronic coupling based on direct chemisorption. Lifetime changes are measured with scanning tunneling spectroscopy as a function of temperature and quantified as arising from a molecule-induced increase in electron-electron scattering rate into bulk bands within Fermi liquid theory. Adsorbate-induced effects extend far beyond the adsorption site of the molecule, decaying exponentially away with a characteristic length scale of  $\sim 2.4$  nm, similar to the carrier mean free path in Cr.

Organic materials offer the possibility to use synthetic chemistry to control spin dependent transport in new devices.<sup>1-4</sup> and to understand fundamental spin transport phenomena in solids with strongly localized carriers.<sup>5, 6</sup> A major challenge in semiconductor spintronic devices is to optimize spin polarized carrier injection from magnetic electrodes<sup>7-9</sup>. In organic materials, direct molecular orbital hybridization with magnetic states at the conducting electrode is widely regarded as a mechanism to promote spin injection.<sup>10, 11</sup> The hope is to use molecular orbital interactions at spin injecting contacts in a manner analogous to the symmetry filtering effects responsible for large magnetoresistance values in oxide tunnel barrier devices<sup>12</sup>. Our motivation in the present Brief Report is to expand the perspective on the type of orbital interactions that need to be considered at spintronic interfaces beyond the simplest intuitive chemisorption bonding picture.

Highlighting the importance of interfaces in organic spintronics, Barraud et al.<sup>7</sup> showed that spin polarized interface states formed by hybridization of molecular orbitals and exchange-split electrode states can control the tunneling magnetoresistance with a sign that is dependent on the strength of interaction.<sup>8</sup> Several studies of metal-molecule interfaces for spintronics have focused specifically on direct organic *p*-derived orbital coupling to metal *d*-bands.<sup>13-16</sup> Similarly, there has been evidence from spin polarized scanning tunneling spectroscopy<sup>17-19</sup> and spin polarized photoelectron spectroscopy<sup>10, 20</sup> that organometallic species with *d*-derived molecular orbitals can create hybrid interface states with electrode *d* bands. Both of these metal-molecule couplings are expected from elementary chemical bonding principles applied to chemisorption at surfaces.<sup>21, 22</sup>

In this letter we identify molecule-electrode interactions that differ conceptually from the simple surface chemical bonding pictures used in previous work.<sup>10, 18, 19</sup> Most importantly, we show that direct *p-d* orbital coupling is not a guaranteed interaction motif for planar aromatics on transition metal surfaces. We begin by noting the interesting metal-molecule interactions found in the coupling of PTCDA to the *sp*-derived Shockley surface state on Ag(111)<sup>23-25</sup>. In this adsorption system, the strong acceptor PTCDA takes charge from the bulk *sp* band of the Ag

substrate in a manner that is essentially traditional direct orbital coupling.<sup>25</sup> The adsorbate modification of the bulk bands correspondingly modifies the  $sp$ -derived Shockley surface state by significantly shifting its energy (by  $\sim 0.4\text{eV}$ ) and slightly changing its effective mass.<sup>23</sup>

We focus attention on a related but more subtle interaction between PTCDA adsorbates and a predominantly  $d_z^2$ -derived Shockley surface state on the Cr(001) surface.<sup>26, 27</sup> This state located near the Fermi level has been observed to be spin polarized<sup>28</sup> and could potentially hybridize with nonmagnetic molecular orbital  $p_z$ -derived states at a metal-organic interface according to the established  $p$ - $d$  resonance type interaction.<sup>17</sup> In addition, the state has some contribution from Cr  $sp$  bands<sup>27</sup> whose less rapid decay away from the surface would promote interaction with molecular adsorbates.

However, we find that the intuitively plausible direct electronic coupling between the molecule and the mostly  $d_z^2$  surface state does *not* occur in this system. Instead, PTCDA accepts charge from the bulk  $sp$ -band of Cr, which only *indirectly* modifies the lifetime of the  $d$ -derived Shockley surface state without directly mixing with it. Moreover, the indirect modification has a spatial range that extends far beyond the length of a single molecular adsorbate and is controlled by the bulk mean free path in the Cr metal.

This indirect and long-range surface state modification is distinct from the more direct and strongly localized modification of  $sp$  Shockley surface states seen for PTCDA on Ag(111). Most importantly, it is distinct from the direct coupling often invoked as a mechanism for spin injection into organic materials.<sup>7</sup> The significance for electronic and spintronic interfaces is that direct orbital coupling ideas do not exhaust the possibilities for electronic metal-molecule interactions near the Fermi level.

Experiments were carried out in a vacuum system housing a commercial STM (Omicron VT-XA100/500). The STM and STS measurements were carried out with typical pressures in low  $10^{-11}$  torr range. The measurements showed good reproducibility with multiple W tips etched in-house. STS spectra were measured using lock-in detection of the first harmonic of the tunneling

current with a tunneling bias modulation of  $V_{\text{mod}} = 0.02 V_{\text{rms}}$  at 10 kHz. A limited bias range was probed in STS to avoid tip-induced perturbations of the molecular adsorbates. A single crystal of Cr(001) was cleaned daily by 2 hours of sputtering with 1 keV Ar<sup>+</sup> ions at  $\sim 1000$  K, followed by a sputtering during cool-down for  $\sim 15$  minutes and then annealing to 1000 K for  $\sim 10$  minutes. Liquid nitrogen was used to cool the STM during measurements. Figure 1(a) shows a typical topographic image of the Cr(001) surface cleaned by the sputter/anneal procedure described above. Dark spots on the surface are trace carbon contamination.<sup>29, 30</sup> All STS measurements were taken to avoid contamination sites and step edges and were repeated on multiple different PTCDA adsorbates. As shown in Figure 1(c), an intense peak is located at 20meV above the Fermi level and is consistent with previous reports of the Shockley *d*-derived surface state.<sup>26, 31</sup> PTCDA molecules (97%, Sigma-Aldrich) were evaporated from a heated quartz crucible and deposited onto a room temperature Cr(001) surface in a preparation chamber (base pressure  $< 1 \times 10^{-9}$  Torr) connected to the UHV STM chamber by a gate valve. Deposition rate was monitored by a quartz crystal microbalance (QCM).

A submonolayer coverage of PTCDA on Cr(001) is shown in Figure 1(b). This very small coverage provides a surface that enables us to compare the linewidth of the surface state at molecular sites directly with the surrounding bare Cr(001) surface. In Figure 1(d), one can see that the near-Fermi-level surface state of Cr(001) survives at the PTCDA adsorption sites. This is already different than expectations for direct molecule-metal interaction that would shift the state in energy such as observed for PTCDA on Ag(111).<sup>23</sup> Although the surface state is not shifted, it is broader than for the clean Cr(001) surface indicating a more subtle electronic interaction. There is also an additional peak located at -370meV. This is assigned as the result of charge transfer into the lowest unoccupied molecular orbital (LUMO) of PTCDA by direct analogy with similar molecular states for PTCDA on Ag surfaces.<sup>23, 24</sup>

In Figure 2(a) we show an STM image with points where local tunneling spectra were measured indicated by symbols both on the PTCDA molecules and extending away from the

center of the molecule by several nanometers. Figure 2(b) shows the corresponding local spectra at each point. The molecular orbital-derived feature at -370 meV is spatially well-localized on the molecular sites as expected for a LUMO-derived state. In contrast to the molecular orbital localization, the PTCDA-induced broadening of the Shockley surface state on Cr(001) extends well beyond the boundaries of the molecular shape.

This effect is shown in more detail in Figure 3 as a plot of Lorentzian linewidth for a large collection of local spectra measured at different distances from the centers of a population of PTCDA molecules (74 total molecules considered). Within the span of the distance from the center to the edge of the molecule, the width is approximately constant and then starts to decay toward the clean surface value. The small increase in going from the center of the molecule to the edge is probably due to a strong and localized interaction between the oxygen atoms on the edge of the molecule and the substrate.<sup>32</sup> We have repeated the measurements in Figure 3 at a variety of different submonolayer coverages, approaching saturation. This does not add new information since it only changes the maximum distance that spectra can be acquired away from adsorption sites.

The dashed (red) line is an exponential fit to all of the data after the edge of the molecule. The fit yields a decay length of  $2.8 \pm 0.4$  nm. This length is of the same order as mean free path estimates for Cr<sup>33</sup>, indicating a strong connection between linewidth and scattering processes in the bulk of the substrate. Importantly, since this length scale is much longer than the size of the molecule, it is clear that local bonding interactions are not sufficient to explain the adsorbate-induced modification of the *d*-derived surface state. In contrast, PTCDA on Ag(111) modifies the *sp*-derived surface state only within the confines of molecular islands.<sup>23</sup>

In order to apply existing surface state lifetime models to the observed molecule-induced broadening, we performed temperature-dependent studies of surface state linewidth for the PTCDA/Cr(001) interface. We measured STS spectra for both PTCDA on Cr(001) and the clean Cr(001) surface at the temperature of 130K, 180K, 230K, 280K and 300K. In Fig 4(a), we

present spectra of the surface state of clean Cr(001) surface and its Lorentzian fit at different temperatures in which clear thermal broadening of the surface state can be seen. The temperature dependent spectra of the clean Cr(001) surface are in agreement with previous work.<sup>29</sup> In Fig 4(b), spectra measured at the center of PTCDA molecule (at least 10 different molecules averaged for each spectrum) on Cr(001) at different temperatures are shown. Spectra on molecules cannot be measured beyond 260K due to thermal instabilities in the STM junction at elevated temperatures. However, thermal broadening of the surface state located at 20meV is still obvious in the more limited temperature range.

As the inverse of lifetime, the linewidth of the Cr(001) surface state  $\Gamma$  is determined by electron-electron (e-e) scattering<sup>34, 35</sup> and electron-phonon (e-ph) scattering<sup>36, 37</sup> rates by the two terms:

$$\Gamma(E, T) = \Gamma_{e-ph}(E, T) + \Gamma_{e-e}(E, T) \quad (1)$$

The e-ph scattering contribution to the total linewidth is given in the Debye model by:

$$\Gamma_{e-ph}(E, T) = \lambda \frac{2\pi}{\hbar\omega_D} \int_0^{\hbar\omega_D} dE' E'^2 [1 - f(E - E') + 2n(E') + f(E + E')] \quad (2)$$

where  $\omega_D$  is the Debye frequency and  $\lambda$  is the electron-phonon mass-enhancement factor,  $f(E)$  the Fermi distribution and  $n(E)$  the Bose-Einstein distribution.

In addition, the e-e scattering contribution to linewidth is given by Fermi liquid theory<sup>29, 34</sup>:

$$\Gamma_{e-e} = 2\beta[(k_B T)^2 + (E - E_F)^2] \quad (3)$$

However, since the factor  $\beta$  should be small, many observations have shown that the change of linewidth contributed by e-e scattering ( $\Delta\Gamma_{e-e}$ ) with varying temperature is very minor.<sup>29, 35, 38</sup> Furthermore, there is no measureable shift in the binding energy of this surface state in our measurement. Therefore we treat  $\Gamma_{e-e}$  as a constant independent of temperature equal to only the second term of Eq. (3).

In figure 4(c), we fit the plot of linewidth vs temperature using equations (1)-(3). The fit to the data of surface state on clean Cr(001) results in  $\lambda=0.9\pm0.4$ ,  $\Gamma_{e-e}=47\pm3$ meV and

$\hbar\omega_D=52\pm 4\text{meV}$ , comparable to previous work,<sup>29</sup> while the fit to the data of surface state on PTCDA molecules result in  $\lambda=0.9\pm 0.2$ ,  $\Gamma_{e-e}=128\pm 6\text{meV}$  and  $\hbar\omega_D=55\pm 4\text{meV}$ . Interestingly, both  $\lambda$  and  $\hbar\omega_D$  are not significantly different in the presence of the organic adsorbate, but only  $\Gamma_{e-e}$  increases for fits to the two sets of data. Similarly, as shown in Figure 4(c), fits to data sets of different distances from molecule give almost equal values of  $\lambda$  and  $\hbar\omega_D$  compared to the clean surface, and only different offsets, i.e,  $\Gamma_{e-e}$ . So we can conclude that the broadening of the surface state by PTCDA molecules comes from the increase of e-e scattering contribution to linewidth.

This is a quantitative measure of the indirect electronic coupling between the molecule and the surface state, mediated by the *sp* bulk bands. By accepting charge into its LUMO from the bulk *sp* band, the PTCDA molecule enhances the scattering rate of surface state electrons into these bulk bands and reduces their lifetime. Notably, the molecule nearly doubles the surface state-bulk scattering rate compared to a clean surface at the adsorption site. The scattering rate (i.e. the vertical offset of each curve in Figure 4(c)) is clearly a function of distance away from molecule. The influence of the local molecular adsorbate on *sp* electrons (and thus indirectly on the surface state) extends about one mean free path, and this is seen in the variation e-e scattering rate contribution to the lifetime at different distances. [It would be extremely valuable to supplement this phenomenological Fermi liquid model with \*ab initio\* calculations. These will be challenging due to the size of the PTCDA molecule and known difficulties of treating the magnetic Cr\(001\) surface,<sup>27</sup> but will provide more specific microscopic insights than the experimentally-determined Fermi liquid scattering rates.](#)

The implications of these observations for spintronic interfaces are very interesting to consider. The Shockley surface state on clean Cr(001) is spin polarized and located close to the Fermi level, making it naively an ideal candidate for promoting spin injection into a molecular system. This is especially true since the surface state is derived from  $d_z^2$  atomic orbitals<sup>26</sup> which should



have good possibilities for sigma bond-like interactions with  $p_z$ -derived  $\pi$  orbitals in the flat-lying PTCDA molecule. In contrast to this intuition, we find that the direct coupling between the surface state and PTCDA is very weak and indirect coupling via bulk  $sp$ -bands dominates the molecule-induced interface modifications. The particular bulk  $sp$  bands that directly couple to the molecule are at best weakly magnetic<sup>39, 40</sup> and thus the PTCDA/Cr(001) interface would not necessarily be expected to enhance spin injection. This observation is likely to apply also to Fe(001) which has a similar Shockley surface state.<sup>31</sup> In short, we identify a clear case where essentially geometric chemical bonding intuition is not sufficient to assess interfacial coupling, in contrast to known cases where it has been valuable.<sup>13, 24</sup> This new complexity is a challenge for design of interfaces for spin injection but also heralds an opportunity to find unexpected modes of coupling.

In conclusion, we report indirect molecular modification of the near-Fermi-level surface state of Cr(001) surface when an organic molecule PTCDA accepts charge from the bulk substrate bands. The temperature-dependence of tunneling spectra shows that the surface state lifetime is reduced when an interaction between the PTCDA LUMO and the Cr bulk  $sp$  band opens new surface state scattering channels. This is quantified as a two-fold increase in the electron-electron scattering rate in a Fermi-liquid model of the surface state lifetime. Moreover, the large spatial range of this broadening effect provides further support for this interpretation of increased e-e scattering since the bulk  $sp$  band is not localized.

The results described here illustrate a subtle new indirect interaction at the interface between an organic molecule and a metal surface. The significance is that simple direct hybridization of molecular orbitals and spin split electrode states is not the only possibility for electronic coupling at magnetic surfaces. Specifically, geometrically intuitive  $p-d$  hybridization<sup>16</sup> is not a guaranteed electronic coupling mechanism between planar organic semiconductors and magnetic electrodes. In designing interfaces for spin injection into organic materials we need to recognize the full range of possible electronic interactions and their magnetic implications.

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**Figure 1.**(color online) (a) STM image ( $250 \times 250 \text{ nm}$ ) with tunneling current  $I_t = 10 \text{ pA}$ , bias  $V_b = -0.7 \text{ V}$  of the clean Cr(001) surface cleaned by sputtering/annealing cycles; (b) STM image ( $25 \text{ nm} \times 25 \text{ nm}$ ) with  $I_t = 10 \text{ pA}$ , bias  $V_b = 0.5 \text{ V}$  of submonolayer PTCDA on Cr(001) surface, showing most PTCDA molecules are lying down and intact; (c) STS spectra on the clean Cr(001) surface shown in (a). The (red) dashed line shows a Lorentzian fit to the spectra with peak position  $\epsilon_0 = 20.4 \pm 0.3 \text{ meV}$ , and width  $\Gamma = 92 \pm 2 \text{ meV}$ ; (d) STS taken with same setting as (c) at molecular sites shown in (b). The Lorentzian fit (red dashed line) gives the peak position of  $\epsilon_0 = 20.8 \pm 1.5 \text{ meV}$  and width  $\Gamma = 180 \pm 5 \text{ meV}$  with a Gaussian fit the additional peak gives the peak position at  $-370 \pm 4 \text{ meV}$ .

**Figure 2.** (a) STM image showing a PTCDA molecule and the positions where spectra were taken. (b) single spectra at the center (black) and edge (blue) of PTCDA molecule as well as bare Cr(001) surface at distance of  $1.2 \text{ nm}$  (green),  $3.2 \text{ nm}$  (purple) and  $5.1 \text{ nm}$  (olive) from the center of PTCDA.

**Figure 3.** Plot of linewidth of surface state vs distance from PTCDA molecule. Experimental points are represented by symbols and the solid line (red) is the best exponential fit. One can see that the broadening effect is not localized at molecular sites but extends to the surrounding bare Cr(001) surface with a decay length much larger than the size of a single PTCDA molecule (shown in the inset to scale).

**Figure 4.** (a) STS of the surface state at different temperature on a clean Cr(001) surface; (b) STS of the molecule modified surface state measured at the center of the molecule for PTCDA/Cr(001) at different temperatures; (c) Temperature dependence study shows linewidth of surface state taken at different distances from PTCDA are offset by e-e scattering rates.

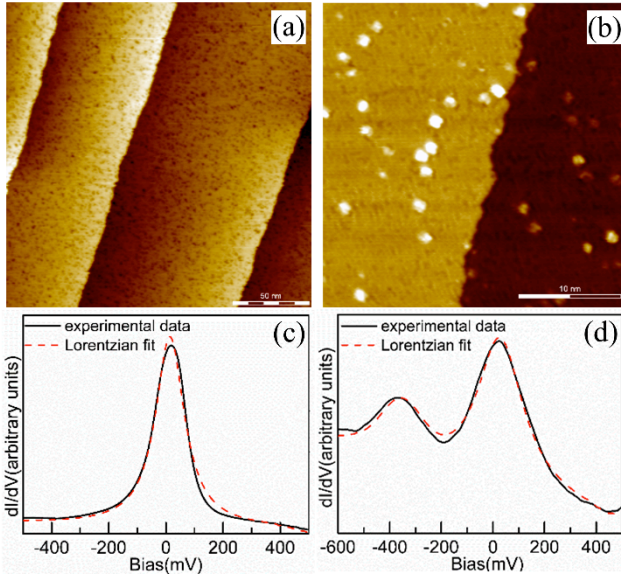


Figure 1. Wang And Dougherty

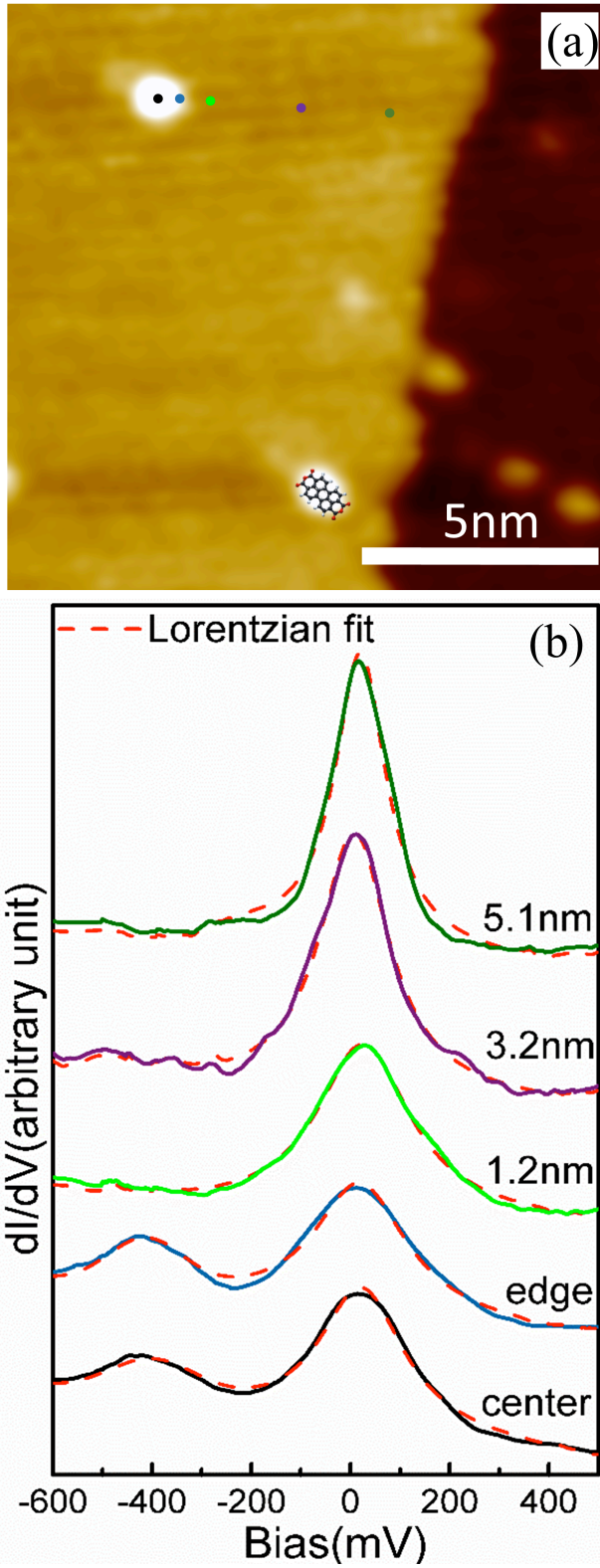


Figure 2. Wang and Dougherty

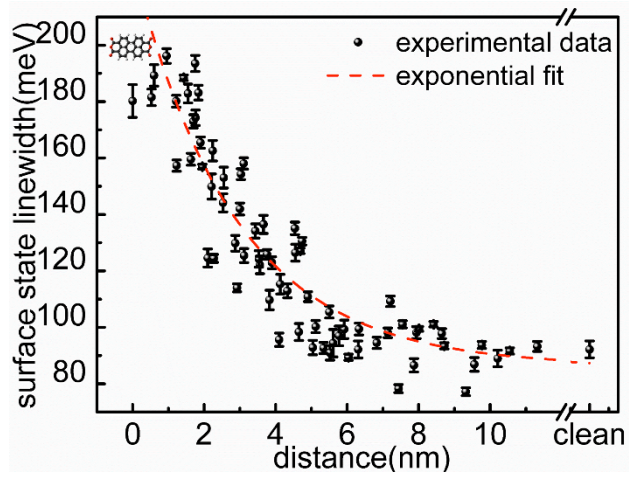


Figure 3. Wang and Dougherty

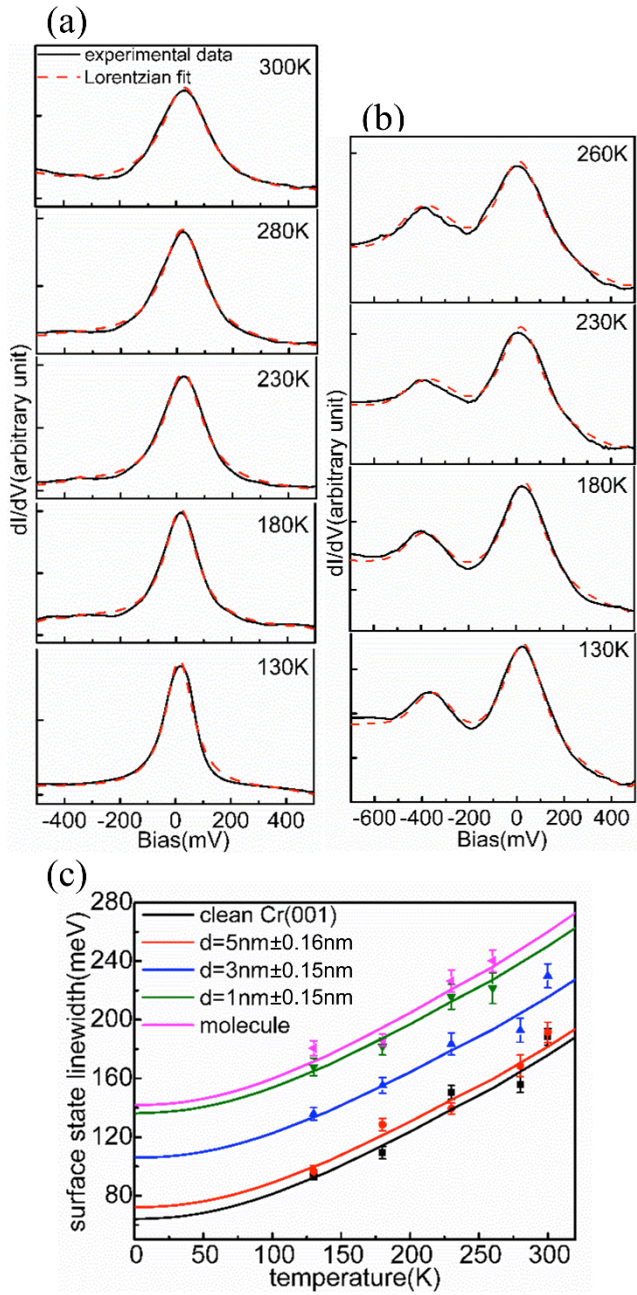


Figure 4. Wang and Dougherty