

Supplementary Information: Incommensurate Quantum Size Oscillations of Oligoacene Wires Adsorbed on Au(111)

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Golden rule calculation of the band broadening

The band structure of the isolated Pac is represented by the Bloch energies, $\varepsilon_{k,b}$, where k is the wave number along the chain and b labels bands. The analogous quantity for adsorbed Pac is the spectral function $A_{k,b}(\omega)$. If for a given k, b the hybridization is weak, the spectral function $A_{k,b}(\omega)$ is a sharply peaked resonance centered at energy $\approx \varepsilon_{k,b}$ with broadening

$\Gamma_{k,b}$. In this section we estimate $\Gamma_{k,b}$ by Fermi's golden rule.

We denote the retarded Green's function of Pac adsorbed on a metallic substrate as $G_{k,b}(\omega)$. The index k is the wave-number along the Pac, it is a symmetry label due to translational invariance. We assume (approximate) compatibility of the substrate and Pac unit cells. b is the Pac band index. The substrate can mix the Pac bands, in principle. However, here we focus only on a segment of the conduction band that is well separated from other bands, so that band mixing can be neglected.

In absence of coupling between substrate and the wire, the Green's function simplifies to $1/(\omega - \varepsilon_{k,b} + i0^+)$. The substrate has bands $\varepsilon_{\mathbf{k}_\perp,k}$ which we label by the longitudinal wave-number k and denote by \mathbf{k}_\perp the wave-numbers in complementary directions of the reciprocal space. We suppress band indices of the substrate for brevity.

Upon coupling, the Green's function becomes

$$G_{k,b}(\omega) = 1/[\omega - \varepsilon_{k,b} - \Sigma_{k,b}(\omega)], \quad (1)$$

$$\Sigma_{k,b}(\omega) = \sum_{\mathbf{k}_\perp} |V_{\mathbf{k}_\perp|k,b}|^2 \frac{1}{\omega - \varepsilon_{\mathbf{k}_\perp,k} + i0^+} \quad (2)$$

where $\Sigma_{k,b}(\omega)$ is the retarded self-energy and $V_{\mathbf{k}_\perp|k,b}$ is the coupling (hybridization Hamiltonian matrix element) of the Pac state k, b and the substrate state \mathbf{k}_\perp . The real part of the self-energy yields a band shift, which can be absorbed in $\varepsilon_{k,b}$. The imaginary part gives the broadening of the Pac band upon adsorption. We introduce $\Gamma_{k,b}(\omega) = \pi \sum_{\mathbf{k}_\perp} |V_{\mathbf{k}_\perp|k,b}|^2 \delta(\omega - \varepsilon_{\mathbf{k}_\perp,k})$. Assuming weak dependence on the wave-number, we can replace the coupling by its average $V_{k,b}$. The broadening factorizes $\Gamma_{k,b}(\omega) \approx \pi |V_{k,b}|^2 \sum_{\mathbf{k}_\perp} \delta(\omega - \varepsilon_{\mathbf{k}_\perp,k}) = \pi |V_{k,b}|^2 \rho_k(\omega)$ where $\rho_k(\omega)$ is a density of substrate states with longitudinal wave-number k .

This form allows to make a quantitative estimate of the band broadening using the super-cell calculation. The coupling can be estimated from Graph 2 by inspecting the crossings of the Pac conduction band and substrate bands. The gaps created by the crossing do not exceed 0.5 eV. From first-order perturbation theory, the gap of a non-avoided band crossing

is $2|V_{k,b}|$, giving an upper bound $|V_{k,b}| < 0.25$ eV. It remains to estimate $\rho_k(\omega)$. We shall consider only the two-dimensional Shockley surface state. Then, $\sum_{\mathbf{k}_\perp} \delta(\omega - \varepsilon_{\mathbf{k}_\perp, k})$ effectively runs just through the wave vectors of the surface perpendicular to the molecular wire. We obtain $\rho_k(\omega) \approx a/\pi\hbar v_F$ where the Fermi velocity $v_F \approx a/\hbar\pi \times 5$. eV (see Graph 2) so that $\Gamma_{k,b} = \pi|V_{k,b}|^2\rho_k(\omega) \approx 0.040$ eV.