

Valence Electron Orbitals of an Oligo(*p*-phenylene-ethynylene)thiol on Gold

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In their paper proposing the field now called molecular electronics, Aviram and Ratner¹ explained rectification in molecules in terms of the frontier orbitals and the shifting of these orbitals upon chemical substitution. The experimental and theoretical work of the ensuing years has reinforced the idea that the location and characteristics of valence electron orbitals are central to the electronic function in molecular systems.²

Although there have been many investigations of the electronic structure for small organic molecules and polymers,^{3–6} including organic thiols and ferrocene phenylene–vinylene, there are no measurements for one of the most prominent systems in the arena of molecular electronics, the oligo(phenylene–ethynylene)s. This communication reports energies of the valence orbitals of the molecular wire, 4,4'-bis-(phenylethynyl)benzenethiol (Figure 1), chemisorbed on gold. One- and two-photon photoelectron spectroscopy were used to make these measurements.

Compound **1** was synthesized using published procedures.⁷ Samples were prepared on a Au(111) crystal and on gold-coated silicon substrates, using methods known to give densely packed monolayers.^{8,9} The crystal was subjected to anneal–sputter cycles, until the photoemission spectrum corresponded to that of clean gold. The gold-coated substrates were cleaned by exposure to ultraviolet light and ozone, rinsed with water, and dried with gaseous nitrogen. Monolayers were grown from a ~1 mM 2:1 CH₂Cl₂:CH₃CH₂OH solution in an inert environment. After growth, the crystal was placed in a load lock and transferred into an ultrahigh vacuum chamber. The gold-coated silicon pieces were used to measure reflection absorption infrared spectra, ellipsometric spectra, and contact angles. These measurements ensured that a monolayer had formed. The light sources were a He(I) lamp [21.2 eV, ~10¹³ photons/s] and the frequency-doubled output of an optical parametric amplifier [tunable 3.2–4.5 eV, pulse duration ~0.1 ps, 2 mW in ~0.6 mm² at sample, rep. rate 0.25 MHz]. A 180° hemispherical analyzer measured the kinetic energy spectrum of the photoelectrons.

One-photon photoemission spectra are shown in Figure 2. The energy axis for each spectrum was set so that the Fermi energy is 0 eV. Structure observed in the gold spectrum could be assigned to known transitions. The work function of the gold decreased to ~4.3 eV after the formation of the monolayer. Two other characteristics are observed in these spectra as well: an increased onset of photoelectrons above ~0.85 eV and peaks centered at 2.0 and 3.9 eV. We shall refer to these as B and O.

A one-color, two-photon photoemission spectrum of **1** on gold is shown in Figure 3. A broad, featureless secondary electron background was fit with an exponential function, and that fit was subtracted from the spectrum shown here. Again, two peaks are observed. We shall refer to these resonances as O* and B*_{obs}.

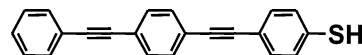


Figure 1. 4,4'-Bis(phenylethynyl)benzenethiol, compound **1**.

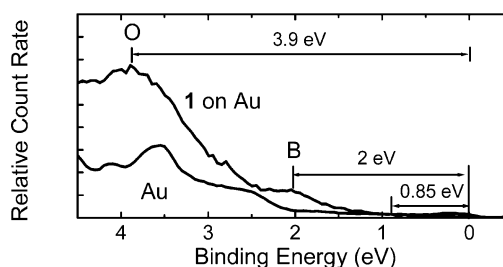


Figure 2. One-photon (21.2 eV) photoemission spectra of clean Au and **1** on Au. Binding energy given relative to Fermi energy.

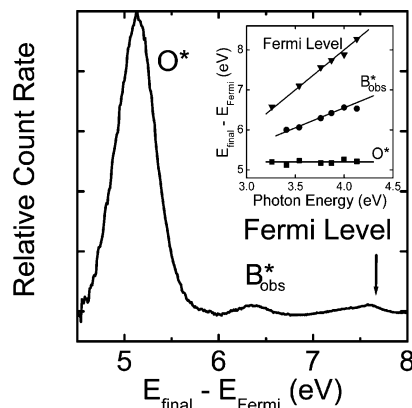


Figure 3. One-color (3.87 eV), two-photon spectrum of **1** on Au. The abscissa is the final state energy relative to the Fermi energy. Inset: Energy of electrons from O*, B*_{obs}, and the Fermi level as a function of photon energy. Lines of slope zero (O*), one (B*_{obs}), and two (Fermi level) are drawn through the data of the inset.

Two-photon photoemission spectra were recorded at photon energies between 3.2 and 4.2 eV. In these spectra, the final state energy (E_{final}) of electrons corresponding to B*_{obs} increased linearly with unit slope as the photon energy ($h\nu$) increased (Figure 3, inset). The energy of electrons corresponding to peak O* did not change. These trends are expected for ionization through levels that are between the vacuum energy and Fermi energy (unit-slope, linear dependence) and above the vacuum energy (independent), respectively.⁶ Additionally, peak B*_{obs} was not observed at photon energies below ~3.4 eV, while peak O* was observed at all photon energies.

An energy-level diagram can be constructed from these spectra. The energies of the occupied levels can be determined directly from Figure 2. As noted, the observed states are 2 and 3.9 eV below the

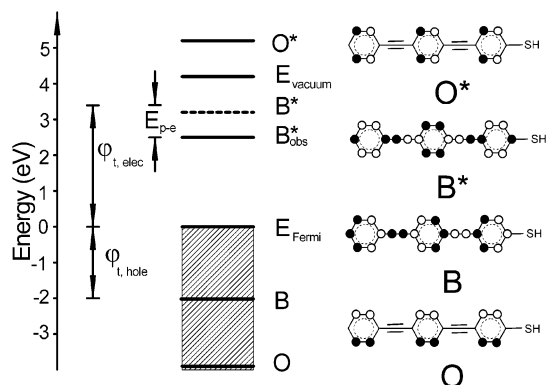


Figure 4. Energy level diagram used to determine charge transport energies. Schematic representations of states are shown at the right.

Fermi energy. The energy of states observed using two-photon photoemission can be determined as follows:⁶ For the state above the vacuum, $E = E_{\text{final}} - E_{\text{Fermi}}$, and for the state between the vacuum and Fermi energies, $E = E_{\text{final}} - E_{\text{Fermi}} - h\nu$. The energies of these observed states are 5.2 and 2.5 eV above the Fermi energy, as shown in Figure 4.

Comparison to para-substituted polyphenylenes allows one to deduce the orbital nature of these energy levels.¹⁰ For this class of polymers, the doubly degenerate e_{1g} molecular orbitals of benzene split and form two sets of bands. One is a localized π -band that involves only the ortho carbons. These are represented in Figure 4, and designated O and O*. The other set is a pair of delocalized π -band that also involves the backbone para and ethynyl carbons, and these are designated as B and B* in Figure 4. These delocalized bands may serve as transport states.

Because times for electronic and intramolecular structure changes are fast compared to the transit time of the photoelectron, the binding energies measured using one-photon photoemission represent the fully relaxed cation, or positive polaron state.^{10,11} Changes of the monolayer structure as a whole may not be complete, but this lattice effect is rather small (meV). Consequently, the binding energies determined from the one-photon spectra are very close to the energies of those levels for the cation.

For states measured in two-photon photoemission that involve an initial excitation to a molecular excited state, a transient charge-separation state, or neutral polaron–exciton, is formed.^{10,11} This first step is equivalent to an optical absorption. The energy level of such a state is stabilized relative to the same level for the anion, or negative polaron state. Thus, the energy measured corresponds to the sum of the electron affinity and the polaron–exciton energy (E_{p-e}).

This is the case for B*, where the initial excitation is to the lowest allowed neutral exciton state.¹² The measured position of B*_{obs} is thus reduced relative to that of B*. One method to determine the energy of B* involves adding the value of E_{p-e} to the optical absorption peak at ~ 4.3 eV.¹² Measured values of E_{p-e} for conjugated polymers are varied,^{10,11} but charge-separation energies between 0.6 eV to 1.4 eV have been reported for small conjugated molecules.¹³ Simply assuming the midpoint value of 1.0 eV, places B* 5.3 eV above B (3.4 eV above E_{Fermi}).

The photoemission spectra provide another means to estimate the position of B*. Specifically, if it is assumed that the separation between O* and B* is close to the measured separation between O and B, the position of B* can be estimated to be ~ 1.9 eV below

O* (3.3 eV above E_{Fermi}). This then gives a polaron–exciton energy of ~ 0.9 eV. This estimate is based on the simplest of models, namely a tight-binding or Hückel model for the electronic structure an isolated system. It is probably an upper bound.

The transport energy-gap, hole- and electron-injection energy for the molecule-derived π -bands can now be determined. Using the peak maximum, the hole-transport barrier into the occupied π -levels ($\varphi_{t,\text{hole}}$) is ~ 2.0 eV. The electron-transport barrier into the unoccupied π -levels ($\varphi_{t,\text{elec}}$), the sum of the observed energy of the unoccupied level and the polaron–exciton energy, is ~ 3.3 eV, when using the estimated ~ 0.9 eV value for E_{p-e} . Finally, the transport gap energy is, $E_t = \varphi_{t,\text{hole}} + \varphi_{t,\text{elec}} \cong 5.4$ eV. Different criteria for the selecting the onset of charge transport would give correspondingly different values for the transport gap. For example, a value of ~ 3.8 eV is obtained for the transport gap when using threshold positions instead of peak maxima. If the polaron–exciton energy is different from the ~ 0.9 eV estimate, $\varphi_{t,\text{elec}}$ and E_t will be correspondingly changed.

Some final observations: First, the center energy of the peaks observed in the two-photon experiment did not change as the collection angle was varied about the surface normal. This indicates that the excited charge is localized on individual molecules.⁶ Second, the occupied and unoccupied orbitals do not line-up symmetrically about the Fermi level. A similar alignment has been observed in alkanethiols on gold.¹⁴ Third, we have not attributed any transition to sulfur-like or Au–S molecular orbitals.^{3,4} Presumably, such states were not observed because electrons from those levels could not escape these densely packed monolayers.^{9,12} Last, the molecular orbital picture presented here is only an approximation. A more realistic model would treat this as a density-of-states problem and include correlation phenomena, in which the molecular orbital picture can break down.¹⁵

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