Measurement of thermopower and current-voltage characteristics of molecular junctions to identify orbital alignment

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We report an experimental technique that concurrently measures the Seebeck coefficient and the current-voltage (*I-V*) characteristics of a molecular junction to determine the identity and the effective energetic separation of the molecular orbital closest to the electrodes' Fermi level. Junctions created by contacting a gold-coated atomic force microscope tip with a monolayer of molecules assembled on a gold substrate were found to have a Seebeck coefficient of $(+16.9 \pm 1.4)\ \mu V/K$. This positive value unambiguously shows that the highest occupied molecular orbital (HOMO) dominates charge transport. Further, by analyzing the (*I-V*) characteristics, the HOMO level is estimated to be ~0.69 eV with respect to the Fermi level. © *2010 American Institute of Physics*. [doi:10.1063/1.3291521]

Understanding the charge and energy transport properties of metal-molecule-metal junctions (MMMJs) is essential to the creation of molecular electronic,[1] photovoltaic,[2] and thermoelectric devices.[3] However, before such devices can be created, it is necessary to answer several fundamental questions regarding the electronic structure of molecular junctions. Two important and related questions [Fig. 1(a)] that need to be elucidated are: (1) is the highest occupied molecular orbital (HOMO) closer to the Fermi level (more accurately the chemical potential) of the electrodes or is the lowest unoccupied molecular orbital (LUMO) closer? (2) What is the energetic separation between the closest molecular orbital and the Fermi level of the electrodes? In this letter we report an atomic force microscope (AFM) based experimental technique that enables us to directly answer these two important questions in molecular junctions created from self-assembled monolayers.

Recent progress in making thermoelectric measurements of single molecule junctions[4,5] using a scanning tunneling microscope (STM) has shown that the sign of the thermopower (Seebeck coefficient) of the junctions can be used to determine the relative position of the molecular orbitals. A positive thermopower indicates a *p*-type junction with the HOMO level being closer, and a negative thermopower indicates a *n*-type junction with the LUMO level being closer.[6] However, this STM based technique cannot be used to directly estimate the energetic separation of the closest molecular orbital with respect to the Fermi level of the electrodes. An experimental technique—transition voltage spectroscopy (TVS)—that can estimate the energetic separation has been established recently.[7–9] In TVS, the current-voltage (*I-V*) characteristics of MMMJs created by trapping molecules between a metal-coated AFM tip and a metal substrate are interpreted using Fowler–Nordheim (FN) plots[9] to estimate the position of the molecular orbital closest to the Fermi level. However, by performing TVS on a given MMMJ, it is not possible to directly determine the identity of the closest molecular orbital.

Here, we describe a simple AFM-based technique that enables, at room temperature and ambient conditions, a direct resolution of both the questions described above. This is achieved by concurrently performing thermopower measurements and TVS on MMMJs created by trapping organic molecules between a metal substrate and a metal-coated AFM tip. We illustrate this technique for the case of gold–1, 1′, 4′, 1″-terphenyl-4-thiol-gold junctions by unambiguously determining (a) the relative alignment of the molecular orbitals with respect to the Fermi level of the electrodes and (b) the energetic separation between the closest molecular orbital and the Fermi level of the electrodes.

Figure 1(b) shows a schematic illustrating a MMMJ created by placing a Au-coated AFM cantilever in soft mechanical contact (~1 nN contact force) with a Au substrate covered with a self-assembled monolayer of molecules,[10] thus creating a molecular junction with multiple trapped molecules[11] (~100). In fact, this technique for creating molecular junctions, called conducting probe atomic force microscopy (CP-AFM), was originally pioneered by Frisbie *et al.*[11] and has been used extensively to characterize the electrical conductance and (*I-V*) characteristics of MMMJs. In our experiment we make two important additions to create an experimental technique called thermoelectric atomic force microscopy (ThAFM): (1) an electrical heater is attached to the gold substrate, making it possible to heat the substrate to an elevated temperature $T+\Delta T$ [Fig. 1(b)] and (2) a short (~125 μm long, 35 μm wide, and 1 μm thick) gold-coated silicon cantilever is anchored to a thermal reservoir at a temperature T. Given the large thermal conductivity of silicon[12] (~150 W/mK) and the relatively poor thermal conductivity of the surrounding air (~0.024 W/mK), our thermal modeling[10] suggests that the temperature of the metal-coated cantilever tip in contact with molecules must be in between T and $T+0.05\Delta T$. This implies that at least 95% of the temperature differential (ΔT) occurs across the molecules trapped in between the metal electrodes (this model was first introduced by Shi and Majumdar[13] and verified by them experimentally).

The thermoelectric voltage of the junction is measured by connecting a custom-built voltage amplifier[10] between the

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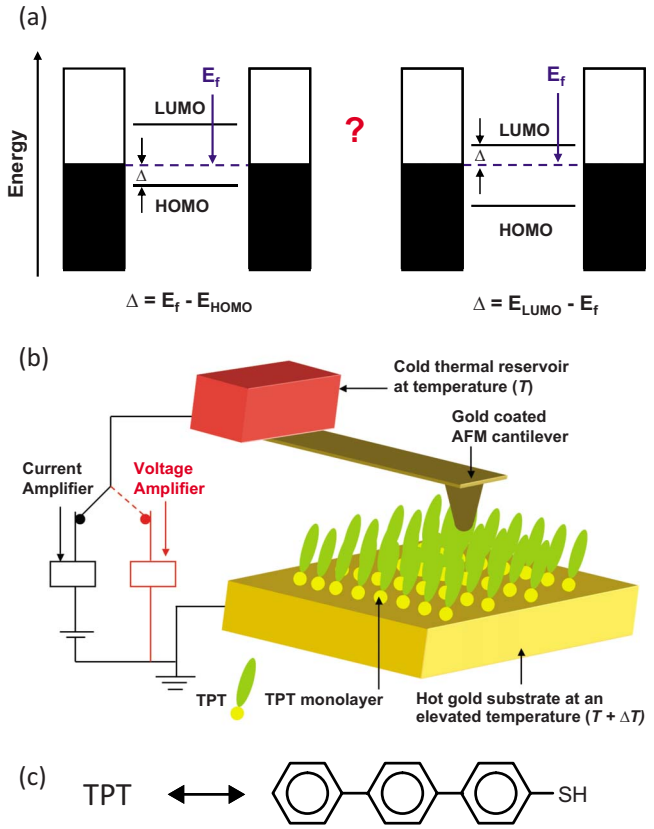

FIG. 1. (Color online) (a) Illustrates the two possible scenarios that the experiment seeks to distinguish. Also shown is the energetic separation, Δ, between the Fermi level and the closest molecular orbital that needs to be determined. (b) Schematic of the experimental arrangement: thiol terminated conjugated TPT molecules are self-assembled on a gold surface and a gold-coated AFM cantilever tip is placed in contact with the molecules to create a metal-molecule-metal junction. The AFM cantilever is in contact with a thermal reservoir at temperature T, while the gold substrate is held at an elevated temperature, $T+\Delta T$. (c) The molecular structure of TPT is shown. (Figures not drawn to scale).

AFM cantilever and the substrate [Fig. 1(b)]. The voltages ΔV [between the AFM tip and the ground[10] in Fig. 1(b)] measured for junctions created by trapping 1, 1′, 4′, 1″-terphenyl-4-thiol (TPT) molecules between gold electrodes are shown in Fig. 2. As can be seen, the magnitude of the measured thermoelectric voltage increases linearly when the temperature differential (ΔT) applied across the molecular junction is increased from 0 to 12 K in steps of 3 K (Fig. 2). Figure 2 shows a representative control experiment where the thermopower of a Au–Au junction with a resistance of ~98 Ω is measured. The thermoelectric voltage measured in these control experiments depends on the resistance of the junction[14] and varies between 0.1 μV/K for low contact resistances (mΩ) and a maximum of ~1.3 μV/K at (~100 Ω). These values are much smaller than the thermoelectric voltage measured for Au–TPT–Au junctions (Fig. 2), clearly demonstrating that the thermoelectric voltage arises from the MMMJs.

For the Au–TPT–Au junctions shown in Fig. 2, the Seebeck coefficient of the junction ($S_{\text{Au-TPT-Au}}$) can be related to the measured thermoelectric voltage of the junction by the following expression:[10]

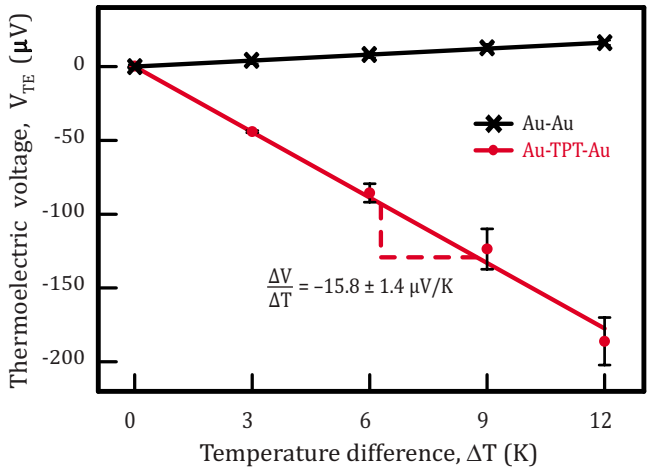

FIG. 2. (Color online) The thermoelectric voltage of a Au–TPT–Au junction, measured using ThAFM, for various temperature differentials. Each data point is obtained by averaging measurements from ten different MMMJs while the errors represent the standard deviations from the mean. The magnitude of the measured thermoelectric voltage increases linearly with the temperature differential. The thermoelectric voltage measured for a substrate with no molecules (Au–Au junctions) is also shown.

$$S_{\text{Au-TPT-Au}} = S_{\text{Au}} - \frac{\Delta V}{\Delta T}. \tag{1}$$

Here, S_{Au} is the thermopower of gold, and ΔV is the measured voltage differential between the tip and the ground. Using this expression and the measured thermoelectric voltage (Fig. 2), the Seebeck coefficient corresponding to Au–TPT–Au junctions is estimated to be $(+16.9 \pm 1.4)$ μV/K. The uncertainty of ±1.4 μV/K arises due to variations in the microscopic details of the metal-molecule contacts across individual junctions[15] and the 5% uncertainty in the tip temperature discussed above. The Landauer formalism,[6] can be applied to relate the relative position of the molecular orbitals (HOMO and LUMO) to the measured value of the Seebeck coefficient. In this formalism, the current and thermopower of MMMJs can be expressed as

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} \tau(E)[f_1 - f_2]dE;$$

$$S_{\text{MMMJ}} = -\frac{\pi^2 k_B^2 T}{3e}\frac{1}{\tau(E)}\frac{\partial \tau(E)}{\partial E}\bigg|_{E=E_f}, \tag{2}$$

where I is the current flowing through the junction, $\tau(E)$ is the transmission function, f_1 and f_2 are the Fermi–Dirac distributions corresponding to the electrodes, k_B is the Boltzmann constant, e is the charge of a proton, h is the Planck constant, T is the average absolute temperature of the junction, and E_f is the energy corresponding to the Fermi level of the electrodes. Past studies[6] have shown that while the details of the transmission function may vary across MMMJs, depending on the chemical composition of the electrodes and the molecular structure, for any given MMMJ the transmission function $\tau(E)$ is well approximated by a combination of two Lorentzian shaped peaks

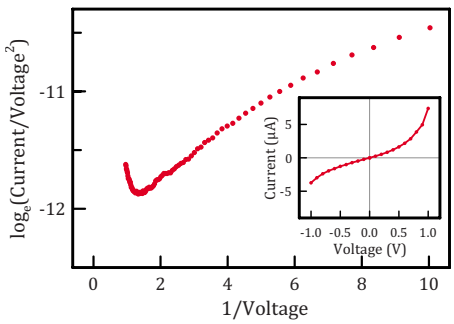

FIG. 3. (Color online) FN plot, $\ln(I/V^2)$ vs $(1/V)$, for Au–TPT–Au junctions. The minimum at 0.69 V suggests that the position of the HOMO level with respect to the Fermi level of the electrodes is ~0.69 eV. The inset shows a $(I\text{-}V)$ curve of the Au–TPT–Au junction. The curve is an average of a total of hundred $(I\text{-}V)$ measurements performed on ten different junctions, where ten $(I\text{-}V)$ measurements were performed at each junction.

$$\tau(E) = \sum_{i=1}^{2} \frac{\Gamma_1 \Gamma_2}{(E-\varepsilon_i)^2 + (\Gamma_1+\Gamma_2)^2/4}, \tag{3}$$

where ε_1 and ε_2 are the energies of the HOMO and LUMO levels, and Γ_1, Γ_2 represent the broadening of the energy levels due to the contacts. From Eqs. (2) and (3) it can be shown[4,6] that the thermopower of a molecular junction is positive if the Fermi level lies closer to the HOMO level and is negative if the Fermi level lies closer to the LUMO level. Given the positive thermopower $(+16.9 \pm 1.4)$ μV/K that was measured for the Au–TPT–Au junction, it is clear that the HOMO level lies closer to the Fermi level than the LUMO level, indicating a *p*-type junction.

While the above measurement of the thermopower of MMMJs clearly identifies the relative alignment of the orbitals, the absolute position of the HOMO level cannot be determined by thermopower measurements alone. In order to accomplish this goal, we adapt a well-established characterization technique—transition voltage spectroscopy[7–9] (TVS)—that enables a direct estimation of the position of the closest molecular orbital with respect to the Fermi level of the electrodes. As outlined above, in TVS, the $(I\text{-}V)$ characteristic of a MMMJ is analyzed by plotting a FN curve, $\ln(I/V^2)$ against $(1/V)$. Such a plot shows a clear minimum, called the transition voltage (V_{trans}), which is expected to indicate, approximately, the energetic separation $(\Delta = eV_{trans})$ between the Fermi level and the closest molecular orbital.[7–9] It must be noted that the TVS measurements are performed under large bias conditions; therefore, the values obtained are an approximation to the zero-bias energetic separation.

To perform TVS on Au–TPT–Au junctions, the $(I\text{-}V)$ characteristics (Fig. 3 inset) of the MMMJs are first obtained by sweeping an applied bias across the MMMJs from −1.0 to +1.0 V while monitoring the electric current flowing through the junctions. The FN plot obtained from the $I\text{-}V$ curve is shown in Fig. 3. While this plot can be drawn for either positive or negative voltages, conventionally,[8] the positive half of the $I\text{-}V$ characteristics are chosen. This corresponds to a *scenario* where the substrate is grounded and a positive voltage is applied to the cantilever tip. The FN plot shows a clear minimum at 0.69 ± 0.3 V suggesting that the HOMO level is 0.69 ± 0.3 eV away from the Fermi level of the electrodes. This value is in excellent agreement with TVS measurements of Au–TPT–Au junctions reported in an earlier study where a voltage of 0.67 ± 0.14 V was reported.[8] It must be noted that while the FN plots in TVS were originally interpreted by modeling the molecule as a tunneling barrier, a recent study[9] has shown that TVS is consistent with the molecular transport model adopted here and allows for an estimation of the position of the closest molecular orbital.

Another important point is that both the measured thermopower and the transition voltage obtained are independent of the number of the molecules trapped in the MMMJ.[6,7] Therefore, the technique described here is not affected by variations in the radii of AFM tips. In addition to answering the important questions regarding the identity of the molecular orbital closest to the Fermi level and energetic separation between the orbital and the Fermi level, the simple AFM based technique described here will enable a variety of studies that will elucidate the dependence of molecular structure, chemical composition of electrodes, and end groups on the thermoelectric properties of molecular junctions.

To summarize, we have demonstrated an experimental technique that unambiguously identifies the molecular orbital closest to the Fermi level of the electrodes by performing thermoelectric measurements using ThAFM. Further, by using TVS, the energetic separation of the closest molecular orbital with respect to the Fermi level is estimated. This ability to simultaneously measure the thermopower and electrical conductance of molecular junctions will not only allow the probing of the electronic structure of MMMJs but will also provide an important tool for exploring the possibility of creating high efficiency organic based thermoelectric materials.[3]

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