

## Thermoelectric effect in molecular electronics

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We provide a theoretical estimate of the thermoelectric current and voltage over a Phenylidithiol molecule. We also show that the thermoelectric voltage is (1) easy to analyze, (2) insensitive to the detailed coupling to the contacts, (3) large enough to be measured, and (4) give valuable information, which is not readily accessible through other experiments, on the location of the Fermi energy relative to the molecular levels. The location of the Fermi-energy is poorly understood and controversial even though it is a central factor in determining the nature of conduction (*n* or *p* type). We also note that the thermoelectric voltage measured over Guanine molecules with a scanning tunneling microscope by Poler *et al.*, indicate conduction through the highest occupied molecular orbital level, i.e., *p*-type conduction.

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### I. INTRODUCTION

Electrical conduction through individual molecules chemically bound to gold contacts has recently been measured using scanning tunneling microscopy (STM),<sup>1,2</sup> break junctions,<sup>3</sup> and nanopores.<sup>4</sup> Theoretical calculations of the current-voltage (*I-V*) characteristics have also been reported; see, for example, Refs. 5–9. However, a detailed quantitative comparison of theoretical and experimental results is made difficult by two factors. First, the low bias conductance depends strongly on the quality of the metal-molecule contacts,<sup>8</sup> which is ill controlled and poorly characterized experimentally. Second, the conductance gap is determined by the location of the Fermi energy relative to the molecular levels—a factor that is poorly understood and controversial.<sup>10,11</sup> One specific example of this controversy is the “Tour wire” where experiment seems to indicate that the Fermi energy is closer to the lowest unoccupied molecular orbital (LUMO),<sup>12</sup> while theory predicts it to be closer to the highest occupied molecular orbital (HOMO).<sup>9</sup> This controversy is particularly unfortunate since the location of the Fermi energy is a central factor in determining the nature of conduction (*n* or *p* type).

The purpose of this paper is to show that a measurement of the thermoelectric voltage (see Fig. 1) can provide new insights into electron transport and allows us to estimate the location of the Fermi energy relative to the molecular levels. Analogous to the hot point probe measurements commonly used to establish the *p* or *n* character of semi-conductors (see, for example, Ref. 13), the thermoelectric voltage yields valuable information regarding the location of the Fermi energy. Previous proposals have suggested that the location of the Fermi energy can be deduced from the asymmetry of the *I-V* caused by asymmetric contacts.<sup>11,14</sup> However, this is a measurement performed far from equilibrium and requires detailed knowledge of the contacts. In contrast the thermoelectric voltage is an easily interpreted linear response, and what makes it particularly useful is that it is relatively insensitive to the quality of the contacts.

In this paper we estimate the thermoelectric current and voltage over a Phenylidithiol (PDT) molecule; see Fig. 1. We

show that the thermoelectric voltage is (1) easy to analyze, (2) insensitive to the contacts, and (3) large enough to be measured. In fact, Poler *et al.*<sup>15</sup> measured the thermoelectric voltage (with a 20-K temperature difference) over a monolayer of Guanine molecules with STM. In this paper we also show that the thermoelectric voltage provide information on where the Fermi energy is relative to the molecular levels, e.g., the sign of the thermoelectric voltage over the Guanine molecule indicate *p*-type conduction.

### II. METHOD

The electrical transport through small conjugated molecules chemically bound to at least one of the contacts can be described by the Landauer formula in terms of the transmission [ $\mathcal{T}(E)$ ]:<sup>16</sup>

$$I = \frac{e}{\pi\hbar} \int_{-\infty}^{\infty} \mathcal{T}(E) [f_1(E) - f_2(E)] dE, \quad (1)$$

assuming that the electronic states in the contacts are filled according to the Fermi distribution of the reservoirs ( $f_1, f_2$ ).

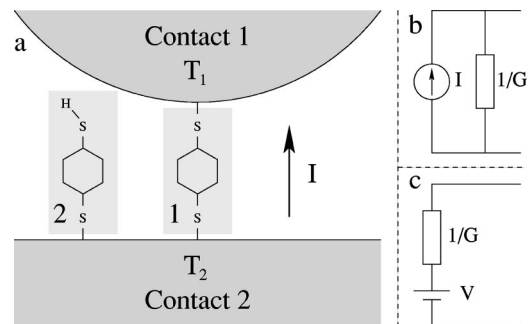


FIG. 1. (a) Proposed experimental setup to measure thermoelectric effects over a molecule with two contacts at different temperatures  $T_1, T_2$ . In this paper we focus on the Phenyl-dithiol (PDT) molecule (1) chemically bound to both contacts (break junction setup) and (2) with one weak contact (STM measurement). (b), (c) Equivalent circuits defining the voltage, conductance, and current.

If the transmission is not constant (as a function of energy), a difference in the Fermi distributions due to a temperature difference ( $\Delta T = T_1 - T_2$ ) will drive a thermoelectric current at zero bias ( $V=0$ ) (also see Ref. 24). For molecules the transmission is often smooth (compared to the thermal energy), which allows us to use the Sommerfeld expansion<sup>17</sup>

$$I = -\frac{e^2}{\pi\hbar} T(E_f) V + \frac{e}{\pi\hbar} \frac{\pi^2 k_B^2 T}{3} \left. \frac{\partial T(E)}{\partial E} \right|_{E=E_f} \Delta T, \quad (2)$$

where  $T$  is the mean temperature of the contacts  $[(T_1 + T_2)/2]$ . Similar expressions are available for heat transport.<sup>17</sup>

The thermoelectric current is usually small enough that we can use a linear equivalent circuit as shown in Fig. 1(b). The current source [see Eq. (2)] has a resistance that is the inverse of the low bias conductance:

$$G = \frac{e^2}{\pi\hbar} T(E_f). \quad (3)$$

Alternatively we could represent the effect in terms of a voltage source ( $V=I/G$ ) with a series resistance as shown in Fig. 1(c):

$$V|_{I=0} = \frac{\pi^2 k_B^2 T}{3e} \left. \frac{\partial \ln(T(E))}{\partial E} \right|_{E=E_f} \Delta T. \quad (4)$$

As we will see below, this open circuit voltage can be large enough to measure and is relatively insensitive to the coupling to the contacts.

To obtain estimates of the low bias conductance and the thermoelectric voltage we need to calculate the transmission as a function of energy for a molecule connected to metallic contacts. Here we calculate the transmission using the non-equilibrium Green's function formalism in conjunction with extended Hückel (EH) theory (see Ref. 25) as described in Ref. 18. This is a simple but sufficient approximation for the transmission through a molecule since, in our experience, the qualitative features of the transmission is not very sensitive to the method (Hückel, EH, or *ab initio*) used, e.g., to compare with *ab initio* calculations see Ref. 8. What may require an *ab initio* model is to theoretically predict the location of  $E_f$  with respect to the molecular levels. However, as explained in the introduction, the purpose of this paper is not to predict the position of  $E_f$ , but to relate the thermoelectric voltage to the location of  $E_f$ . We therefore take  $E_f$  as an adjustable parameter (see Ref. 26) to be determined from experiments.

### III. AN ILLUSTRATIVE EXAMPLE

We choose to estimate the thermoelectric voltage across a phenyl-dithiol (PDT) molecule [Fig. 1(a)] since it has been studied extensively after the experiment by Reed *et al.*<sup>19</sup> In any case, our objective is to provide a reasonable qualitative estimate rather than an accurate quantitative value for a spe-

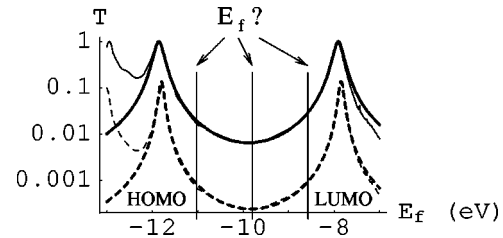


FIG. 2. Logarithmic plot of the transmission as a function of energy. Thin solid line: Transmission calculated from the Extended Hückel model through the PDT molecule strongly bound to both contacts. Thin dashed line: PDT weakly bound to one side (Au-H distance 2.9 Å). Thick lines: The transmission fitted to Lorentzian transmission peaks associated with the molecular energy levels [see Eq. (5)]. Note the widely different positions of the Fermi energy ( $E_f$ ) suggested by different authors.

cific molecule. On gold surfaces, PDT chemisorbs forming a bond between the sulfur and gold. The strength of this bond is difficult to estimate since the precise experimental geometry is unknown. For a STM measurement the contact with the tip is also weaker than the substrate bond. We therefore calculate the transmission through the PDT molecule perfectly bound to the gold contacts [see molecule 1 in Fig. 1(a)] and through a PDT molecule chemisorbed on only one contact with different distances between the molecule and contact 1 [see molecule 2 in Fig. 1(a)].

Figure 2 shows the transmission through the PDT molecule for perfect contacts on both sides (solid line) and one weak contact (dashed line). The position of the Fermi energy ( $E_f$ ) relative to the HOMO and LUMO levels is one of the main parameters affecting the current-voltage characteristics.<sup>10</sup> As pointed out in the introduction, the position of  $E_f$  is difficult to estimate. The suggested positions of  $E_f$  range from (1) closer to the HOMO level,<sup>5,8,9,20,21</sup> (2) midgap, and (3) closer to the LUMO level;<sup>6,12</sup> see Fig. 2. Since the thermoelectric effect depends on the slope of the transmission at  $E_f$  [Eq. (4)], the sign of the thermoelectric voltage and current will be determined by where  $E_f$  is located relative to the molecular levels.

The thermoelectric voltage calculated from Eqs. (4) and (5) is shown in Fig. 3 for a 10-K temperature difference at

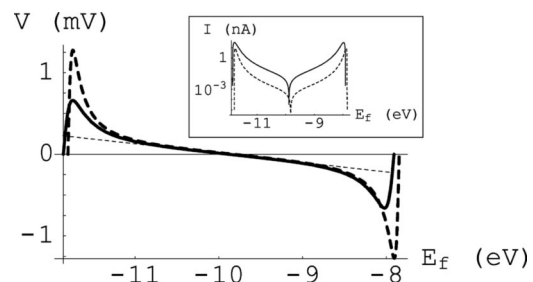


FIG. 3. Thermoelectric voltage generated by a 10 K difference in temperature ( $T_1 = 300$  K,  $T_2 = 310$  K) for different positions of the Fermi energy ( $E_f$ ). Solid line: PDT strongly bound to both contacts. Dashed line: weak bond on one side. Thin dotted line, approximated by Eq. (6). Inset: Logarithmic plot of the thermoelectric current.

room temperature ( $T_1 = 300$  K,  $T_2 = 310$  K). Note that the thermoelectric voltage was calculated from a transmission fitted to Lorentzian peaks (see Fig. 2), this removes the magnification (by taking the derivative) of small numerical errors. Unless  $E_f$  is located very close to the middle of the HOMO-LUMO gap the size of the thermoelectric voltage is of the order 0.5–0.1 mV. Since the thermoelectric voltage is proportional to  $\Delta T$  [Eq. (4)], even smaller temperature differences will give a measurable thermoelectric voltage.

The measured conductance of the PDT molecules<sup>19</sup> is smaller than the theoretical estimates by 2–3 orders of magnitude.<sup>8</sup> This discrepancy indicates that the interaction strength between molecule and contacts is smaller than that assumed in the models (for STM measurements this is obviously true). It is plausible to believe that the molecule forms a strong bond with one of the contacts and only interacts weakly with the second contact (also see Ref. 27). However, the calculated thermoelectric voltage with one weak contact (Fig. 3, dashed line) has almost the same magnitude as the perfectly bound molecule (solid line) and is slightly larger close to the transmission peaks.

To understand why the thermoelectric voltage is unaffected by weak contacts it is instructive to fit the transmission (Fig. 2) to Lorentzian transmission peaks:

$$\mathcal{T}(E) = \sum_{i=1}^2 \frac{\Gamma_1 \Gamma_2}{(E - \epsilon_i)^2 + (\Gamma_1 + \Gamma_2)^2/4}, \quad (5)$$

where  $\epsilon_i$  is the energy of the two levels, and  $\Gamma_1$  and  $\Gamma_2$  the broadenings by contacts 1 and 2. This approximation is useful for the PDT molecule since the transmission around the HOMO-LUMO gap of PDT is mainly determined by two levels that couple approximately equally to the contacts (see Ref. 28). Fitting the transmission to Eq. (5) using a least square fit [of  $\ln(\mathcal{T})$ ] gives  $\Gamma_1 = \Gamma_2 = 0.11$  eV,  $\epsilon_1 = -11.86$  eV, and  $\epsilon_2 = -7.91$  eV. For the weakly coupled PDT molecule (with a Au-H distance of 2.9 Å) the least squares fit gives ( $\Gamma_2 = 0.11$  eV):  $\Gamma_1 = 0.0042$  eV,  $\epsilon_1 = -11.80$  eV, and  $\epsilon_2 = -7.85$  eV. These fits give good approximations to the calculated transmission (see Fig. 2), other Au-H distances (not shown in the figure) in the range 1–5 Å also fit the transmission well.

Assuming the Fermi energy to be situated in between the HOMO and LUMO levels and far from the levels ( $|E_f - \epsilon_{1,2}| \gg |\Gamma_1 + \Gamma_2|$ ) we can Taylor expand Eq. (4) in the energy around the midpoint of the HOMO-LUMO gap [ $E = (\epsilon_1 + \epsilon_2)/2$ ]:

$$V|_{I=0} = \frac{8\pi^2 k_B^2 T}{e} \frac{1}{(\epsilon_1 - \epsilon_2)^2} \left( E_f - \frac{\epsilon_1 + \epsilon_2}{2} \right) \Delta T. \quad (6)$$

This shows that the thermoelectric voltage is, to first order, independent of the strength of the interaction with the contacts, see thin dotted line in Fig. 3. This result is not limited to the PDT molecule but valid for most conjugated molecules (see Ref. 29).

To experimentally measure the thermoelectric voltage, the thermoelectric current has to be larger than any leakage currents. The thermoelectric current [Eq. (2)] through the PDT molecule is shown in the inset of Fig. 3. Since the thermoelectric current is proportional to the transmission ( $\mathcal{T}$ ), the magnitude of the current is strongly dependent on the strength of the interactions between molecule and contacts. It is also important to realize that for very weak coupling to both contacts, i.e., in the Coulomb blockade regime, the simple decomposition of the transmission into HOMO and LUMO peaks (see Fig. 2) might not be enough to describe the thermoelectric effect. However, even for a molecule which is relatively weakly connected to one contact (but chemically bound to the other contact) should give a thermoelectric current of the order of 1–100 pA; see the inset in Fig. 3.

#### IV. SUMMARY AND DISCUSSION

The position of the Fermi energy is one important ingredient in understanding electrical transport through molecules. It is also interesting since shifting the Fermi energy by (1) doping, (2) the addition of side groups, (3) a gate field, or (4) the use of different contact material, can be used to optimize the molecular properties. Phenomena of this type can be probed and evaluated through a measurement of the thermoelectric voltage (coupled with  $I$ - $V$  measurements).

In this study we have only considered a single molecule between the two contacts. However, unless the local structure of each molecule is different, the thermoelectric effect should only be affected trivially. It is possible that the detailed structure of the gold atoms bonding to the molecule affect the charge transfer to the molecule and thus the position of the Fermi energy. If this is the case, the variations could be mapped by STM measurements on different molecules on a single substrate. Another simplification in our work is that we only focus on the PDT molecule. Due to its simple structure the transmission is almost symmetric around the middle of the HOMO-LUMO gap. For other molecules this need not be true. In this case, the interpretation of the thermoelectric voltage still provides an estimate of the Fermi energy even though it is less straightforward.

To our knowledge the only reported measurement of the thermoelectric voltage over a molecule was performed by Poler *et al.*<sup>15</sup> Using a STM tip they measured the thermoelectric voltage over Guanine molecules on a graphite substrate. A detailed analysis of the measurement is not possible since the  $I$ - $V$  characteristic was not measured in this experiment. However, the sign of the thermoelectric voltage indicates that the electrical transport is conducted through the HOMO level and the measured thermoelectric voltage was similar in magnitude to the value estimated here for PDT ( $0.5 \pm 0.01$  mV at  $\Delta T = 26.5$  K).

An intriguing possibility is to use the thermoelectric effect over a molecular SAM as a thermoelectric element. Applications of these elements include thermoelectric coolers (Peltier effect) and power generators. We have performed preliminary calculations on the efficiency of such elements. However, the efficiency is limited (and largely determined)

by the lattice thermal conductivities of the SAM. We therefore believe that until there are reliable estimates of the thermal conductivity any speculations on the efficiency of such elements are premature.

In summary, we have shown that a measurement of the thermoelectric voltage over a molecule is (1) simple to analyze, (2) insensitive to the contacts, (3) feasible, and (4) should give valuable information, which is not readily acces-

sible through other experiments, on the location of the Fermi energy relative to the molecular levels.

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<sup>24</sup>In addition to the current given by the slope of the transmission, the chemical potentials of the contacts shifts slightly. However, this effect is negligible for most metals (Ref. 22).

<sup>25</sup>To compare energy levels with experimental quantities, e.g., work functions, the EH levels should be shifted (towards positive energies) by approximately 4.6 eV since electron-electron interactions are neglected.

<sup>26</sup>In reality the Fermi-energy of the contacts is fixed but charging effects shift the molecular levels. Here we keep the molecular levels fixed and treat the Fermi energy of the contacts as a parameter.

<sup>27</sup>Emberly and Kirczenow have pointed out that the symmetric  $I$ - $V$  curves obtained in measurements on PDT are consistent with a geometry where two weakly interacting molecules are attached to the two different contacts (Ref. 23). We have omitted this case in this paper since the thermoelectric voltage calculated in this geometry is qualitatively the same as for one PDT molecule weakly coupled to one contact.

<sup>28</sup>The transmission peaks actually correspond to the HOMO and LUMO+1 levels since the LUMO level is localized to the benzene ring and give zero transmission.

<sup>29</sup>From the NEGF formalism (Ref. 10),  $\mathcal{T} = \text{Tr}(G\Gamma_1 G^\dagger \Gamma_2)$ . If a weak coupling only scales  $\Gamma_1$  by a constant, it is easy to show that the transmission scales by the same constant when the energy is far from any resonances (due to the molecular energy levels) in  $G$ .