

# Temperature-Dependent Electronic Transport through Alkyl Chain Monolayers: Evidence for a Molecular Signature

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Temperature-dependent transport measurements through alkyl chain monolayers that are directly chemically bound to Si, show that the currents decrease as the temperature increases. We relate this temperature dependence primarily to a gradual un-tilting of the adsorbed molecules, which leads to increasing of the film thickness, resulting in a wider tunnel barrier. Following that, we conclude that a significant part of transport through these alkyl chain monolayers occurs “through space”. The experimental finding and its interpretation result from the high reproducibility and accuracy of the transport results for the semiconductor/alkyl chain/ metal junctions that we study.

## Introduction

Apart from possible applications of molecules as electronic components, understanding electronic charge transport through molecules is a central issue in molecular electronics, as it may reveal new science of these systems. A major problem for arriving at such comprehension is that interfaces can easily dominate transport across molecular junctions, screening the effects of molecules between two conducting electrodes.<sup>1–3</sup> Therefore, one of the challenges is to distill molecular transport information from the experimental data.

Recently, we showed that a monolayer of alkyl chains, chemically bound to Si via a Si–C bond and with a metal top contact to the molecules, yields a very stable and reliable junction with well-defined interfaces.<sup>4–6</sup> Another interesting aspect of this system is that transport is distinctly controlled by the electrodes over one bias voltage range and by the molecular layer over another one, depending on the electrode material and the molecular length. For example, for *n*-Si molecular junctions, transport at low forward and at reverse bias is dominated by thermionic emission over the Schottky barrier inside the Si, whereas at higher bias, where the Schottky barrier is eliminated the current flow is mediated by tunneling through the molecular layer.<sup>4,57</sup> With this system, then, we can distinguish between contributions from the interface and from the molecular film to transport, which, in turn, allows us to learn about the role of the molecular film in transport. Furthermore, the fact that similar transport behavior is observed for comparable molecular junctions, with different electrode materials such as GaAs–alkyl-chains/Hg junctions<sup>8–11</sup> or with different molecule/electrode binding groups such as Si–O–C<sub>n</sub>H<sub>2n+1</sub>/Hg<sup>12</sup> [*n* = 10, 12, 14, 16] suggests a general characteristic of semiconductor/saturated molecules/metal junctions.

Here, we report and analyze the temperature-dependent measurements through alkyl chain monolayers, chemically bound to Si<sup>13,14</sup> or GaAs. The validity of the results relies on the highly reliable, well-defined molecular junctions<sup>5,6,11</sup> al-

lowing detailed data analyses. The results suggest that molecular dynamics are involved in the transport process and that “through space” interactions make a major contribution to tunneling through alkyl chains.

## Background

Linear chains of methylene (CH<sub>2</sub>) units (alkyl chains) present a simple and basic model to study electron transport through molecule-based junctions and, possibly, also through biological systems. Simple as these molecules are, they are very flexible because of the internal rotation along the C–C bond. That is, even though the “all trans” conformation is the most stable one in a monolayer, other conformations can be accessed and may, at room temperature, coexist. Since such a rotation requires energy, it is a thermally activated process, and therefore, the monolayer structure is expected to be temperature-dependent. Indeed, the structural dynamics of alkyl chain monolayers as well as their electronic structure were and still are studied extensively, well before modern experimental interest in molecular electronics.<sup>15–22</sup> Because in the present study the temperature dependence of electronic transport through these molecular based junctions is central, we shall summarize some earlier findings.

**Temperature Dependent Behavior of Alkyl Chains.** (1) At room temperature, alkyl chains bound to Si or Au by Si–C or Au–S–C, respectively, are tilted ~30° with respect to the surface normal. The tilt angle gradually decreases with increasing temperature, giving a corresponding increase in monolayer thickness.<sup>20,23,24</sup> Such behavior was calculated for the above-mentioned cases of alkyl chains, bound to Si (111) (cf. Figure 1) and to Au(111).<sup>20,23,24</sup>

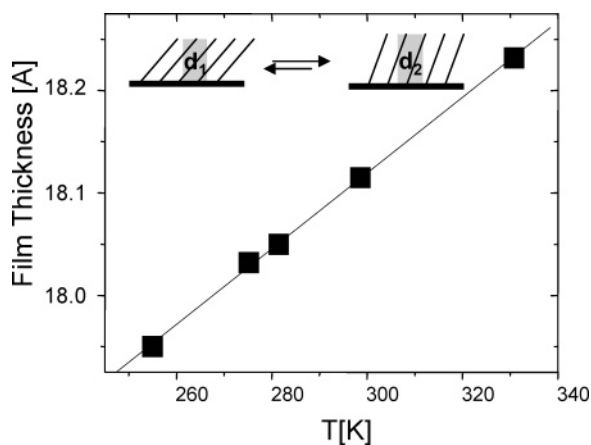
(2) Increasing temperature leads to an increase of nonplanar conformational defects. These defects were identified as “end-gauche”, a gauche defect at the end group, “kink”, a gauche defect in the chain and “double-gauche”, two defects on the same molecule. The “end-gauche”<sup>20</sup> and possibly the “kink” forms<sup>25</sup> are thought to be dominant nonplanar defects under our conditions.

(3) The same types of conformational defects appear to exist in all *n*-alkanes. Their concentration increases significantly with increasing chain length.<sup>20,25</sup>

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**Figure 1.** Expansion of alkyl chain monolayer, bound to Si via Si-C bonds, as a function of temperature. Values were taken from Monte Carlo calculations done by Zhang et al.<sup>24</sup> Inset: Illustration of change in film thickness due to gradual un-tilting of the monolayer with increasing temperature.

(4) The films disorder with increasing temperature,<sup>20</sup> a process that is reversible below a certain temperature.<sup>22,26</sup>

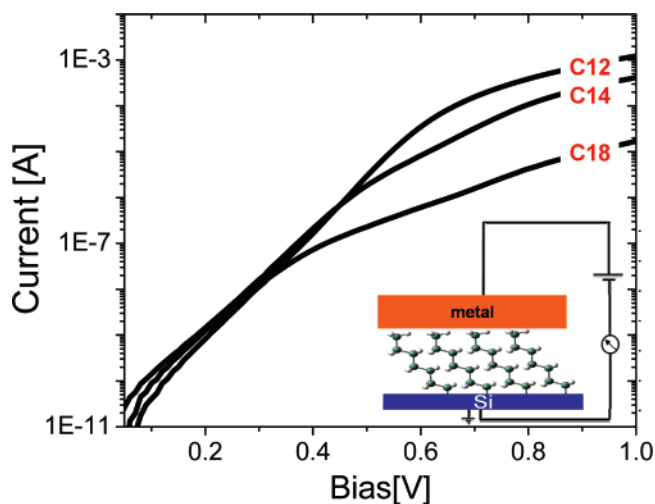
(5) Alkyl chain molecules expand with increasing temperature because of the lengthening of the molecules' C-C bonds. Over the 250–330 K temperature range the monolayer expands  $<0.02\%$ ,<sup>27</sup> that is, an effect that is negligible compared with the  $\sim 2\%$  change due the monolayer tilt angle change.

On the basis of 1 through 4 above, it is likely that transport through these types of molecular junctions will be temperature-dependent<sup>28</sup> for any electronic transport mechanism.

**Electronic Transport through Alkyl Chains.** Transport through alkyl chain monolayers is mostly described by direct tunneling or super-exchange<sup>29–32</sup> because the barrier for transport is much larger than  $kT$ .<sup>33</sup> Strictly speaking, transport via these mechanisms should not depend on temperature if the dynamics of the system are excluded. Indeed, there are reports on temperature-independent transport through alkyl chain molecular junctions, both for single molecule and for monolayer-based junctions. These results<sup>34–36</sup> suggest that molecular dynamics contributions<sup>37</sup> were either negligible or below the detection limit in those experiments. An exception is a report for single alkyl chain junctions, where the tunneling efficiency was found to increase with increasing temperature. This was explained by a decrease in tunnel barrier width with temperature, due to changes in the molecular conformation.<sup>38,39</sup> However, it is difficult to exclude interface contributions to the observed currents from these data, because the longest measured molecule was a nonanedithiol.<sup>40,3</sup> In the following, we will argue that, unlike single molecule junctions, the tunnel barrier for monolayer-based junctions widens with increasing temperature, because of an un-tilting of the molecules (see Figure 1).<sup>20,24</sup>

## Materials and Methods

**Monolayer Synthesis.** Si-C linked monolayers were formed by thermally induced hydrosilylation of alkenes on H-terminated Si(111), as described elsewhere.<sup>6,41,42</sup> Alkyl chain monolayers on GaAs were formed by adsorbing alkyl phosphonates (5 mM in tetrahydrofuran) onto GaAs(100).<sup>8</sup> The molecular junction configuration is shown in the inset of Figure 2. Thorough characterizations of the monolayers, as described in detail in refs 6 and 41, showed them to be of the required high quality.<sup>6</sup> These characterizations, as well as the long-term stability of the monolayers in air, also exclude any significant presence of water or other impurities in the films.



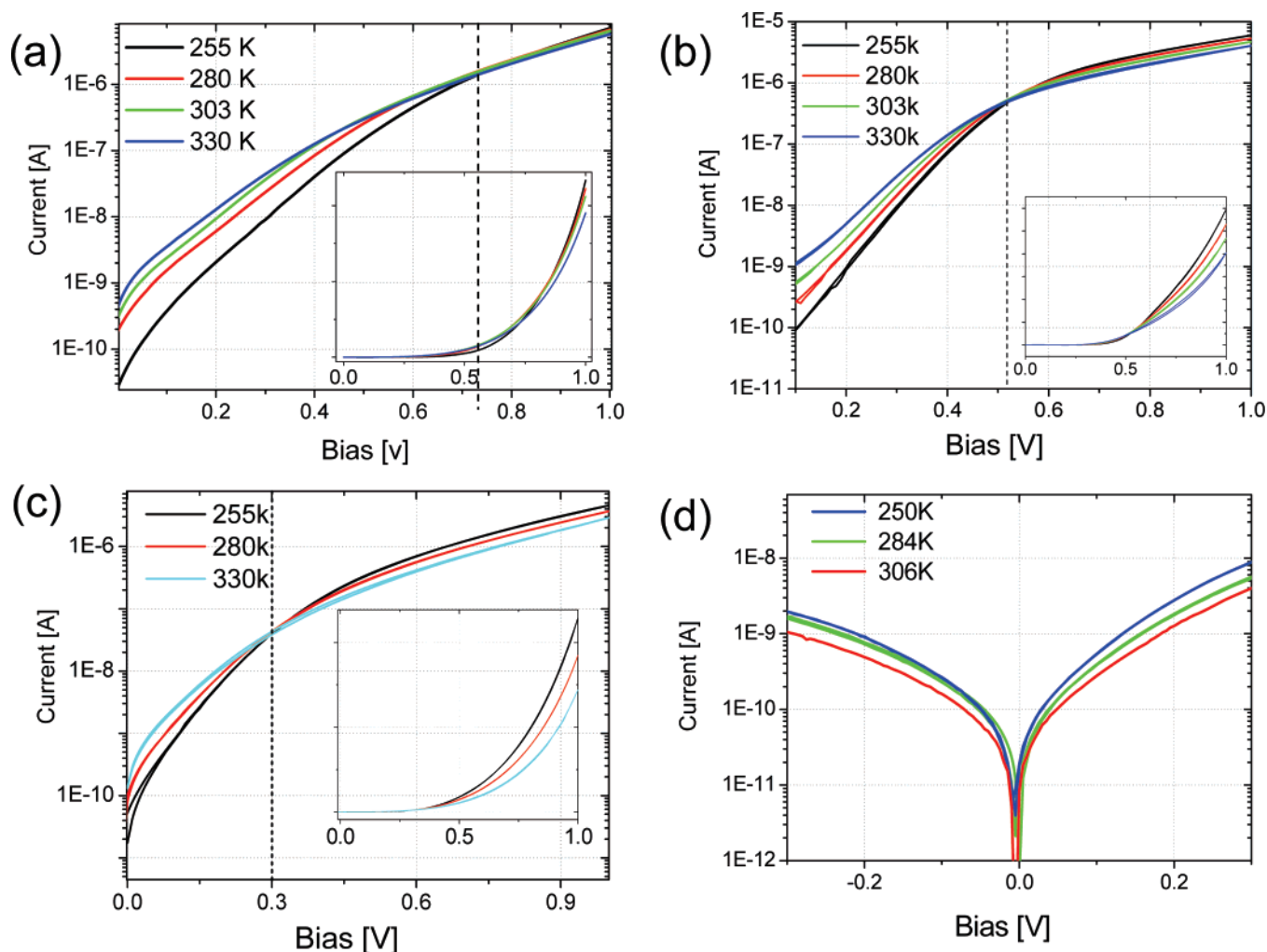
**Figure 2.** Forward bias part of room-temperature current-voltage characteristics for Si-C<sub>n</sub>H<sub>2n+1</sub>/Hg ( $n = 12, 14, 18$ ). At low bias, the currents are limited by the electronic properties of the electrodes and at higher bias regime the currents decrease exponentially with molecular length.<sup>5</sup> Optical measurements show a geometric contact area of  $\sim 10^{-3}$  cm<sup>2</sup>. Inset: Experimental setup of alkyl chain molecular junctions. The top contact is Hg (liquid), Au, or Pd.

**Electrical Transport Measurements.** Temperature-dependent measurements were conducted on molecular junctions with a liquid Hg drop or indirectly evaporated Au or Pd metal contacts,<sup>43</sup> using an MMR variable temperature measurement system. Here, the sample is in a Faraday cage-like sample chamber and can be contacted mechanically by micromanipulators. After sample placement, the sample chamber was flushed a few times in a row with N<sub>2</sub> and pumped down (to 20 mTorr). The sample was then first heated (to 330° K) for  $\sim 10$  min to clean it and to prevent ice clogging upon cooling. The sample holder was cooled by an MMR Joule-Thomson cooler, using a computerized control system. An additional cooling finger was placed in the chamber to prevent water condensation on top of the sample. The electrical contact was made to the back of the semiconductor, using the refrigerator cooling finger connectors. The second metal (top) electrode to the sample was contacted by a micromanipulator. For indirectly evaporated Au and Pd contacts, a drop of GaIn was placed at the tip of the micromanipulator, to prevent mechanical pressure and to ensure good electrical contact. With Hg as top contact,<sup>44</sup> a drop was placed on the sample, after which the sample was gently placed on the sample cooling finger. Because of surface tension, good and stable electrical contacts to the sample could be achieved only if the manipulator needle was placed exactly on the middle of the Hg drop. Current-voltage characteristics were measured, first upon cooling, then upon heating, and then again upon (re)-cooling, to ensure junction stability and reliability of the experimental results. All voltage scans were cyclic to ensure temperature stability of the junction. Scans mostly started from zero voltage. The back contact of the junction was grounded.

## Results and Discussion

**Room-Temperature Transport Data.** The use of a semiconductor as one of the electrodes allows distinguishing between interface and pure molecular effects. This is feasible by considering both metal/semiconductor and metal/insulator/semiconductor (MIS) transport mechanisms that are well-known in the literature.<sup>5,45,46</sup>

Figure 2 shows the forward bias room-temperature transport characteristics for three *n*-Si-alkyl chain monolayer/Hg junctions,



**Figure 3.** Temperature-dependent current–voltage data of (a–c)  $n$ -Si– $C_nH_{2n+1}$ /Hg and (d)  $p$ -Si– $C_{18}H_{37}$ /Hg, on semilogarithmic plots. In a–c at low forward bias, currents increase with temperature, whereas at higher bias, they decrease with temperature. Insets: Same data, but on a linear scale. (a)  $n = 12$ ; (b)  $n = 14$ ; (c)  $n = 18$ . For the  $p$ -Si junction (d) only one type of behavior is observed, the current decreases with increasing temperature. The same behavior was observed also with other metals (Au, Pd), deposited in different ways as top contacts. For clarity's sake only a few of the temperature  $I$ – $V$  curves are shown, but the same behavior was observed if data (with Au contacts) between 200 K and 330 K were included. Curves were recorded in a cyclic mode and measured upon cooling, heating, and re-cooling, to ensure junction stability.

differing in their molecular length and, thus, in their film thickness.<sup>5</sup> At low bias, the semiconductor/metal interface dominates transport. The observed currents are limited by the barrier inside the Si, rather than by the molecules. Increasing the applied bias gradually eliminates the barrier inside the Si; that is, the interface contribution and the currents become limited by tunneling through the molecular barrier.<sup>5,47</sup> In this bias regime, currents decrease exponentially with molecular length, as expected for tunneling through a rectangular barrier.<sup>48</sup> In addition, as the molecular length increases, transport through the whole junction is less and less dominated by the electrodes or the interfaces. For instance, deviation from the main low bias locus (the common line for the 3 junctions) occurs at  $\sim 0.3$  V for octadecane (C18) and at  $\sim 0.7$  V for dodecane (C12) junctions.<sup>49</sup>

These results for Si/alkyl chains monolayer/Hg junctions agree well with theoretical simulations done for an ideal Si/SiO<sub>2</sub>/metal MIS system.<sup>46</sup> Generally speaking, this agreement indicates the following:

(a) Transport through this molecular system is not controlled by monolayer defects such as pinholes that usually scale with the molecular length.<sup>19,50</sup>

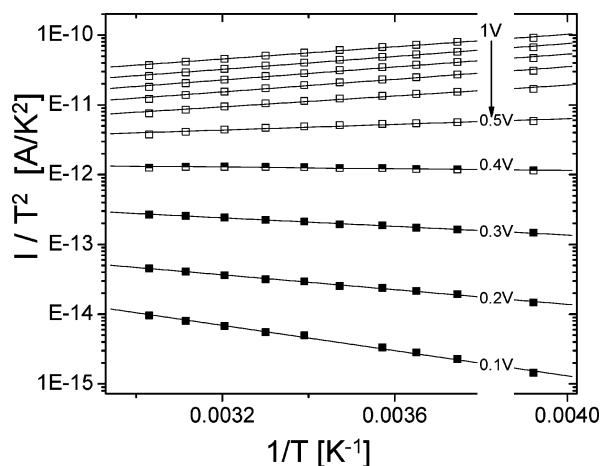
(b) These molecular layers act as sufficiently ideal insulators to produce near-ideal MIS junctions.<sup>47</sup>

(c) Two types of barriers control transport, the Schottky barrier inside the semiconductor<sup>45</sup> and the tunneling barrier due to the insulating property of the molecular monolayer.<sup>5</sup>

We now ask if this molecular system behaves “just” as an ideal insulator. The answer is no, as agreement between the molecular junctions and the prediction for MIS junctions breaks down when we consider the temperature dependence of transport, as is discussed below.

**Temperature-Dependent Current–Voltage Characteristics.** Apart from revealing the molecular signature,<sup>51</sup> temperature-dependent measurements can assist in understanding the transport mechanisms through these molecular junctions. The above-mentioned room-temperature results suggest two transport mechanisms; (i) thermionic emission (TE) over the semiconductor barrier, a temperature activated mechanism, and (ii) tunneling through the molecular layer, a mechanisms that does not depend on temperature to a first approximation.<sup>45</sup> Figure 3a–c shows temperature-dependent current–voltage ( $I$ – $V$ ) characteristics for  $n$ -Si molecular junctions, for three different molecular lengths (C12, C14, and C18). As expected for a TE mechanism over a barrier inside the Si, at low bias, the current increases with temperature. At higher forward bias, where the current is limited by tunneling through the molecular layer, the current decreases with increasing temperature. While the current decreases are





**Figure 4.** Semilogarithmic plots of  $(I/T^2)$  vs  $(1/T)$  at different applied bias voltages for  $n\text{-Si-C}_{14}\text{H}_{29}/\text{Hg}$  junctions. At low bias (closed squares), the slopes are negative, indicating a thermally activated barrier. At high bias (open squares), the slopes are positive, indicating that the transport barrier is reduced as the temperature decreases. For clarity's sake, only results for  $n\text{-Si-C}_{14}\text{H}_{29}/\text{Hg}$  are shown, but the same behavior was observed for other molecular junctions with different molecular lengths and with Au or Pd top contacts.

**TABLE 1: Voltages at Which the Current's Temperature-Dependence Inverts and Where, in the Room-Temperature Data, the Current Starts to Deviate from TE Behavior, for Different  $n\text{-Si}$  Molecular Junctions, as a Function of Molecular Length (or Monolayer Thickness)**

molecular junction	inversion point (V) $\pm 0.1$ V	deviation voltage <sup>a</sup>
$n\text{-Si-C}_{12}\text{H}_{25}/\text{Hg}$	0.7	0.6–0.7
$n\text{-Si-C}_{14}\text{H}_{29}/\text{Hg}$	0.5	0.5
$n\text{-Si-C}_{18}\text{H}_{33}/\text{Hg}$	0.3	0.3

<sup>a</sup> Voltage at which room-temperature  $I$ – $V$  deviates from thermionic emission, TE.

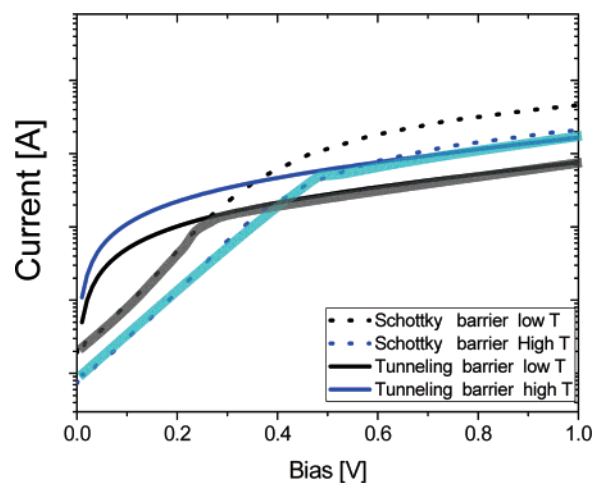
small, they are reproducible and well above the noise in the measurements.<sup>52,53</sup>

For any given molecule, the transition between TE over the barrier inside the Si and tunneling through the molecular layer occurs over a very narrow voltage range, which we define as the inversion point. As summarized in Table 1, the inversion point depends monotonically on the molecular length (or monolayer thickness). A correlation, similar to that between the inversion points and the molecular lengths, can be found in the room-temperature transport data, between the voltage at which the currents start to deviate from the main (TE) locus (see Figure 2) and the molecular length.

The origin of the inversion point can be understood from Figure 5, which illustrates schematically the  $I$ – $V$  characteristics expected for the following: (a) transport through a metal/semiconductor junction dominated by TE mechanism, at two different temperatures;<sup>45</sup> and (b) transport through a rectangular barrier according to the Simmons model,<sup>48</sup> with two different barrier widths. The two barrier widths simulate the above-noted increase in monolayer width with increasing temperature due to un-tilting of the molecules (see Figure 1).

The illustration shows that an “experimental” curve can be obtained by considering curves of the same temperature (same color) and combining them. In this case, the lowest current of the two over the whole voltage range must be considered because it limits the measured current. In this way, inversion is clearly observed.

To examine this behavior the experimental results shown in Figure 3 are re-plotted as  $\log(I/T^2)$  versus  $1/T$ <sup>48,56</sup> for various



**Figure 5.** Illustration of the origin of the “inversion point” in the temperature-dependent semilogarithmic current–voltage curves (cf. Figures 3). The dashed curves are  $I$ – $V$  characteristics for a metal/semiconductor junction, where transport is dictated by thermionic emission over the barrier inside a semiconductor. The solid lines are  $I$ – $V$  characteristics for transmission by tunneling through a rectangular insulating barrier, with two different barrier widths. The bottom line is for the wider barrier (which, within the model used here, corresponds to the higher temperature,  $T_2$ , as the tilt of the molecules decreases with increasing temperature) and the blue line is for the narrower barrier (lower temperature,  $T_1$ ). By taking the minimum current of the dashed and solid curves for each temperature, we get the thick solid lines, which illustrate what is measured experimentally.

bias voltages. Figure 4 shows the transition from a low bias regime in which the transport efficiency increases with temperature, as expected for TE, to a higher bias regime where transport efficiency decreases with increasing temperature. We assign this current reduction with increasing temperature to the dynamics of the molecular system as is discussed below.<sup>48,54,55</sup>

To examine the temperature dependence further, we also measured  $p\text{-Si}$  molecular junctions. By considering our room-temperature results<sup>47</sup> and on the basis of the Schottky theory, at any given applied bias voltage, the barrier inside  $p\text{-Si}$  is expected to be less than that for  $n\text{-Si}$ . Therefore, current through  $p\text{-Si}$  molecular junctions is mostly limited by the molecular barrier and, thus, by tunneling through the molecular film, as we showed recently.<sup>47</sup> Thus, in  $p\text{-Si}$  based junctions, the molecular behavior is expected to be more pronounced than in the  $n\text{-Si}$  based ones. Indeed, Figure 3d shows only one type of temperature behavior. Transport through the molecular junction decreases slightly with increasing temperature, as expected for the temperature-induced changes in monolayer width.

All in all, the results presented in Figure 3 show that in the bias regime where interface effects are minimal or absent, the tunneling current through the molecular layer decreases with increasing temperature.

The results can be rationalized as follows:

(a) Change of the spatial width of the barrier: the tilt angle of the molecule relative to the surface decreases with increasing temperature, yielding a thicker molecular film, and therefore, a wider barrier to tunneling (see Figure 1).<sup>20,24</sup>

(b) Monolayer defects: as the temperature increases, conformational defects are created in the monolayer.<sup>20</sup> Such defects lead to a decrease in charge-transfer efficiency as was shown previously.<sup>57,58</sup>

Explanations a and b refer to two limiting types of interaction for transport, namely, “through-space” and “through-bond” ones, respectively.<sup>29,33,59–63</sup> More explicitly, in the case of transport mediated “through bond”, that is via the C–C  $\sigma$  bonds; a change

in the monolayer tilt angle with temperature should not play a role, while an increase in monolayer defects with temperature is expected to be important if transport is dominated by “through bond” interactions.

To try to distinguish between these two transport processes in our system, we performed the following temperature-dependent measurements:

(1) The first is transport measurements on a molecular system in which the alkyl chain molecules are bound to the electrodes at both sides of the molecules. The idea here is that, if the molecules are restrained at both ends by chemical bonds to the electrodes, the density of gauche defects should decrease and any effect of the temperature-dependence of their density should be diminished.<sup>64</sup> Transport measurements were done on *p*-Si-C<sub>11</sub>H<sub>23</sub>-S-Hg and *p*-Si-C<sub>11</sub>H<sub>23</sub>-S-Au junctions, where the alkyls are bound to both electrodes via Si-C bond and via S-Hg or S-Au bond to the metal electrode.<sup>4,41</sup> The results are shown in Supporting Information (Figure SI-1). No significant differences<sup>65</sup> compared to the molecular junctions shown in Figure 3 were found. That is, the temperature dependence of the *I*-*V* characteristics was the same, whether the molecules were bound to both electrode sides or to only one of them. This result suggests that “end gauche” defects do not play a dominant role for transport through this system.

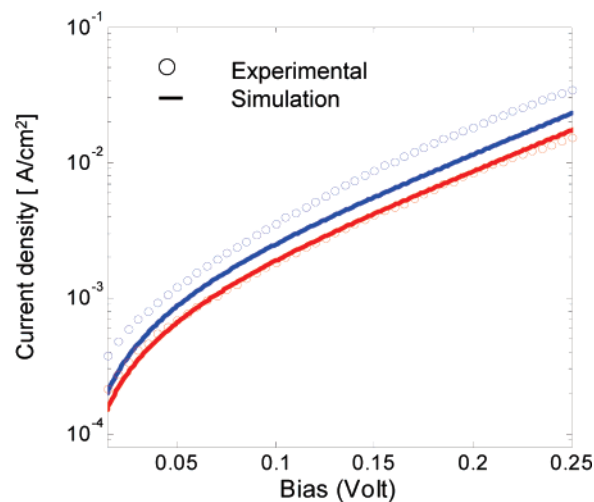
(2) The second is transport measurements on molecular junctions in which the alkyl chains are barely tilted at room temperature, and, thus, the temperature dependence of the tilt angle is expected to be small. Therefore, if transport were mediated by “through space” interactions, the currents through the junction should not show appreciable temperature dependence.

To investigate this issue, we measured the temperature-dependent transport through Hg-contacted alkyl phosphonate monolayers on GaAs(100), a system where the molecular tilt angle is smaller than 15°. This angle is similar to that of alkylthiol monolayers on GaAs,<sup>9,66</sup> but the junctions with the phosphonates are much more robust. Because of the small tilt angle the phosphonate monolayer thickness is not expected to change significantly with temperature. Therefore, any temperature-dependent transport would indicate that we have thermally activated creation of molecular conformational defects.

Experimentally, we find no significant temperature dependence in the voltage regime where tunneling dominates (see Figure SI-2, Supporting Information), while at lower bias voltages, currents increase with temperature, as expected for thermionic emission over the barrier inside the GaAs.

While both types of experiments point to “through space” transport, we can ask if this is the only type of transport through the alkyl chain monolayers. We addressed this question by simulating the voltage dependence of tunneling through a rectangular barrier, according to the full Simmons model, including image force effects (Figure 6).<sup>47,48</sup> We used as the tunneling width a Si-C<sub>18</sub>H<sub>37</sub> monolayer with two different thicknesses, according to the tilt angles at two different temperatures, 255 and 306 K according to Figure 1, together with a barrier height of 0.825 eV and an effective mass of 0.8 *m*<sub>0</sub> for both systems.<sup>47</sup>

Figure 6 shows that the differences between the experimental results are larger than what we find from the simulations, which suggests that, in addition to monolayer expansion due to un-tilting, additional factors affect the temperature dependence. Among those factors, we note changes in the dielectric constant<sup>52</sup> and the above-mentioned thermally activated creation of defects



**Figure 6.** Simulation based on “through space” tunneling. Solid lines: Simulations of experimental results based on tunneling through a rectangular barrier, for two barrier widths, one of 17.9 (blue, top) and one of 18.1 Å (red, bottom), corresponding to the monolayers at 255 and 306 K (see Figure 1). The experimental results (open circles with same color coding: blue, top; red, bottom) are for *p*-Si-C<sub>18</sub>H<sub>37</sub>/Hg (from Figure 3d). The curves were simulated with an effective mass = 0.8 *m*<sub>e</sub>; dielectric constant = 2.6, barrier height = 0.825 eV (cf. 47).

in the monolayer. Further experiments are needed to prove or disprove these possibilities.

## Conclusions

The temperature dependence of electronic transport through alkyl chain monolayers can be ascribed primarily to the temperature dependence of the molecular orientation with respect to the substrate. While additional effects, such as temperature-dependent formation of conformational defects, may also play a role, we have not found clear evidence for that. Thus, transport through this type of molecular junctions appears dominated by through-space interactions. In view of this conclusion, we note a recent quantum mechanical analysis of charge transfer through proteins, which showed that for some proteins the tunneling barriers do not depend on protein structure,<sup>67</sup> whereas for other proteins the electron-transfer pathway is very structure specific.<sup>68</sup> This agrees with earlier work on biological systems.<sup>59</sup> The relevance for charge transport through the molecular systems studied here is that our data can be explained by the whole monolayer acting as a uniform system, where defects inside the monolayer do not appear to play an important role. Such conclusion fits with our recent finding that, by purposely introducing defects, we can “dope” the monolayer.<sup>69</sup>

While using short molecules reduces the complexity of theoretical calculations and is, at times, dictated by experimental limitations, transport through the molecules is then more likely to be influenced by the molecule/electrode interfaces than if longer molecules are used. Therefore, the shorter the molecules, the more difficult it may be to discern effects of the dynamics of the molecules on charge transport.

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**Supporting Information Available:** Temperature-dependent measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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