SUPPORTING INFORMATION

Interpretation of transition voltage spectroscopy

Everardus H. Huisman\textsuperscript{1,}\textsuperscript{1}, Constant M. Guédon\textsuperscript{1,}\textsuperscript{2},
Bart J. van Wees\textsuperscript{1}, and Sense Jan van der Molen*\textsuperscript{,}\textsuperscript{2}

\textsuperscript{1}Physics of Nanodevices, Zernike Institute for Advanced Materials,
University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

\textsuperscript{2}Kamerlingh Onnes Laboratorium, Leiden University,
P.O. Box 9504, 2300 RA, Leiden, The Netherlands

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a. **Analytical expression for** $V_m**$ using Stratton.** We start with eq. 1 in the main text, which expresses the current through a rectangular barrier:

$$I \propto \sinh \left( \frac{eV \tau}{\hbar} \right)$$

To find $V_m$, we put the derivative in a Fowler-Nordheim plot to zero. Substituting $y = 1/V$, we find:

$$
\frac{d \ln(I/V^2)}{d1/V} = \frac{d}{dy}(\ln(\sinh(e\tau y \hbar / \hbar)) + 2\ln(y)) \\
= \frac{2}{y} - \frac{e\tau}{\hbar y^2} \coth(e\tau y \hbar / \hbar) = 0.
$$

Thus:

$$y_m = \frac{e\tau}{2\hbar} \coth(e\tau y_m / \hbar)$$

By re-substituting $y_m = 1/V_m$, equation 2 in the main text is obtained.

b. **Full formulation of the Simmons formula.** According to ref [1], a full expression for the current density, $J$, through a barrier between two similar metal electrodes over the entire voltage range is given by:

$$J = c \{ \tilde{A} + \tilde{B} + \tilde{C} \}$$

$$c = \frac{4\pi me}{\hbar^3}$$

$$\tilde{A} = eV \int_{\eta-eV}^{\eta+eV} \exp(-A\sqrt{\eta + \phi - E_x}) dE_x$$

$$\tilde{B} = -\phi \int_{\eta-eV}^{\eta} \exp(-A\sqrt{\eta + \phi - E_x}) dE_x$$

$$\tilde{C} = \int_{\eta-eV}^{\eta} (\eta + \phi - E_x) \exp(-A\sqrt{\eta + \phi - E_x}) dE_x.$$}

Here, $A = (4\pi \Delta s / h) \sqrt{2m}$, where $\Delta s = s_2 - s_1$ is the width of the barrier at the Fermi energy of the metal and $\phi$ is the average barrier height. In ref [1], parts of the integrands are neglected. The consequence of this is that for small $A$ and/or small $\phi$, the commonly used Simmons expression gives unphysical results. Below, we calculate the full integrands. $\tilde{A}$ and $\tilde{B}$ are of the same form:

$$- \int_{e_1}^{e_2} \exp(-A\sqrt{\eta + \phi - E_x}) d(-E_x) > 0$$

By substituting $y^2 = \eta + \phi - E_x$ and $d(-E_x) = d(\eta + \phi - E_x) = dy^2 = 2y dy$, this becomes:

$$- \int_{y_1}^{y_2} \exp(-Ay) \cdot 2y dy$$

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Here, \( y_{1,2} = \sqrt{\eta + \bar{\phi} - e_{1,2}} \). These integrals can be solved by partial integration \([1]\). Boundaries for \( \tilde{A} \) are \( e_1 = 0, e_2 = \eta - eV, y_1 = \sqrt{\eta + \bar{\phi}}, y_2 = \sqrt{\bar{\phi} + eV} \), yielding:

\[
\tilde{A} = \frac{2eV}{A^2} \{ (A\sqrt{\bar{\phi} + eV} + 1)exp(-A\sqrt{\bar{\phi} + eV}) - (A\sqrt{\eta + \bar{\phi} + 1})exp(-A\sqrt{\eta + \bar{\phi}}) \}.
\]

Boundaries for \( \tilde{B} \) are \( e_1 = \eta - eV, e_2 = \eta, y_1 = \sqrt{\bar{\phi} + eV}, y_2 = \sqrt{\bar{\phi}} \), yielding:

\[
\tilde{B} = \frac{\bar{\phi}}{A^2} \{ (A\sqrt{\bar{\phi} + 1}exp(-A\sqrt{\bar{\phi}}) - (A\sqrt{\bar{\phi} + eV} + 1)exp(-A\sqrt{\bar{\phi} + eV}) \}.
\]

Like \( \tilde{A} \) and \( \tilde{B} \), \( \tilde{C} \) can again be solved by substituting \( y^2 \equiv \eta + \bar{\phi} - E_x \) and \( d(-E_x) = d(\eta + \bar{\phi} - E_x) \) and partial integration.

\[\tilde{C} = -2 \int_{y_1}^{y_2} y^3 exp(-Ay)dy\]

Boundaries for \( \tilde{C} \) are \( e_1 = \eta - eV, e_2 = \eta, y_1 = \sqrt{\bar{\phi} + eV}, y_2 = \sqrt{\bar{\phi}} \), so that:

\[
\tilde{C} = \frac{2}{A} \{ (\bar{\phi}^{3/2} + \frac{3}{A}\bar{\phi}) + \frac{6}{A^2}\sqrt{\bar{\phi}} + \frac{6}{A^2})exp(-A\sqrt{\bar{\phi}})
- (\bar{\phi} + eV)^{3/2} + \frac{3}{A}(\bar{\phi} + eV) + \frac{6}{A^2}\sqrt{\bar{\phi} + eV} + \frac{6}{A^2})exp(-A\sqrt{\bar{\phi} + eV}) \}.
\]

Taking all integrals together, we can calculate \( J \). Note that for relatively high and/or thick barriers, i.e. if \( A\sqrt{\bar{\phi} \pm eV} \gg 1 \), the full expression for \( J \) reduces to eq. (26) of reference [1]:

\[
J = J_0 \{ (\phi - eV/2)exp(-A\sqrt{\phi - eV/2}) - \\
(\phi + eV/2)exp(-A\sqrt{\phi + eV/2}) \}.
\]

where, \( J_0 = e/(2\pi hs^2) \).

Figure 1 shows \( V_m \) versus \( 1/d \) for each of the three equations mentioned above; eq. 26 of ref [1], (black), eq. 1 (Stratton) in the main text (blue) and the full Simmons expression (red). For thick barriers all three collapse on a single line. The maximum deviation between the three is in the order of a few percent for thin barriers (around \( d = 5\bar{A} \)). These differences are negligible compared to the spread in the experimental data as discussed in the Letter.

c. The inclusion of an image potential using Simmons. For the calculations including the image potential it is essential to use the full formulation of Simmons. Eq. 35 of reference [1] was used to calculate \( \bar{\phi} \):

\[
\bar{\phi} = \frac{1}{\Delta s} \int_{s_1}^{s_2} \{ \phi_0 - \frac{eVx}{s} - \frac{1.15\lambda s^2}{x(s-x)} \} dx.
\]
Here, $\lambda = e^2ln2/8\pi\epsilon_r s$, where $\epsilon_r$ is the dielectric constant. $s_1$ and $s_2$ are the positions where the barrier is equal to the Fermi energy of the metal and were found numerically. Figure 2 shows the dependence of $V_m$ on d for different $\phi_0$ (see figure 2a) and different $\epsilon_r$ (see figure 2b) using these equations.

\textit{d. $V_m$ for alkanes using a simple coherent model of molecular transport.} In Figure 3 of the Letter, we assumed $E_{HOMO} = -4$ eV [2]. We also calculated $V_m$ versus d for $E_{HOMO} = -2.14$ [3] and -3 eV (see Figure 3a). $V_m$ saturates at a voltage $V_{sat}$ above $d > 9\text{Å}$ for all three cases. $V_{sat}$ scales linearly with $E_{HOMO}$, thereby justifying TVS as a spectroscopic tool (see Figure 3b).

FIG. 1: $V_m$ versus $1/d$ for a barrier with $\phi=4eV$ and $d=1\text{nm}$. Clearly, $V_m$ is roughly proportional to $1/d$ using the three equations mentioned above; eq. 26 of ref [1] (black), eq. 1 in the main text (Stratton, blue) and the full Simmons expression (red).
FIG. 2: $V_m$ versus $1/d$ for a) different $\phi_0$ (figure 2a, $\epsilon_r = 2.1$) and b) different $\epsilon_r$ (figure 2b, $\epsilon_r = 4eV$) using the full Simmons expression with image potential.

FIG. 3: a) $V_m$ calculated using our coherent level model (see main text) for several positions of the HOMO. For $d > 9\AA$, $V_m$ saturates to a value $V_{sat}$ b) Plot demonstrating that $V_{sat}$ scales linearly with the position of the molecular HOMO level.