# Interpretation of Transition Voltage Spectroscopy

Huisman, Everardus H.; Guedon, Constant M.; van Wees, Bart; van der Molen, Sense Jan

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# SUPPORTING INFORMATION

## *Interpretation of transition voltage spectroscopy*

Everardus H. Huisman†,[1] Constant M. Guédon†,[2]

Bart J. van Wees,[1] and Sense Jan van der Molen*,[2]

[1]*Physics of Nanodevices, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

[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:

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

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

$$\begin{aligned} \frac{dln(I/V^2)}{d1/V} &= \frac{d}{dy}(ln(sinh(\frac{e\tau}{y\hbar})) + 2ln(y)) \\ &= \frac{2}{y} - \frac{e\tau}{\hbar}\frac{1}{y^2}coth(\frac{e\tau}{\hbar y}) = 0. \end{aligned}$$

Thus:

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

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:

$$\begin{aligned} J &= c\{\tilde{A} + \tilde{B} + \tilde{C}\} \\ c &= \frac{4\pi me}{h^3} \\ \tilde{A} &= eV\int_0^{\eta - eV} exp(-A\sqrt{\eta + \bar{\phi} - E_x})dE_x \\ \tilde{B} &= -\bar{\phi}\int_{\eta - eV}^{\eta} exp(-A\sqrt{\eta + \bar{\phi} - E_x})dE_x \\ \tilde{C} &= \int_{\eta - eV}^{\eta} (\eta + \bar{\phi} - E_x)exp(-A\sqrt{\eta + \bar{\phi} - E_x})dE_x. \end{aligned}$$

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 $\bar{\phi}$ 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:

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

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

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

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:

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

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:

$$\begin{aligned}\tilde{C} = & \frac{2}{A}\{(\bar{\phi}^{3/2} + \frac{3}{A}\bar{\phi} + \frac{6}{A^2}\sqrt{\bar{\phi}} + \frac{6}{A^3})exp(-A\sqrt{\bar{\phi}}) \\ & -((\bar{\phi} + eV)^{3/2} + \frac{3}{A}(\bar{\phi} + eV) + \frac{6}{A^2}\sqrt{\bar{\phi} + eV} + \frac{6}{A^3})exp(-A\sqrt{\bar{\phi} + eV}))\}\end{aligned}$$

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

$$\begin{aligned}J = & J_0\{(\phi - eV/2)exp(-A\sqrt{\phi - eV/2}) - \\ & (\phi + eV/2)exp(-A\sqrt{\phi + eV/2})\}.\end{aligned}$$

where, $J_0 = e/(2\pi h s^2)$.

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 $d = 5\AA$). 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, $\lambda = e^2 ln2/8\pi\epsilon_r s$, 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.

*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 $d > 9\AA$ for all three cases. $V_{sat}$ scales linearly with $E_{HOMO}$, thereby justifying TVS as a spectroscopic tool (see Figure 3b).

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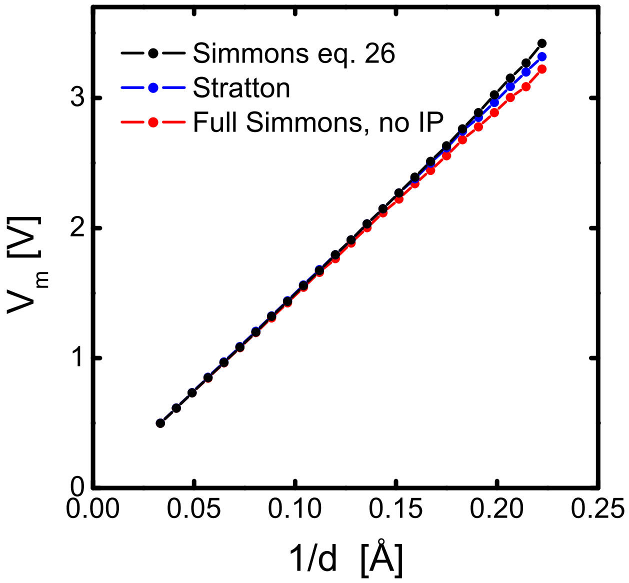


FIG. 1: $V_m$ versus 1/d for a barrier with $\phi$=4eV and d= 1nm. Clearly, $V_m$ is roughly proportional to 1/d using the three equations mentioned above; eq. 26 of ref [1] (black), eq. 1 in the main text (Stratton, blue) and the full Simmons expression (red).

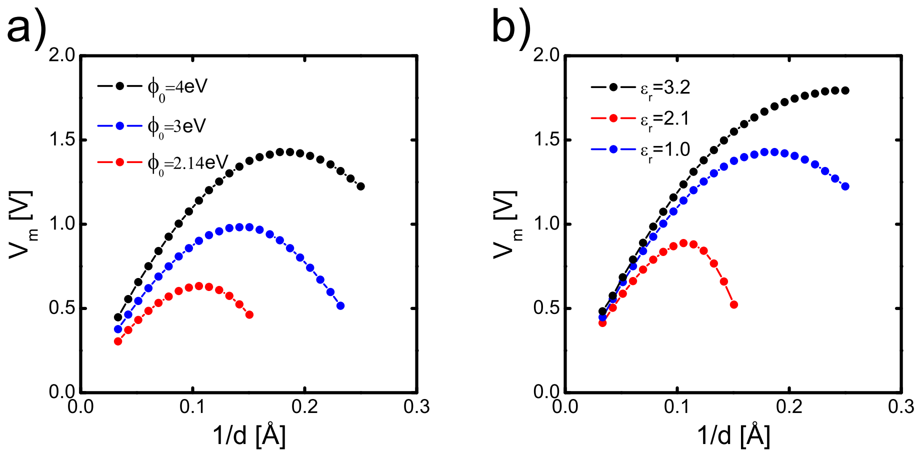


FIG. 2: $V_m$ versus $1/d$ for **a)** different $\phi_0$ (figure 2a, $\epsilon_r = 2.1$) and **b)** different $\epsilon_r$ (figure 2b, $\bar{\phi} = 4eV$) using the full Simmons expression with image potential.

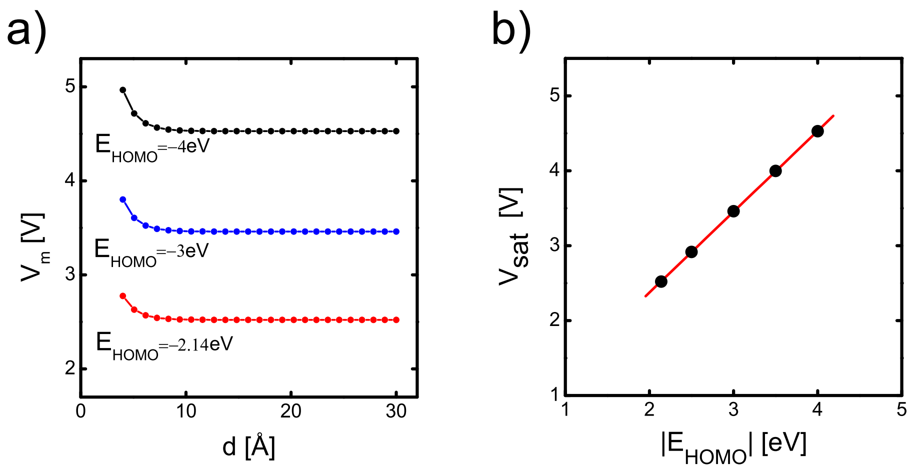


FIG. 3: **a)** $V_m$ calculated using our coherent level model (see main text) for several positions of the HOMO. For $d > 9\mathring{A}$, $V_m$ saturates to a value $V_{sat}$ **b)** Plot demonstrating that $V_{sat}$ scales linearly with the position of the molecular HOMO level.