

# Transition voltage spectroscopy scrutinized

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In the first part of this contribution I will report on recent<sup>[1-8]</sup> theoretical work of the author on transition voltage spectroscopy (TVS). In the second part several new results will be presented.

TVS is a method proposed by the groups of Kushmerick and Frisbie<sup>[9]</sup> to estimate the energy offset  $\varepsilon_0 = \min(E_F - E_{HOMO}, E_{LUMO} - E_F)$  relative to the electrodes' Fermi energy  $E_F$  of the frontier molecular orbital (HOMO or LUMO), which dominates the charge transport through a single-molecule junction.

$\varepsilon_0$  is a key quantity, because it determines the charge transfer efficiency. Unfortunately,  $\varepsilon_0$  can not be determined from low (ohmic) conductance  $G$  alone, which is commonly measured experimentally; in the case wherein the transport is determined by a single molecular orbital,  $G$  depends not only on  $\varepsilon_0$ , but also on the broadening functions  $\Gamma_{L,R}$  caused by the couplings to (say,) left and right electrodes,  $\Gamma = \Gamma_L = \Gamma_R$ , assumed equal for simplicity. So,  $I$ - $V$ -transport measurements beyond the linear regime are necessary. In principle,  $\varepsilon_0$  could be "easily" determined from a full  $I$ - $V$  curve; this curve should display current steps (abrupt if  $\Gamma \ll \varepsilon_0$ ) at voltages  $V = V_r$  where the molecular level becomes resonant with the Fermi energy of one electrode. For symmetric potential profiles (voltage division factor  $\gamma = 0$ ), this occurs at voltages satisfying  $eV_r = \pm 2\varepsilon_0$ . Practically, this is impossible, because molecular junctions can hardly withstand such high voltages.

Typical transport measurements yield  $I$ - $V$ -curves without structure (no maximum, no inflection point, *etc*), not seldom with substantial noise, which do not straightforwardly suggest how to determine  $\varepsilon_0$ .

Beebe et al<sup>[9]</sup> suggested that the energy offset can be estimated from the so-called transition voltage  $V_t$ , which is defined as the source-drain voltage at the minimum of the Fowler-Nordheim (FN) plot, *i. e.*, the curve  $\log(I/V^2)$  vs.  $1/V$ . According to the initial claim,<sup>[9]</sup> a transition from direct tunneling to field-emission (FN) tunneling occurs at  $V_t$ , which corresponds to a change in the shape of the tunneling barrier from trapezoidal to triangular. Although such a change is not essential,<sup>[8,10,11]</sup> this "barrier-shape conjecture"<sup>[4]</sup> turned out to yield a reasonable estimate ( $\varepsilon_0 \approx eV_t$ ).

To give support to the "barrier-shape conjecture", TVS initially invoked results based on the Simmons model. The interpretation of TVS within the Simmons model has been challenged.<sup>[10]</sup> However, that approach turned out to have serious drawbacks, as demonstrated in a series of works.<sup>[4-7]</sup> *E. g.*, it ignored the lateral constriction and exaggerated the image effects by using an approximate image potential proposed by Simmons, which is in error by a factor of two.

As recently shown by the author,<sup>[1-3,8]</sup> a variety of  $I$ - $V$ -curves measured in molecular junctions can be excellently reproduced within the Newns-Anderson model; an example is presented in Fig. 1. Pleasantly for the experimentalist colleagues, simple analytical expressions can be deduced, which conveniently allow to deduce both the MO energy offset and the voltage division factor from the measured transition voltages  $V_{t+}$  and  $V_{t-}$  at positive and negative biases<sup>[2]</sup>

$$|\varepsilon_0| = 2 \frac{e|V_{t+}V_{t-}|}{\sqrt{V_{t+}^2 + 10|V_{t+}V_{t-}|/3 + V_{t-}^2}},$$
$$\gamma = \frac{\text{sign}\varepsilon_0}{2} \frac{V_{t+} + V_{t-}}{\sqrt{V_{t+}^2 + 10|V_{t+}V_{t-}|/3 + V_{t-}^2}}.$$

The above formula holds for realistic cases, where  $\Gamma \ll |\varepsilon_0|$ . The leading corrections to the above results,

which are of the order  $\mathcal{O}(\Gamma/\varepsilon_0)^2$ , can also be expressed in closed analytical form<sup>[3]</sup>

$$V_{t+} = \frac{2}{3} \frac{\sqrt{4\gamma^2 + 3} + 4\gamma}{1 - 4\gamma^2} \varepsilon_0 + \frac{99 + 192\gamma\sqrt{4\gamma^2 + 3} \left[ \left(\gamma^2 - \frac{1}{3}\right)^2 + \frac{191}{144} \right] + 624\gamma^2 + 112\gamma^4 - 384\gamma^6}{(1 - 4\gamma^2) \left\{ \sqrt{4\gamma^2 + 3} \left[ \frac{63}{256} + \left(\gamma^2 - \frac{3}{16}\right)^2 \right] - 2\gamma \left(\gamma^4 - \frac{9}{16}\right) \right\}} \frac{\Gamma_a^2}{96\varepsilon_0},$$

$$V_{t-} = -\frac{2}{3} \frac{\sqrt{4\gamma^2 + 3} - 4\gamma}{1 - 4\gamma^2} \varepsilon_0 - \frac{99 - 192\gamma\sqrt{4\gamma^2 + 3} \left[ \left(\gamma^2 - \frac{1}{3}\right)^2 + \frac{191}{144} \right] + 624\gamma^2 + 112\gamma^4 - 384\gamma^6}{(1 - 4\gamma^2) \left\{ \sqrt{4\gamma^2 + 3} \left[ \frac{63}{256} + \left(\gamma^2 - \frac{3}{16}\right)^2 \right] + 2\gamma \left(\gamma^4 - \frac{9}{16}\right) \right\}} \frac{\Gamma_a^2}{96\varepsilon_0}.$$

Whatever the fabrication method, stochastic fluctuations are inherent, and they play an essential role in the interpretation of the transport data in single-molecule junctions. In an important experimental work,<sup>[12]</sup> relying upon an impressive statistics (thousands of junctions), simultaneous  $G$ - and  $V_t$ -measurements have demonstrated that the  $G$  and  $V_t$ -histograms are affected in a completely different manner by stochastic fluctuations. On the basis of the above results, the different impact of fluctuations observed<sup>[12]</sup> can be quantitatively explained.<sup>[1]</sup> These results also demonstrate that, unlike  $G$ ,  $V_t$  represents a molecular signature.<sup>[1]</sup>

In the second part of this presentation I will present some new results demonstrating the usefulness of TVS for quantifying solvent effects and to interpret recent transport data in redox metalloproteins.<sup>[13]</sup>

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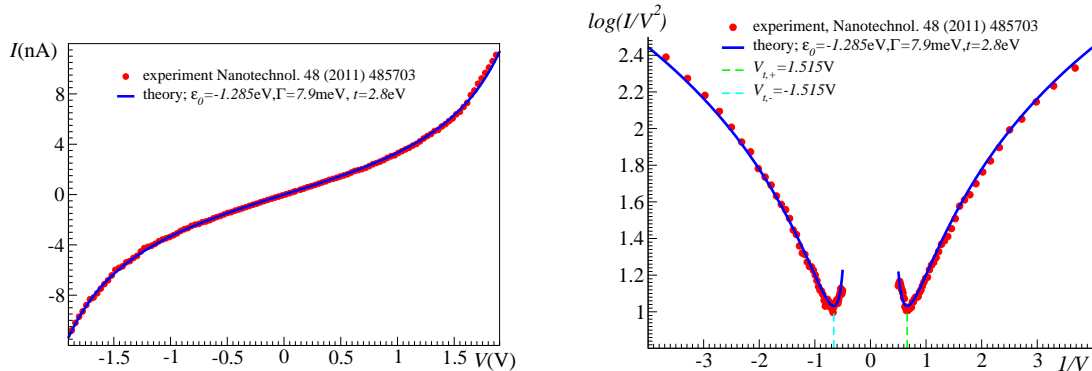


Figure 1: An example demonstrating that the Newns-Anderson model is able to excellently reproduce full  $I$ - $V$  transport data in general and the TVS in particular (after Ref. 3).