Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

—Electronic Supporting Information—

Gaining insight into molecular tunnel junctions with a pocket calculator without I–V data fitting. Five-thirds protocol

Ioan Bâldea

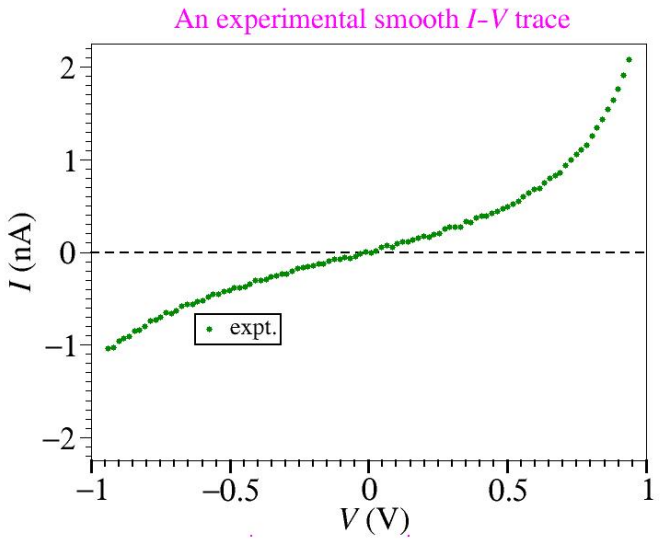
Theoretical Chemistry, Heidelberg University, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany. Fax: +49 6221 545221; Tel: +49 6221 545219; E-mail: ioan.baldea@pci.uni-heidelberg.de

Practical guide for applying the five-thirds protocol

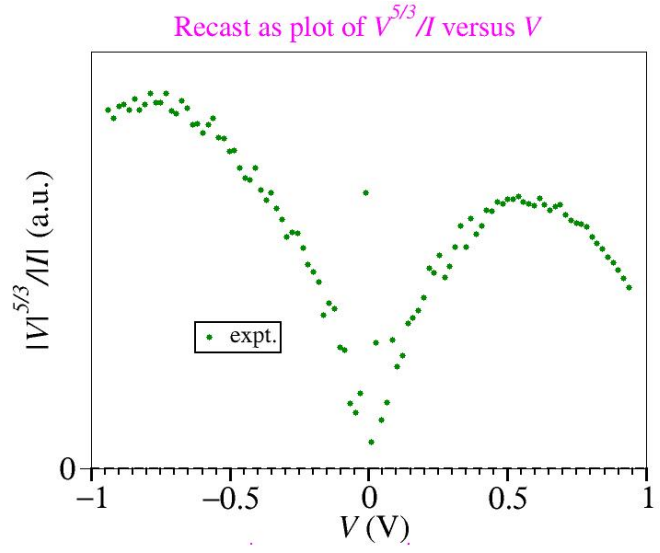
N.B.: The numerical data underlying the figures presented below are included in the EXCEL file "Simulation_Protocol_5by3.xlsx" uploaded as additional ESI file.

S1 Processing a smooth experimental $\mathrm{I}-\mathrm{V}$ curve

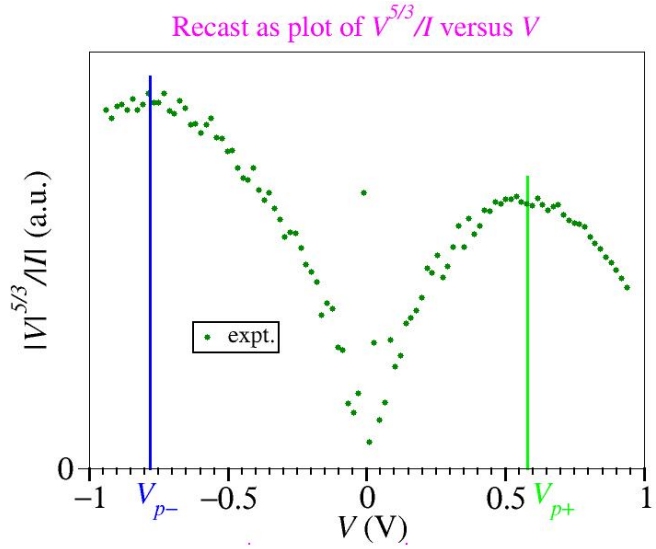
Consider a smooth experimental curve



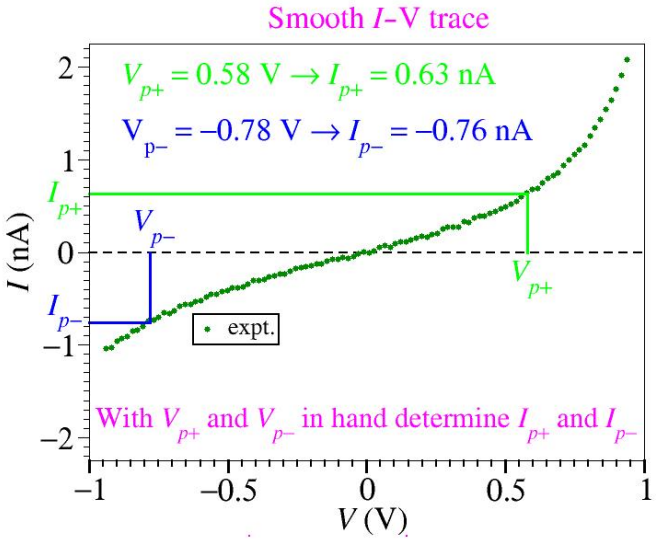
Recast the $I-V$ curve as curve of $V^{5/3}/I$ versus V. Notice the more pronounced noise exhibited by the curve of $V^{5/3}/I$ versus V



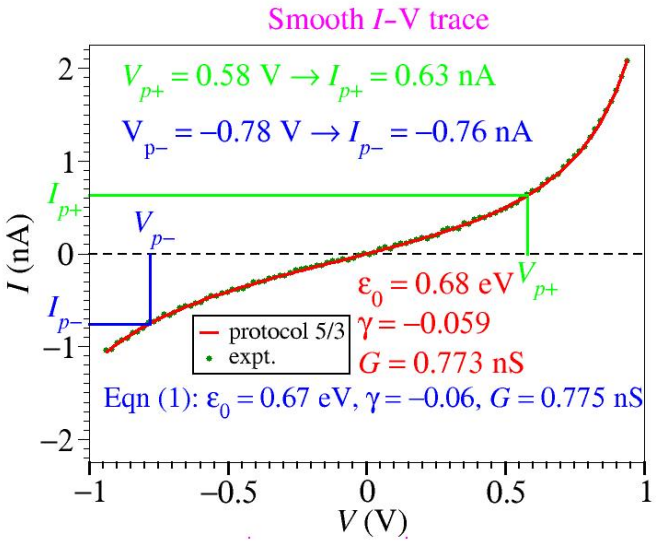
Determine the voltages V_{p+} and V_{-} from the position of the peaks at positive and negative bias



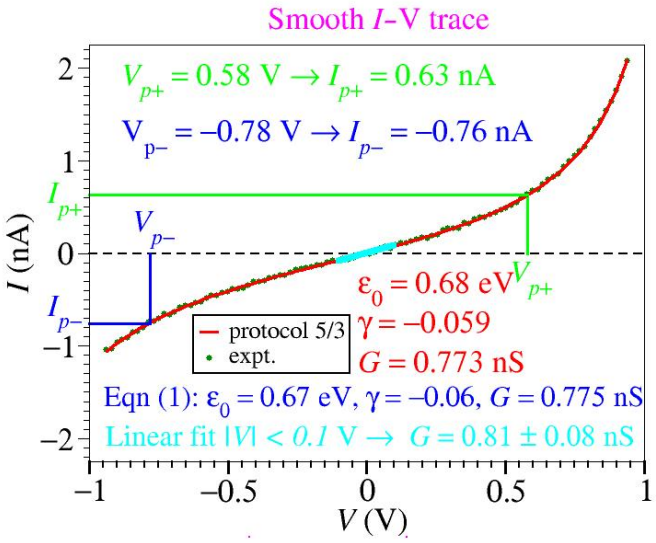
Return to the original $I - V$ curve and determine the currents I_{p+} and I_{p-} corresponding to the voltages V_{p+} and V_{-}



Plug the values V_{p+}, V_{-}, I_{p+} and I_{p-} determined above into eqn (9) and obtain the parameters ε_0, γ and G characterizing the junction considered. Notice that the values obtained by applying the five-thirds protocol excellently agree with the values obtained by data fitting to eqn (1).

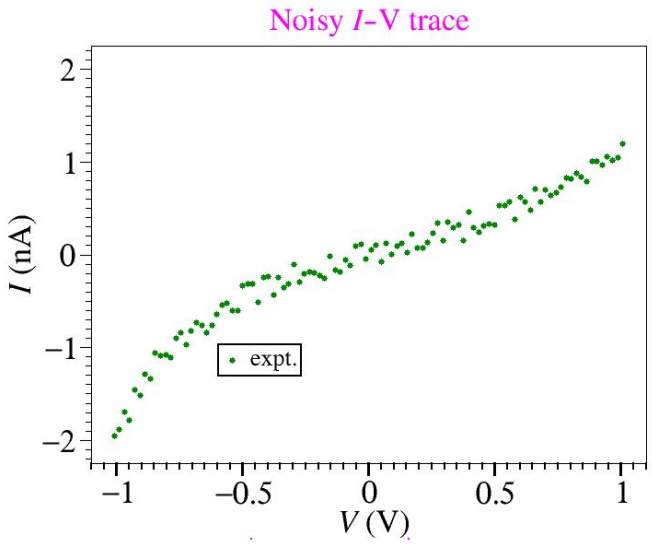


Remark: Noteworthily, despite the smoothness of the $I-V$ curve considered, the value of the low bias estimates using the five-thirds protocol ($G = 0.773\,$nS) is closer to the "most exact" value ($G = 0.775\,$nS) obtained by data fitting to eqn (1) than the value extracted from the slope of the $I-V$ curve deduced from linear fitting in the "low" bias range $-0.1\,\text{V} \leq V \leq +0.1\,\text{V}$.

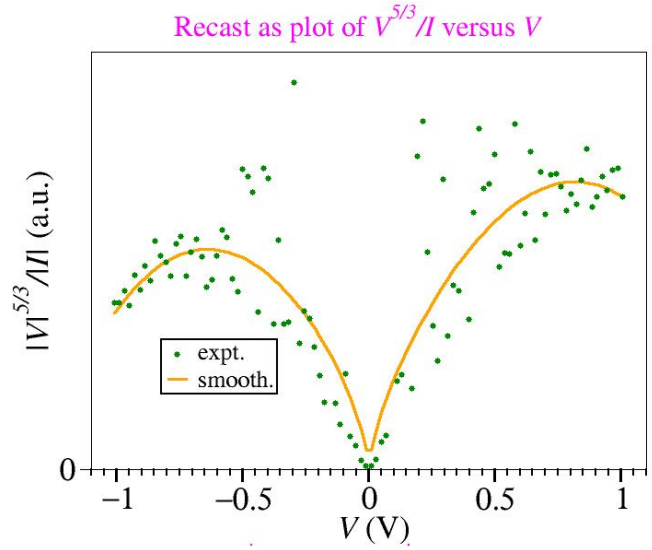


S2 Processing a noisy experimental $\mathrm{I}-\mathrm{V}$ curve

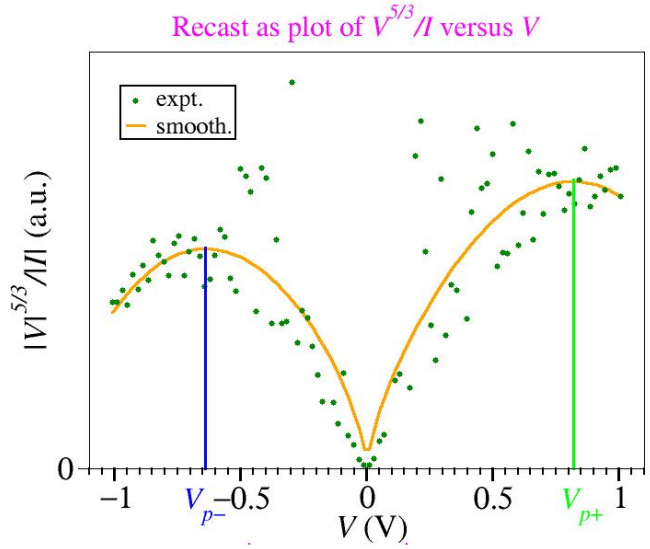
Consider a noisy experimental $I-V$ curve



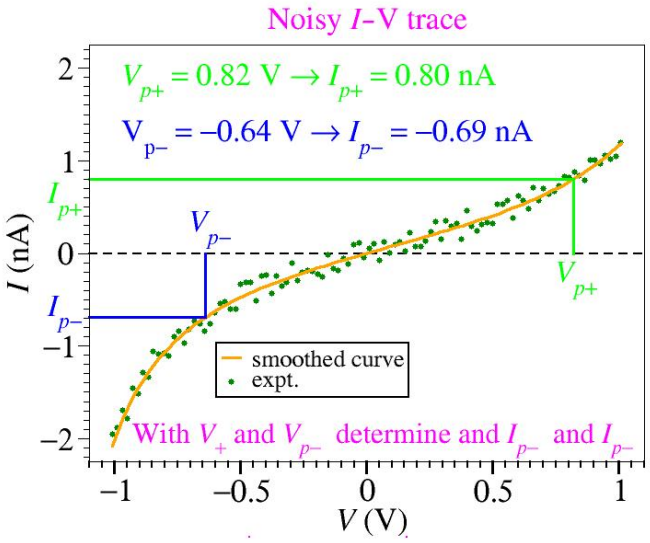
Recast it as curve of $V^{5/3}/I$ versus V



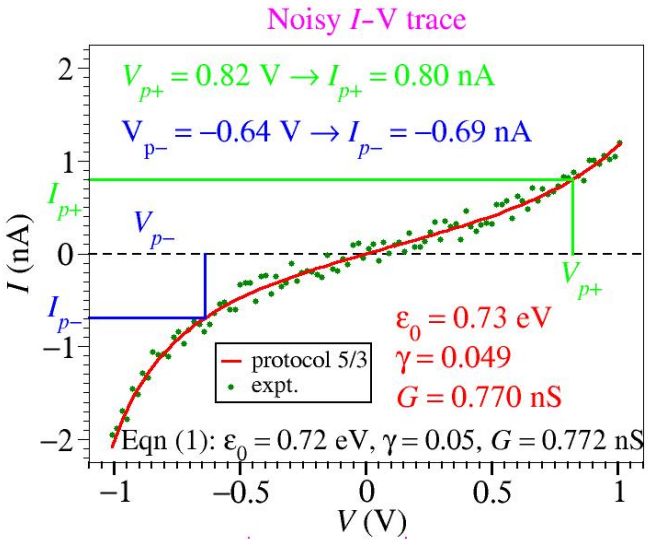
Determine the voltages V_{p+} and V_{-} from the position of the peaks of the smoothed curve at positive and negative bias



Return to the original $I - V$ curve and determine the currents I_{p+} and I_{p-} corresponding to the voltages V_{p+} and V_{-}. Use the smoothed curve to this aim



Plug the values V_{p+}, V_{-}, I_{p+} and I_{p-} determined above into eqn (9) and obtain the parameters ε_0, γ and G characterizing the junction considered. Notice that the values obtained by applying the five-thirds protocol excellently agree with the values obtained by data fitting to eqn (1).



Remark: Notwithstanding the very pronounced noise exhibited by the experimental data, the value of the low bias conductance G estimated using the five-thirds protocol ($G = 0.770\,$nS) is very closer to the "most exact" value ($G = 0.772\,$nS) obtained by data fitting to eqn (1), while the value extracted from the slope of the $I - V$ curve deduced from linear fitting in the "low" bias range $-0.1\,\text{V} \leq V \leq +0.1\,\text{V}$ is very inaccurate.