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Quantifying transition voltage spectroscopy of molecular junctions: *Ab initio* calculations

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Transition voltage spectroscopy (TVS) has recently been introduced as a spectroscopic tool for molecular junctions where it offers the possibility to probe molecular level energies at relatively low bias voltages. In this work we perform extensive *ab initio* calculations of the nonlinear current-voltage relations for a broad class of single-molecule transport junctions in order to assess the applicability and limitations of TVS. We find, that in order to fully utilize TVS as a quantitative spectroscopic tool, it is important to consider asymmetries in the coupling of the molecule to the two electrodes. When this is taken properly into account, the relation between the transition voltage and the energy of the molecular orbital closest to the Fermi level closely follows the trend expected from a simple, analytical model.

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Molecular electronics holds the promise of continuing the miniaturization of electronic devices beyond the limits of standard silicon technologies by using single molecules as the active elements.[1,2] In the design and characterization of molecular devices, the electronic structure of the molecule is naturally of vital importance. In fact, when quantum interference effects are disregarded,[3] there is a direct relation between a junction's conductance and the distance of the molecular energy levels to the electrode Fermi level. The latter may, in principle, be determined from peaks in the dI/dV curve, where I is the current and V is the bias voltage. Assuming that the molecular level closest to the Fermi level is the highest occupied molecular orbital (HOMO) it would require a voltage of $V\sim 2|E_F-\varepsilon_H|$ to probe the HOMO position in a symmetric junction. However, in practice the molecular junction often becomes unstable and breaks down due to the large current density before the peak in the dI/dV is reached.

Transition voltage spectroscopy (TVS) was introduced as a spectroscopic tool in molecular electronics by Beebe *et al.*[4] They found that the Fowler-Nordheim graph of a molecular junction, i.e., a plot of $\ln(I/V^2)$ against $1/V$, showed a characteristic minimum at a bias voltage $V_{\min}$, which scaled linearly with the HOMO energy obtained from ultraviolet photo spectroscopy (UPS). Importantly, the TVS minimum is obtained at relatively low bias voltage before electrical breakdown. TVS is now becoming an increasingly popular tool in molecular electronics.[2,5–9]

The original interpretation of TVS introduced by Beebe[4] and applied in most later experimental work, is based on a Simmons tunnel barrier model.[10] Within this interpretation, the TVS minimum is obtained, when the tunnel barrier, due to the applied bias potential, changes from being trapezoidal to triangular. The transition voltage equals the barrier height, which is interpreted as the distance from the Fermi level to the closest molecular level. However, it has recently been pointed out by Huisman *et al.*[11] that the barrier model is inconsistent with experimental data which on the other hand is more appropriately described by transport via a single electronic level. In the single-level model the transmission function was assumed to have a Lorentzian shape, and all nonlinear effects due to the finite bias, were neglected. While these assumptions may be reasonable, they are not obviously fulfilled in a realistic molecular junction at high electric fields. It is therefore of interest to compare the simple Lorentzian transmission model with more realistic calculations.

In this Rapid Communication, we present a quantitative analysis of TVS based on extensive *ab initio* calculations of the nonlinear current-voltage relations for a broad class of molecular junctions. The ratio of the TVS minimum to the HOMO level position is found to vary between 0.8 and 2.0 depending on the junction asymmetry, i.e., quite different from the one-to-one relation assumed so far. The large variation is due to the difference in the nonlinear response of the molecular level to the bias voltage. The importance of asymmetry effects is further signified by the fact that many of the experiments using TVS were performed on asymmetric molecules in an asymmetric conductive atomic force microscopy (AFM) measurement setup.[4–6,8] Indeed, as we show below a larger degree of consistency between TVS measurements and UPS data is obtained when the asymmetry is taken into account.

We begin our analysis by considering a simple model for transport via a single electronic level equivalent to the work in Ref. 11. The transmission function is assumed to be a Lorentzian

$$T(E;\varepsilon_0,\Gamma)=\frac{f}{(E-\varepsilon_0)^2+\Gamma^2/4}, \tag{1}$$

where ε_0 and Γ are the molecular level energy and broadening, respectively. f is a constant factor to account for multiple molecules in the junction, asymmetric coupling to the electrodes, etc. Our analysis will not be dependent on the actual value of f. We shall assume that the molecular level is the HOMO level, i.e., $\varepsilon_0<E_F$. This is the typical case for thiol bonded molecules (as considered in this work), where

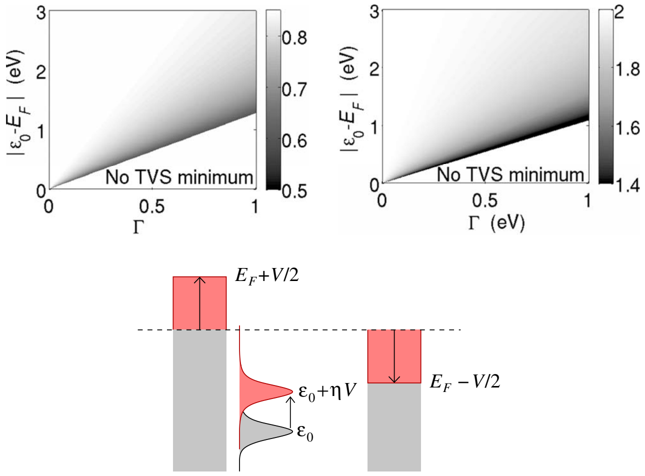


FIG. 1. (Color online) Upper panels: Ratio between molecular level energy and transition voltage, $|\varepsilon_0 - E_F|/V_{\min}$, vs molecular level energy, ε_0 and broadening, Γ, for a symmetric junction, $\eta=0$, (left), and a completely asymmetric junction, $\eta=1/2$, (right). Note the different scales of $|\varepsilon_0 - E_F|/V_{\min}$ for the symmetric and asymmetric junctions. The lower part illustrates how the molecular level moves under a finite bias voltage. At zero bias the level is located at ε_0 but when a bias voltage is applied, the level follows to some degree the chemical potential of the left electrode, due to a stronger coupling to this electrode.

electron transfer from the metal to the sulfur end group shifts the molecular levels upward in energy.[12] At finite bias voltage, the molecular level may be shifted relative to the zero-bias position, as shown schematically in Fig. 1 (lower part). Such nonlinear effects express themselves differently in symmetric and asymmetric junctions.[13,14] For example, if the molecule is only strongly coupled to the left electrode, the molecular levels will follow the chemical potential of the left contact. On the other hand, for a symmetric junction the molecular level will remain at the zero-bias position. We describe the degree of asymmetry by the parameter $\eta \in [-1/2;1/2]$ such that the current is given by

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} T(E;\varepsilon_0 + \eta V, \Gamma)[f_L(V) - f_R(V)]dE, \tag{2}$$

where $f_{L/R}(V) = 1/[\exp(E_F \pm eV/2)/k_BT + 1]$ are the Fermi-Dirac distributions for the left and right contact, respectively. The dependence of the level position on the bias voltage is the main difference between our model and the one considered in Ref. 11.

Using Eq. (2) we calculate $\ln(I/V^2)$ and find the minimum at the bias voltage $V_{\min}$. At this voltage, the slope of the current depends quadratically on the bias voltage, $I \propto V^2$, and $d[\ln(I/V^2)]/dV = 0$. An example of a calculated Fowler-Nordheim plot can be seen in the inset of Fig. 4. In Fig. 1 we plot the ratio $|\varepsilon_0 - E_F|/V_{\min}$ as a function of broadening, Γ and molecular level energy, ε_0, for a symmetric junction ($\eta=0$) and a completely asymmetric junction ($\eta=1/2$). Figure 1 illustrates two main points: First, the ratio $|\varepsilon_0 - E_F|/V_{\min}$ is nearly constant over a large range of Γ and ε_0 values. For a given degree of asymmetry (value of η), the TVS minimum can therefore be used as a direct measure of the molecular level position, independently of Γ. Note, however, that for $\Gamma/|\varepsilon_0 - E_F| \gtrsim 1$, there is no minimum in the Fowler-Nordheim plot since the molecular level is too close to the Fermi level, and the current increases slower than $\propto V^2$ at all bias values. The second conclusion from Fig. 1 is that the ratio $|\varepsilon_0 - E_F|/V_{\min}$ ranges from 0.86 to 2.0 depending on the asymmetry of the molecular junction. In order to use TVS as a quantitative tool, knowledge of the asymmetry factor is therefore needed. On the other hand, if the molecular levels can be determined by other means, the TVS can be used to measure the asymmetry factor.

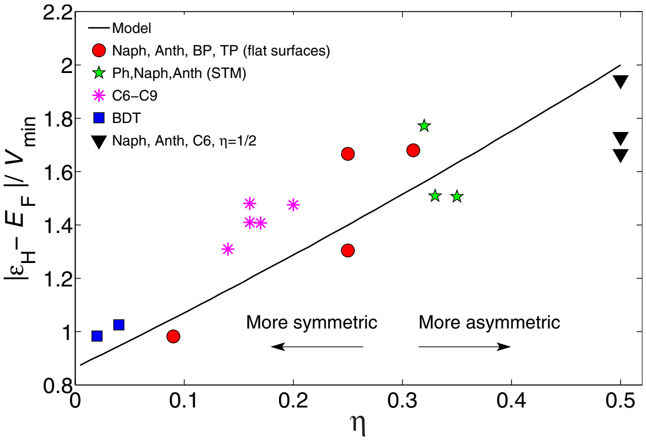
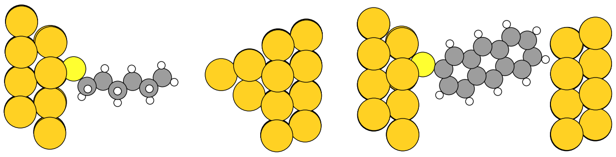


FIG. 2. (Color online) Ratio between the HOMO energy (at zero bias) and the transition voltage, $V_{\min}$, vs asymmetry parameter, η. Solid line is obtained from a Lorentzian transmission function using Eqs. (1) and (2) and symbols are results of *ab initio* finite bias calculations.

We now turn to our *ab initio* finite bias calculations and Fig. 2, which is our main result. It shows the ratio of $|\varepsilon_H - E_F|/V_{\min}$ vs η for the 17 molecular junctions listed in Fig. 3. The solid line is the result obtained from the one-level model using Eqs. (1) and (2). Although there are deviations between the model and the *ab initio* results, both data sets clearly follow the same trend. This result further supports TVS as a spectroscopic tool but it also underlines that quantitative information about the molecular level position can only be obtained from TVS provided some knowledge of the junction asymmetry. The calculated numbers for the data points are listed in Fig. 3.

The current at finite bias voltage is calculated using density functional theory (DFT) in combination with a nonequilibrium Green's function (NEGF) method, as described in Ref. 15. Our DFT-NEGF method is implemented in GPAW, which is a real-space electronic structure code based on the projector-augmented wave method.[16,17] We use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,[18] and a 4×4 k-point sampling in the surface plane. The electronic wave functions are expanded in an atomic-orbital basis.[17] In all calculations, the molecule and the closest Au layers are described by a double-zeta plus polarization basis set while the remaining Au atoms are described by a single-zeta plus polarization basis.

The upper panel of Fig. 3 shows the atomic structure of two representative junctions: a hexanethiol (left) in a scan-



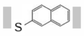
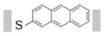
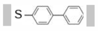
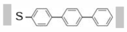
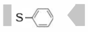
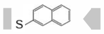
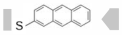
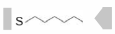
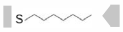
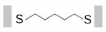
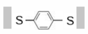
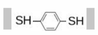
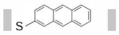
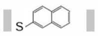
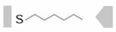
Molecule	Structure	Calculated values $V_{\min}$ (V)	 ε_H-E_F (eV)	 η
Naph-S		0.63	-1.05	0.31
Anth-S		0.56	-0.55	0.09
BP-S		0.69	-0.90	0.25
TP-S		0.48	-0.80	0.25
Ph-S		1.69	-2.55	0.33
Naph-S		1.27	-2.25	0.32
Anth-S		1.56	-2.35	0.35
C6-S		2.44	-3.60	0.20
C7-S		2.38	-3.35	0.17
C8-S		2.33	-3.45	0.16
C9-S		2.27	-3.20	0.16
S-C6-S		2.94	-3.85	0.14
S-Ben-S		1.56	-1.60	0.04
HS-Ben-SH		1.22	-1.20	0.02
Anth-S^a		0.26	-0.45	0.5
Naph-S^a		0.71	-1.38	0.5
C6-S^a		2.16	-3.60	0.5

FIG. 3. (Color online) Top: atomic structure of two of the major groups of molecular transport junctions investigated in this work and in experiments (Refs. 2, 4, and 5), namely, alkanes in an STM-like configuration (top left), and anthracenethiol (Anth) between two flat Au (111) surfaces (top right). The table in the lower part shows schematically all the considered molecular junctions together with calculated values of $V_{\min}$, $\varepsilon_H - E_F$, and η. The electrode configurations are indicated with gray boxes showing both the flat Au surface (rectangles) and STM-like geometries (pentagons). The superscript ^{a} indicates that the data are obtained from nonself-consistent calculations by manually setting $\eta = 1/2$. The HOMO energy, ε_H, refers to the first peak in the Kohn-Sham (PBE) projected density of states. See text for more details.

ning tunnel microscope (STM)-like configuration with the STM tip ~4 Å away from the molecule, and anthracenethiol (right) between two flat Au (111) surfaces with a distance of 1.5 Å between the right Au electrode and the closest H atom of the molecule. For all STM setups, we initially relax the molecule on a single Au(111) surface and subsequently add the STM electrode without further relaxations. For the systems with two flat Au surfaces, we relax the molecule and the two closest Au layers. Except for the benzene junctions (S-Ben-S and HS-Ben-SH), the linking S atom relaxes into a bridge site of the Au(111) surface shifted slightly toward the hollow site. The structure of the symmetric benzene-dithiol (S-Ben-S) junction is taken from Ref. 19 where the molecule binds to an Au adatom together with a SCH_3 unit. In the other benzene junction (HS-Ben-SH) the hydrogenated sulfur atoms bind to Au adatoms of the Au(111) surfaces following Ref. 20.

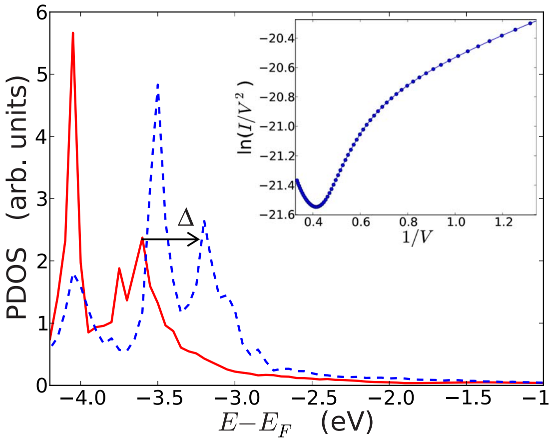


FIG. 4. (Color online) Projected density of states on the C atoms in the C_6-alkane junction shown in Fig. 3. The solid red line refers to $V_{\text{bias}} = 0$ V and the dashed blue line refers to $V_{\text{bias}} = 2.0$ V. The HOMO level (at $V_{\text{bias}} = 0$ V) is located at $E - E_F = -3.6$ eV. We determine the asymmetry factor, η, from the shift, Δ, of the HOMO level with the bias voltage. The inset shows the calculated Fowler-Nordheim plot with the characteristic TVS minimum at $V_{\min} = 2.4$ V.

In Fig. 3 we also list for each junction the obtained TVS minimum voltage, $V_{\min}$, the position of the HOMO level relative to E_F, and the calculated asymmetry parameter. Figure 4 illustrates how we determine these quantities, in the case of the C6-S junction. The TVS minimum is simply found from the minimum in the Fowler-Nordheim plot, as show in the inset. To determine the HOMO level, we project the density of states onto the carbon atoms. Molecular levels then appears as clear peaks in the projected density of state (PDOS) vs energy plot as shown in Fig. 4. We note that there are situations where a peak in the PDOS does not show in the transmission function due to symmetry mismatch between the molecular-orbital and the electrode wave functions. This is indeed the situation for Ph-S, Naph-S, and Anth-S in the STM setup where a peak in the PDOS is observed at $E - E_F \sim -0.55$ eV but only a vanishingly small transmission peak occurs at this energy. In these three cases we take the second PDOS peak at $E - E_F = -2.35$ eV as the HOMO level. At this energy, the Au tip wave functions also have d character, which enables nonzero coupling to the molecular π orbital.

At finite bias voltage, the energy of the HOMO level is shifted by the bias voltage. (cf. Fig. 1). Figure 4 shows the PDOS of the C_6-alkane junction under bias voltage $V = 0$ V (red solid) and $V = 2.0$ V (blue dashed). The equilibrium HOMO energy of $\varepsilon_H - E_F = -3.6$ eV shifts upward by $\Delta = 0.4$ eV when the bias is applied. The asymmetry factor, η, is calculated from the shift, Δ, according to $\eta = \Delta / V = 0.2$.

Notice that even for the very asymmetric STM configurations, the asymmetry factor is never larger than 0.35. This is due to the relatively small distance between the molecule and the Au tip (4.0 Å). Increasing this distance would increase η further, however, this is computationally problematic due to the finite range of the atomic-orbital basis. Instead we simulate a completely asymmetric junction ($\eta = 0.5$), by using the zero-bias transmission function and fixing the electrode chemical potentials to $\mu_L = E_F$ and $\mu_R = E_F - V$. The data for the three last junctions in Fig. 3 are obtained in this way and are thus nonself-consistent results.

The deviations of the numerical data from the analytical result in Fig. 2 may be due to several reasons. (i) The *ab initio* transmission functions do not have a perfect Lorentzian shape as assumed in the analytical model. (ii) The dependence of the HOMO energy on the bias voltage is not strictly linear. (iii) The bias voltage influences the shape of the molecular orbitals which in turn affects the coupling strength. (iv) It may in some cases be difficult to accurately determine ε_H and η, as discussed above.

The TVS minimum voltage was originally interpreted as a transition from tunneling to field emission.[4] However, according to our calculations, $V_{\min}$ does not mark such a transition, and in line with Refs. 11 and 21 we do not view $V_{\min}$ as a special transition voltage. Rather the usefulness of TVS relies on the direct relation between $V_{\min}$ and ε_H when the transmission function can be well described by a Lorentzian.

In the conducting AFM measurements of Ref. 4, the ratio $|\varepsilon_H - E_F| / V_{\min}$ was found to vary between 2.1 and 2.6 for a set of molecules which included Naph-S, BP-S, and TP-S also considered in this work. This is significantly larger than the value of 1 predicted by Simmons barrier model. According to our model the ratio should be smaller than 2.0 which is obtained for a completely asymmetric junction ($\eta = 0.5$). To resolve this puzzle, we first note that our *ab initio* calculations yield $\eta \sim 0.3$ for the three molecules (cf. Fig. 3) giving $|\varepsilon_H - E_F| / V_{\min} \sim 1.6$ according to our model. Next, we note that the presence of the AFM tip in the transport measurements will lead to a renormalization of the HOMO energy due to an image charge effect,[22] which is not present in the UPS measurements. Based on the method described in Ref. 23 we estimate the image charge interaction to be 0.35–0.5 eV depending on the size of the molecule. Correcting the UPS values for ε_H by these values lead to ratios $|\varepsilon_H - E_F| / V_{\min}$ in the range 1.6–1.8 in good agreement with the model prediction of ~ 1.6.

Finally, we note that the well-known inability of DFT to describe energy gaps and level alignment of molecules at surfaces[22] does not affect the conclusions of the present work. This is because, according to Fig. 1, the *ratio* $(\varepsilon_H - E_F) / V_{\min}$ is independent of the value of ε_H. In particular, the dependence of $(\varepsilon_H - E_F) / V_{\min}$ on asymmetry is expected to be a general result independent of the absolute position of the molecular levels.

In conclusion, we have performed extensive *ab initio* DFT transport calculations to simulate transition voltage spectroscopy for a large number of molecular junctions. The numerical data closely follow the trend expected from an analytical model with a Lorentzian-shaped transmission function. We have explicitly shown that in order to use TVS as a quantitative spectroscopic tool to probe the molecular levels, it is necessary to take the asymmetry of the molecular junction into account. The present analysis should therefore be considered in future applications of transition voltage spectroscopy.

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[1] K. Moth-Poulsen and T. Bjornholm, Nat. Nanotechnol. **4**, 551 (2009).

[2] H. Song, Y. Kim, Y. H. Jang, H. Jeong, M. A. Reed, and T. Lee, Nature (London) **462**, 1039 (2009).

[3] R. Baer and D. Neuhauser, J. Am. Chem. Soc. **124**, 4200 (2002).

[4] J. M. Beebe, B. S. Kim, J. W. Gadzuk, C. D. Frisbie, and J. G. Kushmerick, Phys. Rev. Lett. **97**, 026801 (2006).

[5] J. M. Beebe, B. Kim, C. D. Frisbie, and J. G. Kushmerick, ACS Nano **2**, 827 (2008).

[6] C. D. Zangmeister, J. M. Beebe, J. Naciri, J. G. Kushmerick, and R. D. van Zee, Small **4**, 1143 (2008).

[7] S. Ho Choi, B. S. Kim, and C. D. Frisbie, Science **320**, 1482 (2008).

[8] A. Tan, S. Sadat, and P. Reddy, Appl. Phys. Lett. **96**, 013110 (2010).

[9] Y. Noguchi, T. Nagase, R. Ueda, T. Kamikado, T. Kubota, and S. Mashiko, Jpn. J. Appl. Phys. **46**, 2683 (2007).

[10] J. G. Simmons, J. Appl. Phys. **34**, 1793 (1963).

[11] E. H. Huisman, C. M. Guédon, B. J. van Wees, and S. J. van der Molen, Nano Lett. **9**, 3909 (2009).

[12] G. Peng, M. Strange, K. S. Thygesen, and M. Mavrikakis, J. Phys. Chem. C **113**, 20967 (2009).

[13] S. J. van der Molen and P. Liljeroth, J. Phys.: Condens. Matter **22**, 133001 (2010).

[14] C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga, and C. Joachim, Phys. Rev. B **59**, 12505 (1999).

[15] J. Enkovaara *et al.*, J. Phys.: Condens. Matter **22**, 253202 (2010).

[16] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Phys. Rev. B **71**, 035109 (2005).

[17] A. H. Larsen, M. Vanin, J. J. Mortensen, K. S. Thygesen, and K. W. Jacobsen, Phys. Rev. B **80**, 195112 (2009).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] M. Strange, O. Lopez-Acevedo, and H. Häkkinen, J. Phys. Chem. Lett. **1**, 1528 (2010).

[20] Z. Ning, W. Ji, and H. Guo, arXiv:0907.4674 (unpublished).

[21] M. Araidai and M. Tsukada, Phys. Rev. B **81**, 235114 (2010).

[22] J. M. Garcia-Lastra, C. Rostgaard, A. Rubio, and K. S. Thygesen, Phys. Rev. B **80**, 245427 (2009).

[23] D. J. Mowbray, G. Jones, and K. S. Thygesen, J. Chem. Phys. **128**, 111103 (2008).