Conductance of Au-BDT-Au molecular wires: A quantitative analysis

Zhanyu Ning[1], Wei Ji[1] and Hong Guo[1]

[1] *Centre for the Physics of Materials and Department of Physics, McGill University, Montreal, QC, Canada H3A 2T8*

ningz@physics.mcgill.ca

The conductance of gold-benzenedithiol(BDT)-gold molecular junctions has been extensively studied since 1997[1]. However, the difference between the experimental measurements and theoretical calculation are still within 1 or 2 orders of magnitudes. Even the theoretical investigations themselves have hardly been able to reach a consensus. The calculated results vary by 1 or 2 orders of magnitudes, depending on the adopted atomic models and/or *ab initio* methods[6–18]. This controversial situation persisted for more than ten years so far, although the non-equilibrium green's function combined with density functional theory(NEGF+DFT) method has achieved many successes in quantitative modeling of transport problems in many other molecular systems[19–22]. Some straight-forward questions might be raised: What makes the gold-BDT-gold system so special? Is our current *ab initio* technique lacking of some basic ingredients for this particular system? In this work, we attempt to resolve these issues.

First of all, using NEGF+DFT method(Generalized Gradient Approximation with Perdew-Burke-Ernzerhof 96 functional (GGA-PBE) is adopted), we calculated the transmission coefficient following the atomic model widely assumed in literatures[1,4]. The result($0.4G_0$) ,which is consistent with the previous calculation[11,16,18], is found to be much higher than the experimental value($0.01G_0$)[4]. According to the analysis of density of states, it appears that the electronic hybridization between gold and BDT in this commonly adopted atomic model is overestimated, which results in the calculated high conductance through the junctions. It was reported that the conductance is very sensitive to the atomic geometry in molecular junctions[25]. However, the detailed local geometry in this junction has not been well investigated so far. We thus performed a very careful surface calculation using standard PAW-PBE method as implemented in VASP. It was discovered that the $S-H$ bond is non-dissociative when BDT molecules attach to the gold surface via a gold ad-atom. After considering a plenty of representative atomic configurations, the non-dissociative structures are found to be always more stable than the H-dissociated structures by at least $0.2eV$. This non-dissociative adsorption is also supported by the previous experimental and theoretical work[23,24]

Afterward, a further transport calculation based on the new atomic model with non-

dissociative $S-H$ bond has been carried out with the NEGF+PBE method. The calculated conductance of Au-BDT-Au junctions is found to be about $0.02G_0$, which is comparable with the experimental data of $0.011{G_0}^4$. Our results strongly suggest that the non-dissociative $S-H$ bond plays an important role in describing the Au-BDT electronic coupling.

Finally, since the experiment was done in some solutions, it is considerably important to introduce the solvent effects, as discussed in this work.

---

[1] M. A. Reed, *et al.*, Science **278**, 252 (1997).

[2] M. Tsutsui,*et al.*, Appl. Phys. Lett. **89**, 163111 (2006).

[3] E. Lörtscher, *et al.*,Phys. Rev. Lett. **98**, 176807 (2007).

[4] X. Y. Xiao, *et al.*, Nano. Lett. **4**, 267 (2004).

[5] M. Kiguchi, *et al.*, Appl. Phys. Lett. **89**, 213104 (2006).

[6] M. Di Ventra, *et al.*, Appl. Phys. Lett. **76**, 3448 (2000).

[7] K. Stokbro, *et al.*, Comp. Mat. Sci. **27**, 151 (2003).

[8] S. W. Huang, *et al.*, J. Chem. Phys. **121**, 6485 (2004).

[9] T. Tada, *et al.*,J. Chem. Phys. **121**, 8050 (2004).

[10] P. Delaney and J. C. Greer, Phys. Rev. Lett. **93**, 036805 (2004).

[11] S. H. Ke, *et al.*,J. Chem. Phys. **123**, 114701 (2005). S. H. Ke, *et al.*, J. Am. Chem. Soc. **126**, 15897 (2004). S. H. Ke, *et al.*,J. Chem. Phys. **127**, 144107 (2007).

[12] G. C. Solomon, *et al.*,J. Chem. Phys. **122**, 224502 (2005).

[13] R. B. Pontes, *et al.*,J. Am. Chem. Soc. **128**, 8996 (2006).

[14] J. Jiang, *et al.*,J. Chem. Phys. **124**, 34708 (2006).

[15] D. Q. Andrews, *et al.*,J. Chem. Phys. **125**, 174718 (2006).

[16] C. Toher and S. Sanvito, Phys. Rev. Lett. **99**, 56801 (2007). Phys. Rev. B **77**, 155402 (2008).

[17] D. Q. Andrews, *et al.*, Nano. Lett. **8**, 1120 (2008).

[18] M. Strange, *et al.*, J. Chem. Phys. **128**, 114701(2008).

[19] C. C. Kaun,*et al.* , Rhys. Rev. B **67**, 121411(R) (2003).

[20] C. C. Kaun and H. Guo, Nano Lett. **3**, 1521 (2003).

[21] T. Frederiksen, *et al.*, Phys. Rev. Lett. **93**, 256601 (2004).

[22] Z. Ning, *et al.*, Phys. Rev. Lett. **100**, 056803 (2008).

[23] I. I. Rzeznicka, *et al.*, J. Phys. Chem. B **109**, 15992 (2005).

[24] J. G. Zhou and F. Hagelberg, Phys. Rev. Lett. **97**, 045505 (2006).

[25] M. Kamenetska, *et al.*, Phys. Rev. Lett. **102**, 126803 (2009).