RAPID COMMUNICATIONS

PHYSICAL REVIEW B **79**, 081404(R) (2009)

Probing charge transport in single-molecule break junctions using inelastic tunneling

Maryam Rahimi[1,2,*] and Michael Hegg[2]
[1]*Microscale Life Sciences Center (MLSC), University of Washington, Seattle, Washington 98195, USA*
[2]*Department of Electrical Engineering, University of Washington, Seattle, Washington 98195, USA*

(Received 18 August 2008; published 12 February 2009)

Inelastic electron-tunneling spectroscopy (IETS) is used to study charge transport in molecular break junctions. Based on the differences in IETS and conductance measurements, we report the existence of two distinct types of junctions. Earlier IETS measurements by Kushmerick *et al.* [Phys. Rev. Lett. **98**, 206803 (2007)] showed that incorporation of metal nanoparticles into the tunnel junctions leads to enhanced IETS intensity and changes in the line shape of some vibrational modes. The presence of gold nanoparticles in some of our devices could therefore explain the differences in the measured IET spectra in addition to the complex response exhibited by these junctions to illumination with light.

DOI: 10.1103/PhysRevB.79.081404 PACS number(s): 73.61.Ph

Molecules have been proposed as an alternative in post-complementary metal-oxide semiconductor (CMOS) devices. Molecular electronics is an active area of research concerned with building electronic devices using individual molecules.[1] In the past few years, electromigrated gold break junctions have been used to study transport properties of a single molecule with some groups reporting the observation of Coulomb blockade and Kondo effects in these systems.[2,3] However, there have been reports of observations of both Coulomb blockade and Kondo effects in bare-electromigrated break junction devices.[4,5] Therefore it is of great importance for single-molecule experiments to demonstrate that tunneling electrons indeed pass through the molecule positioned in the gap and to be able to verify the molecular component of any observed phenomena.

An extensive study of optical properties of nanoscale break junctions has been performed in recent years.[6–9] Electromigration has been reported to produce metal nanoclusters, which show very intriguing optical properties such as electroluminescence under dc, ac, and pulsed excitation. The several-atom gold clusters have exhibited asymmetric optical response with applied electric field polarity.[6,9] The observed asymmetry has been attributed to the asymmetric proximity of these metal nanoclusters with respect to the electrodes as well as the observed energy-level asymmetry of the electrodes (different oxygen content measured for anode and cathode electrodes) to which the electrons are injected.[9] The fabrication process is performed under constant polarity. Therefore the forces generated by the external electric field can cause the structural and chemical polarization of metal wires, which in turn can result in structural asymmetry in the junction.

Inelastic electron-tunneling spectroscopy (IETS) (Ref. 10) is a powerful technique for measuring the vibrational spectra of molecules, which can be used to identify molecules or molecular fragments based on the characteristic absorption frequencies of functional groups. Similar to Raman and infrared spectroscopy, IETS relies on the excitation of the active vibrational modes and energies of a molecule adsorbed on a surface. Tunneling electrons can lose their energy through excitation of vibrational modes of molecules contained within a tunnel junction structure. When applied voltage exceeds a characteristic vibrational energy of a molecule, the opening of a new inelastic conduction channel—in addition to the elastic one—results in a change in the slope of the current, an increase in the conductance value, and peaks in the second derivative of current versus voltage. Peaks in (d^2I/dV^2) versus V correspond to molecular vibrations that are excited by the tunneling electrodes.

In recent years, IETS has been used as an *in situ* probe of molecular junctions in order to verify the actual presence of the molecule and therefore the *molecular character* of a junction.[11–14] These IETS measurements were performed on ordered self-assembled monolayers (SAMs) consisting of thousands of molecules. A scanning tunnel microscope (STM) setup has been used to measure the IETS signal of a single molecule.[15]

Here, we report on differential conductance and IETS measurements of empty break junction devices and devices coated with 11-Mercapto-undecanoic acid $[HS(CH_2)_{10}COOH]$ molecules. Gold wires with width of 40 nm, lengths of 200 nm, and thickness of 30–35 nm were fabricated on a Si/SiO_2 wafer by electron-beam lithography. The wires were cleaned with acetone, isopropyl alcohol, and oxygen plasma and then placed in a cryogenic probe station (TTP4, Lake Shore Cryogenics Inc.) connected to a LABVIEW controlled sourcemeter to perform electromigration. We used a voltage ramping LABVIEW program, which uses conductance as a feedback parameter, to perform electromigration on gold nanowires in order to make the nanogaps. Details of this voltage ramping algorithm have been reported elsewhere.[16]

Electromigration was performed at room temperature. After measuring the *I*-*V* curves of the devices at room temperature, they were immediately cooled to 4.2 K. Subsequently the *I*-*V* characteristics of the devices were measured at 4.2 K. In more than half of the devices, tunneling current dropped by 2–3 orders of magnitude after cooling down to 4.2 K, possibly due to the widening of the gap or restructuring of the formed electrodes.[17] Differential conductance and inelastic electron-tunneling spectra (IETS) were obtained via standard ac modulation techniques using a Stanford Research Model 830 lock-in amplifier. We used an ac modulation of 10 mV at a frequency of 500 Hz to obtain the first-harmonic (dI/dV) and second-harmonic (d^2I/dV^2) signals.

The conductance and *I*-*V* measurements on about 90% of

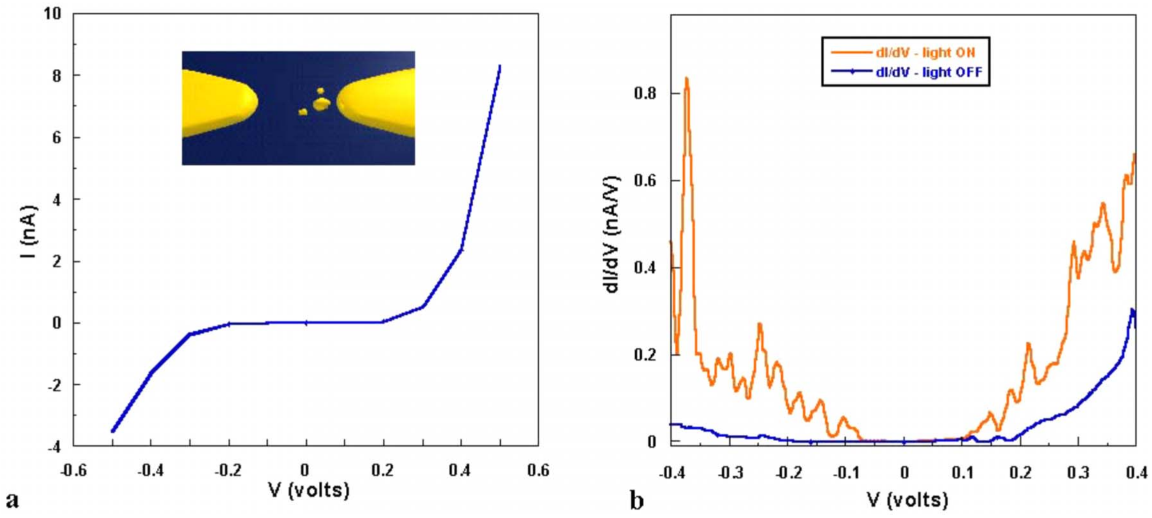

FIG. 1. (Color online) (a) *I-V* characteristics and (b) conductance measurements for a bare (no organic molecule) break junction device measured at 4.2 K. The red plot in (b) is the conductance response of this junction illuminated with light from the microscope lamp. The blue/dark gray plot in (b) is the conductance measurement of the same device with the light off. The asymmetric *I-V* and conductance curves are suggestive of asymmetric nature of the tunnel junction due to the likely presence of gold nanoparticles in the junction [inset of a].

more than 200 devices fabricated for this study show an asymmetric response with respect to bias polarity. Figure 1 shows the *I-V* and conductance measurements on a bare device with no organic molecules deposited on it. Incidentally, we observed that these bare devices (which show strong voltage polarity dependence) exhibit a complicated response to light as well. Our probe station is equipped with a microscope lamp in order to observe the devices being measured.[18] Figure 1(b) shows that upon illuminating this device with light from the microscope lamp, a series of oscillations are seen in the conductance. Such behavior is not expected from a device which only consists of two electrodes a few nanometers apart. Coulomb blockade and resonant tunneling oscillations are expected where a charge trap with variable energy level is positioned between two electrical leads.[19] Normally, a gate voltage is used to vary the average number of electrons on the trap (e.g., metal particle). Illuminating with light capable of exciting electrons within the discrete energy levels of charge traps can change the measured conductance [which is a measure of the local density of states (DOS) available for tunneling electrons] of devices.

Our setup is not capable of performing optical measurements with a controlled spectroscopic source to determine the wavelength dependence of the response. However, the light emission from small gold nanoparticles in different system such as thin metal films[20,21] and electromigrated break junction devices[7] has been studied extensively in the past. The measured electroluminescence spectra of gold nanoparticles (typically an array of 18–22 gold atoms) range from 650 to 750 nm in emission maximum. Illumination with white light from microscope lamp can therefore cause excitation of electrons within the discrete energy levels of gold nanoclusters,[22] which in turn can change the number of electrons (holes) in these clusters and causes the conductance oscillations or even photoconductivity.

In less than 10% of devices measured for this study, we observe *I-V* and differential conductance curves, similar to what is seen in Fig. 2. The *I-V* and differential conductance measurements for these devices are symmetric with applied voltage polarity, with little change in conductance upon illumination with light. The absence of any Coulomb blockaded region or oscillations in the measured differential conductance, in addition to being symmetric with respect to the applied bias polarity and demonstrating no significant reaction to light, suggests that this device is free of charge traps and therefore suitable for single-molecule studies. However, it remains a challenge of how to control the electromigration (which is a relatively random process) parameters in order to increase the yield for clean devices.

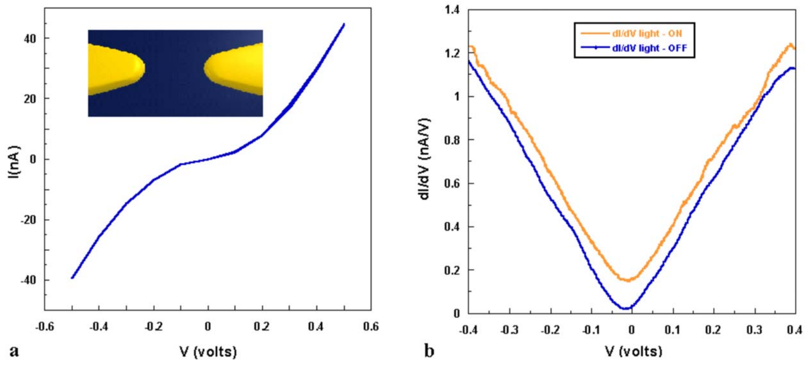

FIG. 2. (Color online) (a) *I-V* and (b) conductance plots of a bare device measured at 4.2 K. The symmetric *I-V* and conductance curves in addition to the absence of Coulomb blockade and any significant change upon illumination with light suggest that this device is free of charge traps [inset of Fig. 1(a)].

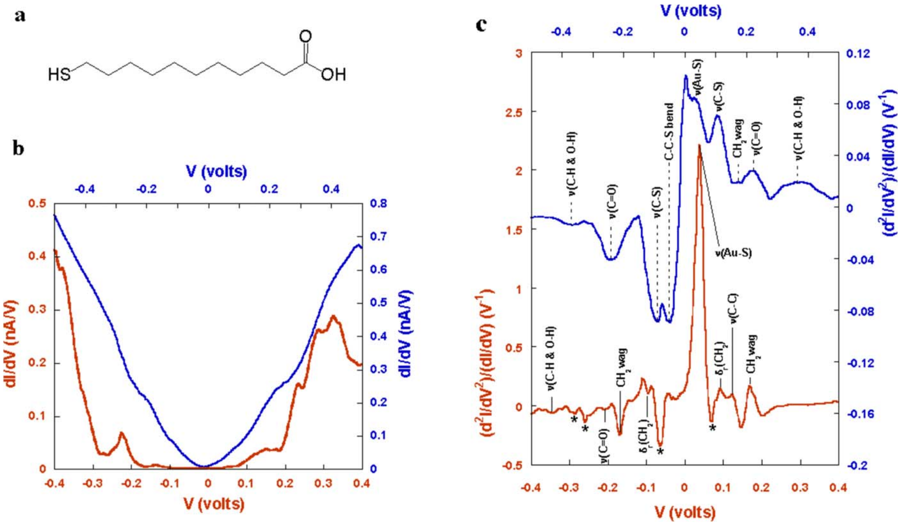

FIG. 3. (Color online) (a) Chemical structure of 11-Mercapto-undecanoic acid, [b and c] conductance, and IET spectra of this molecule in two different break junction devices. Peaks labeled $*$ in (c) (red/gray plot) do not originate from the molecule and are likely due to modes associated with the molecule-metal particle hybrids. Note that υ=stretch and δ=rocking. Numbers in blue/dark gray represent the values for the blue/dark gray plots and numbers in red represent the plots in red/gray.

Figure 3 displays the differential conductance and inelastic electron-tunneling (IET) $[(d^2I/dV^2)/(dI/dV)]$ measurements on two different devices with 11-Mercapto-undecanoic acid molecules in the junctions. After performing electromigration at room temperature, the devices were immersed in 10 mM solution of 11-Mercapto-undecanoic acid in ethanol for about 1 hr in order to form a molecular junction. There are striking differences between the conductance and IET spectra of the two junctions. The conductance of one is symmetric with bias polarity with no resonant tunneling peaks [blue plot, Fig. 3(b)], while the other device shows an asymmetric conductance with resonant tunneling peaks [red plot, Fig. 3(b)]. There are clear differences in the line shapes, presence, or absence of some molecular modes and intensity of the IET spectra of two junctions. Mode assignments of the observed features are based on the computation of the IETS for an idealized junction using the methodology and computational details described elsewhere[23] and supported by the Fourier transform infrared (FTIR) spectra of this molecule provided by Sigma Aldrich. However, full interpretation of IETS results is difficult since there are no clear propensity rules available and, without computational results, one does not know which vibrations will be visible in the IET spectra.[24]

While all the observed features in one junction [Fig. 3(c), blue curve] have only a peak (dip for negative bias) shape, the other junction (red curve) has peak-derivative-like features. The intensity of some vibrational modes such as Au-S has increased more than 20 times for the junction depicted in red. The C=O stretch (appears as a peak in the 1670–1780 cm^{-1} or 208–222 mV range) in addition to O–H and C–H vibrational modes (overlap and appear as one peak in the 2500–3300 cm^{-1} or 312–412 mV) are only seen for the negative bias in the red plot. The C=O and O–H vibrational modes are characteristic vibrational modes for carboxylic acid functional group which is the present functional group in the molecule under study.

The possibility of observing asymmetry in IETS measurements due to differences in contact density of states or different energy dependence of the coupling (e.g., STM-like geometry or asymmetric positioning of molecular vibrational modes in the junction with respect to the electrodes) has recently been studied.[25] However, the observed asymmetry in Fig. 3(c) (red spectra) could be partially due to the inherent asymmetry observed in these devices even prior to the deposition of molecule (asymmetric *I*-*V* and conductance with respect to bias polarity).

Previous IETS measurements performed with monolayers in crossed wire[12] or microsphere[14] junctions have shown only peak shape features, similar to what we observed in Fig. 3(c) (blue spectra). Recent IETS experiments by Kushmerick and co-workers with monolayers in a crossed-wire junction showed that incorporation of metal nanoparticles into tunnel junctions leads to an enhanced IET intensity and changes in the line shape for some of the vibrational modes.[26–28] Junctions with metal nanoparticles in them exhibited vibrational features with *peak-derivative-like* line shapes, while junctions with no incorporated metal nanoparticles had a simple peak shape features in their spectra.

It is interesting to note that no Coulomb blockade or resonant tunneling peaks are observed in the differential conductance at least up to 500 mV for the device depicted in blue [Fig. 3(b)], even though the molecule's signature is detected in its IET spectra [Fig. 3(c), blue spectra]. The peaks in the differential conductance [Fig. 3(b) red plot] could be due to the resonant tunneling into an empty state of gold clusters since they have been observed in empty devices as well.

The existences of gold nanoparticles in these electromigrated break junctions can explain their very high Raman sensitivity which was recently reported.[29] Surface enhanced Raman scattering (SERS) was first observed on molecules adsorbed on a specially prepared rough silver surface; since then, SERS has been reported on many molecules and with a number of other metals (e.g., Au, Cu, and Pt).[30] Inelastic electron tunneling is also known to generate light through excitation of optically coupled surface-plasmon modes in tunnel junctions consisting of rough Au and Ag surfaces.[31] However, the complex geometric and electronic structures of these metal nanoparticles make the comprehensive description of their behavior very challenging.

A likely mechanism that could give rise to the enhancement and change in the line shape in the IET spectra is the change in the energy level of a molecule-metal particle hybrid which is closer to the Fermi level than the highest occupied molecular orbital (HOMO) level of the molecule. Theoretical and computational results have showed that a resonant level close to the Fermi level could give rise to larger IETS intensity and change the line shapes for some vibrational modes.[28,32]

In summary, we have studied the charge transport in molecular break junctions using IETS technique and have been able to identify two types of junctions. In one group of junctions, we observed no Coulomb blockade or resonant tunneling features in their conductance and their IET spectral features had only simple peak shapes. Illumination with white light caused little changes in their conductance. In the second group, we observed asymmetric conductance with *peak-derivative-like* line shapes in their IETS spectra. Illumination with white light caused drastic changes in the conductance of these devices when measured bare. Incorporation of metal nanoparticles in crossed-wire junctions in Ref. 26 leads to changes in the line shape and intensity in the IET spectra in the measured devices. By comparing the IET spectra of our devices with those from crossed-wire junctions, we feel that the presence of gold nanoparticles (leftover from electromigration) in addition to molecules in some of our devices can explain the observed differences in the IETS measurements in addition to their observed reaction to illumination with white light.

We are grateful to D. Ryan and L. Y. Lin for helpful discussions and suggestions. A. Troisi for providing us with the computed IETS spectra of the molecule and J. A. Lund for valuable technical assistance. This work was performed in part at the University of Washington Nanotechnology User Facility (NTUF). M.R. gratefully acknowledge financial support from the Gordon and Betty Moore Foundation.

---

*Author to whom correspondence should be addressed; mrahimi@u.washington.edu

[1] C. Joachim and M. R. Ratner, Proc. Natl. Acad. Sci. U.S.A. **102**, 8801 (2005).

[2] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, Nature (London) **407**, 57 (2000).

[3] J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, and D. C. Ralph, Nature (London) **417**, 722 (2002).

[4] A. A. Houck, J. Labaziewicz, E. K. Chan, J. A. Folk, and I. L. Chaung, Nano Lett. **5**, 1685 (2005).

[5] R. Sordan, K. Balasubramanaian, M. Burghard, and K. Kern, Appl. Phys. Lett. **87**, 013106 (2005).

[6] T. Lee, C. D. Hladik, and R. M. Dickson, Nano Lett. **3**, 1561 (2003).

[7] J. I. Gonzalez, T. Lee, M. D. Barnes, Y. Antoku, and R. M. Dickson, Phys. Rev. Lett. **93**, 147402 (2004).

[8] J. I. Gonzalez, T. Vosch, and R. M. Dickson, Phys. Rev. B **74**, 064305 (2006).

[9] J. I. Gonzalez, T. Vosch, and R. M. Dickson, Phys. Rev. B **74**, 235404 (2006).

[10] R. C. Jaklevic and J. Lambe, Phys. Rev. Lett. **17**, 1139 (1966).

[11] W. Wang, T. Lee, I. Kretzchmar, and M. A. Reed, Nano Lett. **4**, 643 (2004).

[12] J. G. Kushmerick, J. Lazorcik, C. H. Patterson, R. Shashidhar, D. S. Seferos, and G. C. Bazan, Nano Lett. **4**, 639 (2004).

[13] A. S. Blum, J. G. Kushmerick, D. P. Long, C. H. Patterson, J. C. Yang, J. C. Henderson, Y. Yao, J. M. Tour, R. Shashidhar, and B. R. Ratna, Nature Mater. **4**, 167 (2005).

[14] D. P. Long, J. L. Lazorcik, B. A. Mantooth, M. H. Moore, M. A. Ratner, A. Troisi, Y. Yao, J. W. Ciszek, J. M. Tour, and R. Shashidhar, Nature Mater. **5**, 901 (2006).

[15] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **280**, 1732 (1998).

[16] J. Dong and B. A. Parviz, Nanotechnology **17**, 5124 (2006).

[17] D. R. Strachan, D. E. Smith, M. D. Fischbein, D. E. Johnston, B. S. Guiton, M. Drndic, D. A. Bonnell, and A. T. Johnson, Nano Lett. **6**, 441 (2006).

[18] The microscope's light source uses a 150 W EKE bulb to deliver white light via fiber optic cabling for illumination of specimens with an intensity of 0.016 $\mathrm{W/cm^2}$ at specimen's distance.

[19] M. A. Kastner, Rev. Mod. Phys. **64**, 849 (1992).

[20] A. Adams and P. K. Hansma, Phys. Rev. B **23**, 3597 (1981).

[21] R. W. Rendell, D. J. Scalapino, and B. Muhlschlegel, Phys. Rev. Lett. **41**, 1746 (1978).

[22] S. Chen, R. S. Ingram, M. J. Hostetler, J. J. Pietron, R. W. Murray, T. G. Schaaff, J. T. Khoury, M. M. Alvarez, and R. L. Whetten, Science **280**, 2098 (1998).

[23] A. Troisi and M. A. Ratner, J. Chem. Phys. **125**, 214709 (2006).

[24] G. Gagliardi, G. C. Solomon, A. Pecchia, T. Frauenheim, A. Di Carlo, N. S. Hush, and J. R. Reimers, Phys. Rev. B **75**, 174306 (2007).

[25] M. Galperin, A. Nitzan, M. A. Ratner, and D. R. Stewart, J. Phys. Chem. B **109**, 8519 (2005).

[26] L. H. Yu, C. D. Zangmeister, and J. G. Kushmerick, Phys. Rev. Lett. **98**, 206803 (2007).

[27] L. H. Yu, C. D. Zangmeister, and J. G. Kushmerick, Nano Lett. **6**, 2515 (2006).

[28] M. Galperin, A. Nitzan, and M. A. Ratner, Nano Lett. **4**, 1605 (2004).

[29] D. R. Ward, N. K. Grady, C. S. Levin, N. J. Halas, Y. Wu, P. Nordlander, and D. Natelson, Nano Lett. **7**, 1396 (2007).

[30] M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).

[31] J. Lambe and S. L. McCarthy, Phys. Rev. Lett. **37**, 923 (1976).

[32] A. Baratoff and B. N. J. Persson, J. Vac. Sci. Technol. A **6**, 331 (1988).