

Spin-polarized inelastic electron tunneling spectroscopy of a molecular magnetic tunnel junction

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Molecular electronic devices with spin-dependent tunneling transport behavior offer an innovative and extremely enticing direction towards spin electronics, both from fundamental and technological points of view. In this work, inelastic electron tunneling spectroscopy provides unambiguous experimental evidence of the existence of molecular species in the fabricated molecular magnetic tunnel devices. Tunneling spectroscopy is also utilized to investigate the spin-polarized inelastic electron tunneling processes in the molecular device. The results show that inelastic scattering due to molecular vibrations, instead of magnon excitations, may be the main cause of the observed junction magnetoresistance bias dependence. [DOI: 10.1063/1.2360908]

Spin-dependent transport through nanometer scale organic systems has recently attracted increased attention.¹ Due to the weak spin-orbital and hyperfine interactions in molecules, the spin coherence over time and distance could be preserved much longer in molecular nanosystems than in traditional semiconductors, which makes them a suitable playground for spin manipulations.^{1,2} In a single recent report,² an octanethiol [$\text{CH}_3(\text{CH}_2)_7\text{SH}$] self-assembled monolayer^{3,4} (SAM) has been used between two ferromagnetic electrodes to create an organic spintronic system, leading to the expectation that single molecules could be used as the ultimate building blocks for spintronic devices.¹ However, although it is widely accepted that alkanethiols can form robust SAMs on gold surfaces,³⁻⁶ the SAM formation on ferromagnetic metals or metal oxide surfaces is still under investigation. Therefore, as was for the case of SAMs on gold,^{3,6} critical controls are needed to confirm the presence of desired molecules in the device area. In this work, we realize such verification via the application of inelastic electron tunneling spectroscopy^{6,7} (IETS) and present unambiguous experimental evidence of the existence of molecular species in the molecular magnetic tunnel junctions (MTJs). A strong bias dependence of the molecular junction magnetoresistance (JMR) was observed in the previous experiment, but the origin of this dependence is unclear.² In this study, we have further applied spin-polarized IETS to investigate spin-dependent inelastic scatterings in molecular spintronic devices, and we show that inelastic scattering due to molecular vibrations may be the origin of the strong JMR bias dependence observed in our device.

Figure 1(a) shows the device structure, where Ni and Co are the electrodes and octanethiol molecules form the tunnel barrier.^{2,3,8,9} Figure 1(b) shows the current-voltage [$I(V)$] characteristics of an octanethiol-MTJ device at 4.2 K. Positive bias corresponds to electrons injected from the bottom Co contact to the top Ni contact. The Ni-octanethiol-Co devices generally exhibit a minor thermally activated transport behavior, but at temperatures below 50 K conduction is via pure tunneling. Figure 1(c) shows the IETS spectrum of

the device obtained at 4.2 K before applying the magnetic field, where the magnetizations of the two ferromagnetic electrodes are likely in a random configuration. An ac modulation of 9.8 mV (rms value) at a frequency of 503 Hz was applied to the sample to acquire the second harmonic signals. Measurements at different dc resolutions and ac modulations were also performed to confirm the validity of the observed IETS spectra. The peaks at 81, 139, and 176 mV are assigned to $\nu(\text{C-S})$, $\nu(\text{C-C})$, and $\delta_s(\text{CH}_2)$ modes of a surface-bound alkanethiolate from comparison with previously reported IETS, infrared, Raman, and high resolution electron energy loss data.^{6,10} The shoulder appearing at ~ 40 mV is assigned to the $\nu(\text{Ni-S})$ mode according to published reports.^{11,12} This $\nu(\text{Ni-S})$ peak became more pronounced after the application of the external magnetic field. The peak at 262 mV is associated with the Si-H vibration related to the silicon nitride membrane that confines the SAM.⁶ The peak at 17 mV is possibly due to the contribution from nickel phonons.¹³ The obtained tunneling spectra in this study exhibited vibrational signatures of the molecules, thus confirming the presence of the molecular species confined inside the Ni-octanethiol-Co magnetic tunnel junction.

Tunneling magnetoresistance measurements were carried out to investigate the spin-dependent transport in the molecular junction. Figure 2(a) is the plot of the change of the junction resistances ($R=V/I$)² of the same device as a function of magnetic field at a dc bias of 10 mV at 4.2 K. Similar traces have been observed at other biases. The field was applied out of the sample plane. Catastrophic damage to the molecular devices has been encountered at high magnetic fields; therefore, in order to preserve the device for spin-polarized IETS measurements the applied field for JMR measurements was restricted to $|H| < 0.6$ T. When the applied magnetic field was swept from positive to negative polarity, the junction resistance initially increased and showed a maximum at low magnetic fields. It then decreased at larger negative fields until the resistance became independent of the applied field at a value comparable to that observed at the initial high positive field [Fig. 2(a)]. Based on these observations, we argue that an antiparallel configuration has been achieved at the low magnetic field where the junction showed the maximum resistance and a parallel con-

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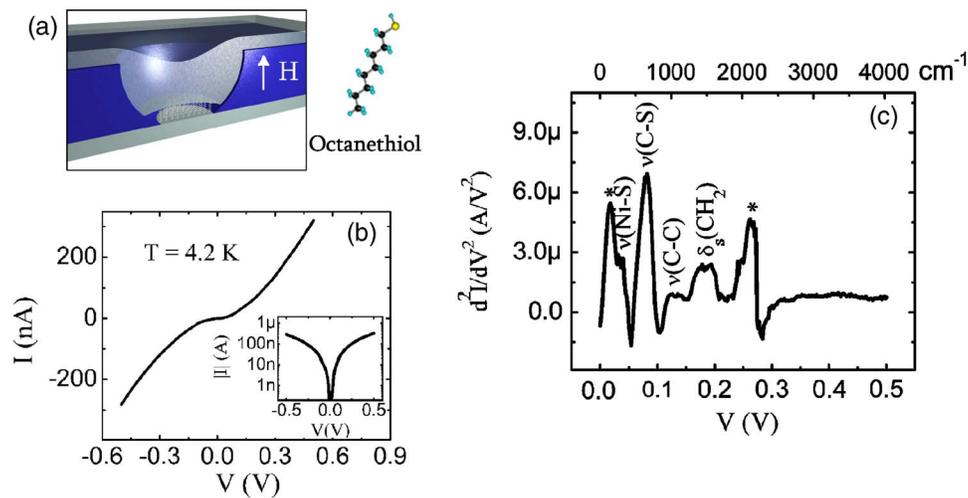


FIG. 1. (Color online) (a) Schematics of the nanopore device and chemical structure of the octanethiol molecule. The arrow shows the magnetic field direction. (b) $I(V)$ characteristic of the octanethiol-MTJ device at 4.2 K. Inset shows the same data on a logarithmic scale. (c) Inelastic electron tunneling spectrum of the MTJ at 4.2 K. Molecular vibrational features from $\nu(\text{Ni-S})$, $\nu(\text{C-S})$, $\nu(\text{C-C})$, and $\delta_s(\text{CH}_2)$ modes are identified in the spectrum. Peaks labeled “*” are possibly due to a Ni phonon and the encasing Si_3N_4 membrane, respectively.

figuration has been achieved at the negative field polarity where the junction resistance became independent of the applied field. Under the conservative magnetic field conditions, the JMR trace did not show a full saturation at the positive field side. Asymmetric JMR behavior¹⁴ similar to that in Fig. 2(a) has been observed previously in similar molecular MTJs, where a higher magnetic field was needed for one polarity to realize a parallel magnetization configuration.² In nanopore-based molecular MTJs this asymmetry is possibly related to the specific device geometry that makes the magnetization of either electrode along one direction easier than the opposite direction. Such effects of the device geometry on magnetization processes in nanostructures have been discussed recently.^{15–17} In light of the asymmetry previously reported,² we presume that the positive field JMR would continue to decrease at fields larger than +0.6 T and a saturation would be achieved at a slightly higher magnetic field. Thus, we attribute the observed magnetoresistance to spin-dependent transport through the molecular barrier.

Figure 2(b) shows the junction magnetoresistance at different dc biases. JMR was calculated according to the definition² $\text{JMR} \equiv (R_{\text{max}} - R_p)/R_p$, where R_{max} is the maximum resistance and R_p is the resistance at the parallel configuration. In our calculation we have assumed the maximum resistance measured at low negative field on the negative field direction sweep as the R_{max} and the resistance that

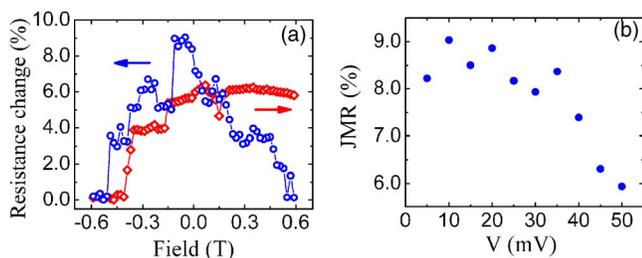


FIG. 2. (Color online) (a) Junction resistance change as a function of magnetic field at a dc bias of 10 mV and 4.2 K. The data were recorded when the magnetic field was swept from +0.6 to -0.6 T (circles) and then back to +0.6 T (diamonds). The arrows denote the field sweeping directions. (b) Device JMR as a function of bias at 4.2 K. A sharp decrease of JMR occurred around 40 mV.

showed field independence at the negative field polarity as the R_p . As Fig. 2(b) shows, the device JMR has strong bias dependence, especially at voltages higher than 40 mV. Such JMR bias dependence has been observed in most traditional MTJs,^{14,18} and it has been reported recently in molecular MTJs as well.² Mechanisms of spin-flip scattering by magnon excitations,^{18,19} impurity-assisted tunneling,^{20,21} and ferromagnet density of states changes¹⁸ have been proposed to explain this bias dependence in traditional MTJs. However, a consensus as to which of these mechanisms is the fundamental cause has yet to be reached.¹⁴

We utilized the spin-polarized IETS technique to investigate the JMR bias dependence of the molecular MTJs. Figure 3 shows the IETS spectra of the octanethiol MTJ at different magnetic fields. These spectra are characterized by four dominant peaks that were reproducibly observed at magnetic fields of -0.25, -0.5, and -0.75 T. The peaks at 42, 80, and 176 mV arise from molecular vibrations and are assigned as the molecule's $\nu(\text{Ni-S})$, $\nu(\text{C-S})$, and $\delta_s(\text{CH}_2)$ vibrational modes, respectively. The peak at 270 mV is from the silicon nitride membrane. The initial application of the magnetic field modifies the IETS spectra. The small shoulder at 40 mV due to $\nu(\text{Ni-S})$ became a distinct peak at a slightly

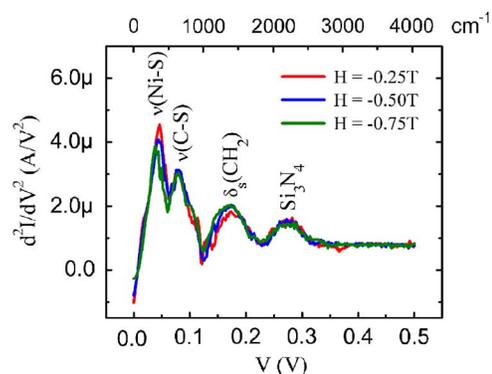


FIG. 3. (Color online) Spin-polarized IETS spectra at magnetic fields of -0.25, -0.5, and -0.75 T. Four pronounced peaks appear, and the first peak position corresponds well to the onset of the abrupt decrease of the JMR at 40 mV shown in Fig. 2(b).

higher position after the field was applied, while the peaks at 17 mV from Ni phonon and 139 mV from $\nu(\text{C}-\text{C})$ became less dominant features. All of the spectra taken before and after the introduction of the magnetic field were obtained under the same test conditions and were stable and repeatable upon successive measurements. The changes in the IETS spectra are possibly related to changes of the molecule-metal contact geometry or the electronic structures of the ferromagnetic electrodes or both, which could be introduced upon the initial application of the magnetic field. After the two electrodes have been magnetized, the IETS spectra (Fig. 3) remain essentially the same at biases larger than 50 mV as the device was changed from the antiparallel to the parallel magnetization configurations. As Fig. 3 shows, no magnon excitation²²⁻²⁴ was observed in the spectra, which suggests that the JMR bias dependence shown in Fig. 2(b) was not caused by spin-flip scattering processes. However, well-defined peaks due to electron-molecule couplings have been detected, and the first peak position at 42 mV corresponds very well to the onset of the rapid JMR decrease at about 40 mV; therefore, the JMR bias dependence in this molecular-MTJ device was attributed to the inelastic scattering due to the molecular vibrations. The inelastic scatterings from intrinsic molecular vibrations or nonmagnetic impurities are spin-independent processes and contribute conductance increases for both parallel and antiparallel magnetization configurations, which decrease the junction tunneling magnetoresistance.¹⁸

In this study we have presented a complete data set of IETS and JMR characterizations of a molecular-MTJ device. Although the effort to conduct a statistics study has been hampered by low device yield and the difficulties of performing these critical measurements, our obtained data unambiguously confirmed the presence of molecular components in the measured sample and the related magnetic behavior. The spin-polarized IETS measurements revealed that inelastic scattering due to molecular vibrations is likely the main cause of the observed JMR bias dependence. These results illustrate that such inelastic scattering events must be accounted for when predicting the performance of practical molecular spintronic devices.

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- ¹A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lamberty, J. Ferrer, and S. Sanvito, *Nat. Mater.* **4**, 335 (2005).
- ²J. R. Petta, S. K. Slater, and D. C. Ralph, *Phys. Rev. Lett.* **93**, 136601 (2004).
- ³W. Wang, T. Lee, and M. A. Reed, *Phys. Rev. B* **68**, 035416 (2003).
- ⁴A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly* (Academic, Boston, 1991).
- ⁵*Molecular Electronics: Science and Technology*, edited by A. Aviram and M. A. Ratner (New York Academy of Sciences, New York, 1998), Vol. 852.
- ⁶W. Wang, T. Lee, I. Kretzschmar, and M. A. Reed, *Nano Lett.* **4**, 643 (2005).
- ⁷J. G. Kushmerick, J. Lazorcik, C. H. Patterson, R. Shashidhar, D. S. Seferos, and G. C. Bazan, *Nano Lett.* **4**, 639 (2004).
- ⁸Z. Mekhalif, F. Laffineur, N. Couturier, and J. Delhalle, *Langmuir* **19**, 637 (2003).
- ⁹See EPAPS Document No. E-APPLAB-89-283641 for the experimental details associated with the fabrication and electrical characterization of the nanopore-based molecular-MTJs. This document can be reached through a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
- ¹⁰M. J. Hostetler, J. J. Stokes, and R. W. Murray, *Langmuir* **12**, 3604 (1996).
- ¹¹T. S. Rufael, D. R. Huntley, D. R. Mullins, and J. L. Gland, *J. Phys. Chem.* **99**, 11472 (1995).
- ¹²H. Yang, T. C. Caves, J. L. Whitten, and D. R. Huntley, *J. Am. Chem. Soc.* **116**, 8200 (1994).
- ¹³R. J. Birgeneau, J. Cordes, G. Dolling, and A. D. B. Woods, *Phys. Rev.* **136**, A1359 (1964).
- ¹⁴J. S. Moodera, J. Nassar, and G. Mathon, *Annu. Rev. Mater. Sci.* **29**, 381 (1999).
- ¹⁵B. Tadic, K. Malarz, and K. Kulakowski, *Phys. Rev. Lett.* **94**, 137204 (1997).
- ¹⁶C. C. Wang, A. O. Adeyeye, and N. Singh, *Nanotechnology* **17**, 1629 (2006).
- ¹⁷It is possible that the observed magnetoresistance was due to a mechanical change of the device structure, which could be caused by the ferromagnetic electrode domain walls changing under the applied field. However, we feel this is unlikely the case because in these fragile devices magnetically induced mechanical changes appear to cause catastrophic damage.
- ¹⁸E. Y. Tsymlal, O. Mryasov, and P. R. LeClair, *J. Phys.: Condens. Matter* **15**, R109 (2003).
- ¹⁹S. Zhang, P. M. Levy, A. Marley, and S. S. P. Parkin, *Phys. Rev. Lett.* **79**, 3744 (1997).
- ²⁰A. M. Bratkovsky, *Phys. Rev. B* **56**, 2344 (1997).
- ²¹J. Zhang and R. White, *J. Appl. Phys.* **83**, 6512 (1998).
- ²²J. S. Moodera, J. Nowak, and R. J. M. van de Veerdonk, *Phys. Rev. Lett.* **80**, 2941 (1998).
- ²³J. Murai, Y. Ando, M. Kamijo, H. Kubota, and T. Miyazaki, *Jpn. J. Appl. Phys., Part 2* **38**, L1106 (1999).
- ²⁴J. Schmalhorst, S. Kammerer, G. Reiss, and A. Hutten, *Appl. Phys. Lett.* **86**, 052501 (2005).