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Probing local electric field and conformational switching in single-molecule break junctions

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By performing inelastic electron tunneling spectroscopy on single-molecule junctions fabricated through electromigration, we were able to detect polarity-dependent frequency shifts in the molecular vibrational spectra. This observation in conjunction with a simple theoretical model is used to infer the magnitude of local electric field (a crucial and previously inaccessible parameter for understanding charge transport in single-molecule junctions) on the molecule. Electric field induced conformational changes are also detected within this set of measurements.

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Understanding charge transport through organic molecules is essential for various reasons such as rationalizing charge transfer in biological molecules,[1] developing molecular electronics,[2] and fabricating nanoelectronic devices and sensors. Methods for selective and rapid identification of single molecules can greatly impact progress in areas of significant interest such as human genome analysis.[3] In recent years different methods such as laser-induced florescence,[4] electrochemical detection of redox-active species,[5] and surface enhanced raman scattering (SERS) (Ref. 6) have been used for single-molecule studies.

Inelastic electron tunneling spectroscopy (IETS) is a method that records the vibrational spectra of individual molecules using information obtained from monitoring the electron-tunneling current.[7] Similar to Raman and infrared spectroscopy, IETS relies on the excitation of the active vibrational modes and energies of molecules adsorbed on a surface or trapped between two metallic electrodes. 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 tunneling channel 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.

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.[8–10] IETS is an extremely sensitive method and can provide information regarding the internal structure of a single molecule on a conductive surface far superior to what is obtained from a scanning tunneling microscope (STM). A STM setup capable of performing IETS measurements has been used to identify the vibrational spectra of specific single bonds on metal surfaces.[11] This sensitivity can be used to identify single molecules or molecular fragments based on the characteristic frequencies of functional groups and infer information on their orientation or electron-tunneling pathways.[12] Similar to other single-molecule spectroscopy techniques, IETS can use the single molecule as a *probe* of its local environment.

The full interpretation of the IETS spectra is difficult since most organic molecules have many vibrational modes in a narrow energy range that can contribute to their spectra. However, specific functional groups have characteristic absorption energies which do not change much from one compound to another and these signals can be used to univocally identify the functional groups.

We studied charge transport through 11-Mercapto-1-undecanol [$HS(CH_2)_{11}OH$, Aldrich; 97% purity and 11-Mercapto-undecanoic acid [$HS(CH_2)_{10}CO_2H$, Aldrich; 99% purity] molecules in electromigrated nanogaps (hereafter we refer to them briefly as alcohol and acid, respectively). Gold wires with width of 40 nm, length of 200 nm, and thickness of 30–40 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. The gaps were formed at room temperature and subsequently immersed in 10 mM solution of acid or alcohol in ethanol (100% purity) for about 1 h in order to form a molecular junction. The –S–H group will undergo some changes upon attachment to gold electrodes by forming a covalent S–Au bond, while a weaker (physisorption) interaction between alcohol and acid groups at the other end of molecule causes the molecule to form a connection with the other electrode, if the electrode geometry is favorable.[13,14]

After measuring their *IV* characteristics at room temperature, the devices were immediately cooled to 4.2 K. Subsequently the *IV*s of the devices were measured at 4.2 K. In some devices the current dropped by 2–3 orders of magnitude, possibly due to the widening of the gap or restructuring of the formed electrode.[15] We measured the *IV* characteristics both at room temperature and at 4.2 K in order to verify that the change in conductance is modest.[16] The average of $\frac{\Delta I}{I}=\frac{I(295\ \mathrm{K})-I(4.2\ \mathrm{K})}{I(295\ \mathrm{K})}$ measured at $V=0.1$, 0.2, 0.3, 0.4, and 0.5 V for the junctions depicted in Figs. 2 and 3 are 0.7 and 0.6, respectively. Differential conductance and IETS spectra were obtained via a standard ac modulation technique using a lock-in amplifier. An ac modulation of 10 mV rms at a frequency of 500 Hz was used to obtain the first harmonic (dI/dV) and second harmonic (d^2I/dV^2) signals. The voltage was changed at a 6 mV/s rate and the integration time was set to 300 ms.

A majority (about 90%) of more then 200 devices fabricated for this study produce IETS spectra with a character-

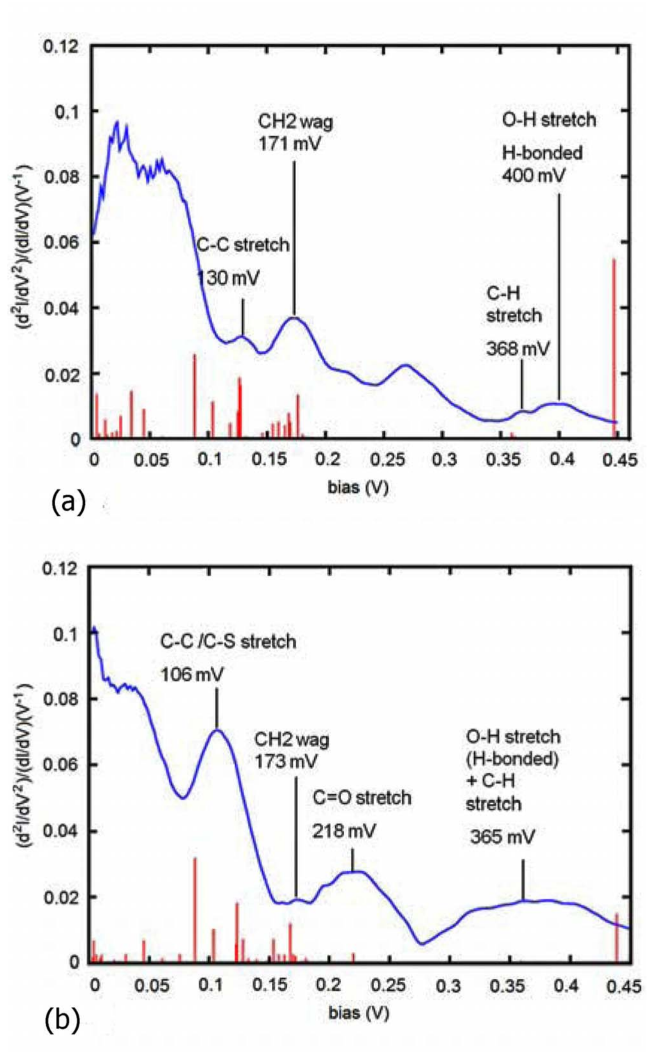

FIG. 1. (Color online) The IET $(d^2I/dV^2)/(dI/dV)$ spectra of (a) alcohol and (b) acid molecules measured at 4.2 K. The O–H peak in (a) detected at 400 mV is the characteristic O–H stretching mode of an alcohol in an environment where it can form hydrogen bond (Ref. 31). The C═O and O–H peaks (b) which are characteristic vibrational modes for the carboxylic acid group are observed at 218 and 365 mV. The computed frequencies and intensity are also indicated with vertical sticks. The O–H stretching frequency is higher in the computational model which does not include the effect of hydrogen bonds related to the presence of SiO_2 surface bound water (Ref. 34).

istic gold nanoparticle signature in the junction. The existence of gold nanoparticles in the junction leads to an enhanced inelastic electron-tunneling (IET) $[(d^2I/dV^2)/(dI/dV)]$ intensity and changes the line shape for some of the vibrational modes.[17–20] These junctions with gold nanoparticles normally show vibrational features with peak-derivative-like line shapes.[19] In this Brief Report, we only discuss IETS results for junctions which are free of gold nanoparticles.

Figures 1(a) and 1(b) show the IET spectra for alcohol and acid molecules in two different junctions. The O–H stretch which is a characteristic vibration for an alcohol is detected at 400 mV (3200 cm^{-1}, 1 eV is equivalent to 8066 cm^{-1}) in one of the devices, while the C═O and O–H stretches for carboxylic acid are observed at 218 and 365 mV (1752 and 2936 cm^{-1}, respectively) in the other one. The assignment of the spectra was helped by computation of the IETS for an idealized junction using the methodology and computational details described elsewhere.[21] The signal at 263 mV in Fig. 1(a) does not originate from the molecule and it is likely due to Si–H vibration of the substrate. The Si–H could be formed on the silica surface by a reaction following the stripping of OH group by large electric fields or high temperatures during electromigration. However, the presence of signals that can be exclusively of molecular origin (such as O–H, CH_2 wagging, and C═O stretching in the case of the acid molecule) confirms that we are measuring the transport through a molecular moiety regardless of the possible presence of shunt currents. Therefore we are able to identify single molecules in different junctions by identifying their constituent functional groups.

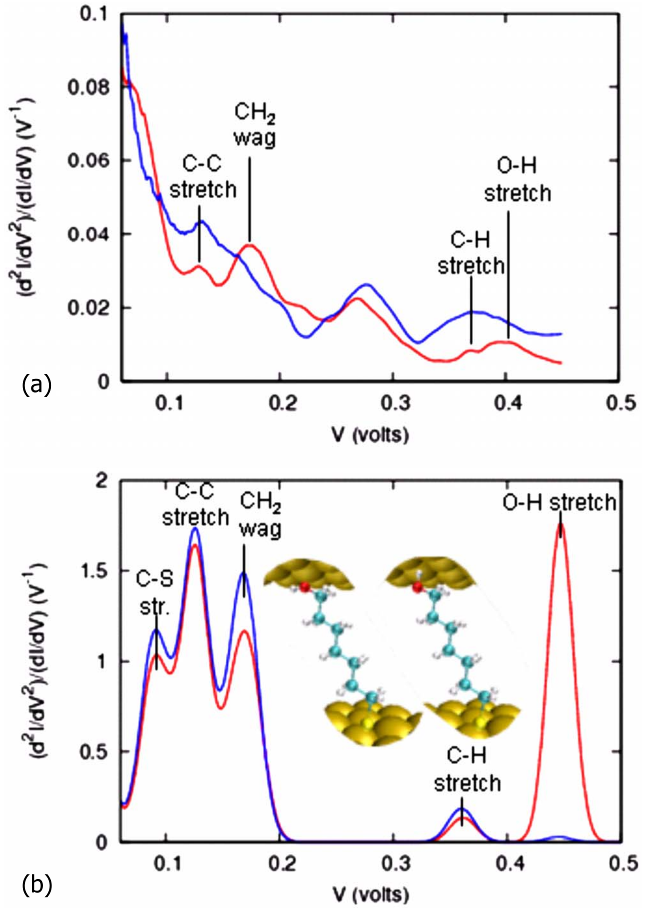

FIG. 2. (Color online) Measured IET spectra of alcohol molecule for positive (red) and negative (blue) biases (a). The O–H peak which is present for the positive bias is not seen for negative bias. The C–H peak seen at +368 mV as a small peak is a bigger and wider peak (−369 mV) for negative voltage. Computed IET spectra (b) for this molecule in two different conformations with the O–H bond pointing away from the electrode (blue spectrum), and toward it (red spectrum). The computed spectra do not include the effect of frequency shifts due to external electric field and broadening and shifting of the O–H signal due to hydrogen bonding. The spectra in (a) are average of 15 scans from +450 to −450 mV.

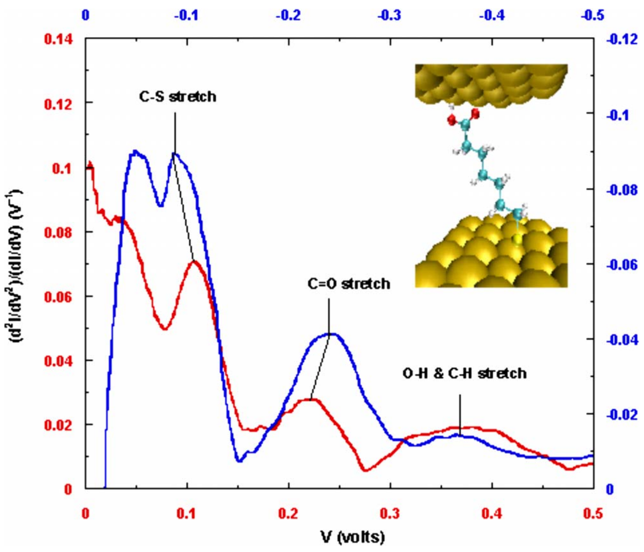

FIG. 3. (Color online) Experimental IET spectra of acid for positive (red) and negative (blue) bias. The C=O vibrational mode has shifted from +218 to −236 mV. The C–S vibration has been excited at its higher energy for positive bias. The spectra are a average of 19 scans from +500 to −500 mV.

Previous IETS studies on monolayers of organic molecules on the oxide of metal-oxide-metal junctions had shown that the tunneling intensities and peak positions could be sensitive to the junction environments.[22–24] It was proposed that the IETS intensities for those systems could give insights into the tunnel junctions' environments and the ratios of intensities could give orientational information.[25] In recent years, STM has been used to study structural conformational changes in single molecules and the degree of coupling between molecular vibrational energies to changes in conformation of molecules under study.[26,27] The conformational and orientational structures of molecules are dictated by a delicate balance between the molecule and local environment interactions in addition to the internal mechanics of the molecules.

We studied the bias polarity dependence of the IET spectra for both acid and alcohol molecules. Figure 2 shows the IET spectra for positive and negative biases for the alcohol molecule. The O–H stretch which is seen at positive bias is not seen for the negative bias. Instead, the C–H stretch which is seen as a small peak in the positive bias is more intense when the bias polarity is reversed to negative. The C–H and O–H vibrations for alcohol were observed at 366 ± 3.67 and 430 ± 20.15 mV, respectively, in four measured devices, with the O–H peak intensity being higher for one polarity than the other. This polarity dependence can be explained in terms of conformational changes in this molecule with respect to the electrode when the bias polarity is reversed.[28,29] The strong dipole moment of the O–H bond at the end of the alcohol molecule can cause different conformations of this molecule to be more stable at different voltage biases. In order to be able to observe the conformational changes in a molecule, the energy levels of two conformations should be close with respect to thermal energy k_BT and the difference in the dipole moment of the two conformations needs to be of the order of few Debye.[30] Computational results show that the IET spectra for the alcohol molecule in two different conformations (with the O–H pointing toward and away from the gold electrode) are different [Fig. 2(b)]. The intensity of the O–H stretching mode is greatly reduced when O–H points away from the electrode. This explains why the O–H stretch is not seen in our experiment when the bias polarity is reversed to negative.

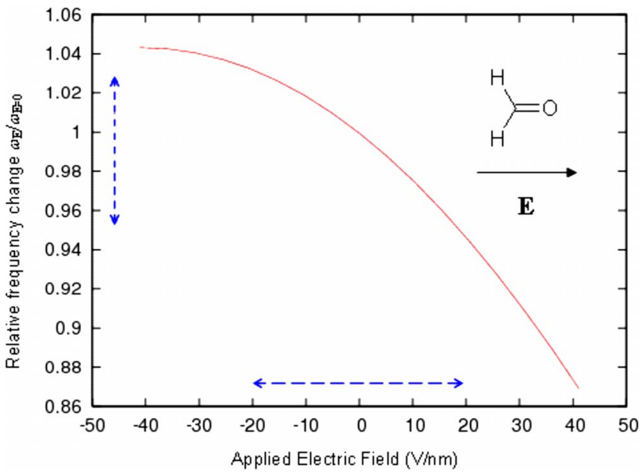

FIG. 4. (Color online) The computed change in relative frequency of the C=O bond in formaldehyde (H_2CO) as a function of an applied electric field E parallel to the C=O bond. All computations are performed at the B3LYP/6–31G* level. The ratio between the frequency at a given field ω_E and the frequency at zero applied field field $\omega_{E=0}$ was computed as $[(\partial^2 U/\partial R_{CO}^2)_E/(\partial^2 U/\partial R_{CO}^2)_{E=0}]^{1/2}$, where U is the total electronic energy of the molecule, R_{CO} is the C=O distance, and the derivatives have been evaluated at the equilibrium position at each field. In order to achieve a frequency shift of 8% (observed experimentally) between positive and negative biases, the local electric field should vary between +18 and −18 V/nm.

The O–H stretching mode of the carboxylic acid group is responsible for the broad signal seen in 2500–3300 cm^{-1} (312–412 mV) range, which partially overlaps with the C–H stretching [Figs. 1(b) and 3]. The C=O stretch is normally seen in the 1705–1780 cm^{-1} (213–222 mV) range. In our experiment with the acid molecule, we observe the O–H stretching mode at +365 and −366 mV. There is also a difference in the intensity and width of this peak for positive and negative biases with the former being more intense and wider compared to the latter.

The striking feature in Fig. 3 is the shift in the frequency of the C=O stretch detected at +218 and −236 mV. We observed an average of 18 ± 8.6 mV shift in the energy of C=O stretching mode in three measured devices. It is very well known to experimental organic chemists that the frequency of the C=O stretching is very sensitive to the local chemical environment and this sensitivity is used to differentiate between functional groups (e.g., amine, acid, ester) containing the carbonyl (C=O) group.[31] These shifts in frequency are due to the polarization of the C=O bond induced by other chemically connected groups. Local electric fields (such as neighboring ions) can cause a similar shift in frequency. The experimentally observed shift of about 8% in the frequency of the C═O stretching mode in Fig. 3 can be caused by the strong local electric field in the vicinity of this bond. The change in polarity of bias voltage can cause orientational changes at one end of this molecule which contains the O–H and C═O bonds with respect to the neighboring electrode.[32] The O–H stretch is seen as a wider and bigger peak for positive bias while it becomes much smaller for negative bias. In return, the C═O stretch which is detected at +218 mV has shifted to higher energy (236 meV) and intensity when the polarity is reversed to negative.

Figure 4 displays the change in vibrational frequency of C═O bond in the presence of an electric field parallel to this bond computed for a simple model molecule (formaldehyde, H_2CO). In order to achieve the experimentally observed 8% shift in the frequency of C═O vibration, the local electric field should be about 18 V/nm. This field is about 150 times bigger than what one would expect to have between two planar electrodes separated by the length of the molecule (1.9 nm) with an applied voltage of 220 mV (the vibration energy of the C═O stretching). However, our experimental setup is made of two metallic tips rather than two parallel planes. The enhancement of local field for metallic tips in dc current has been extensively studied in the area of field electron emission and field-emission microscopy (FEM). Field enhancement factors depend on the tip geometries and can take values of several hundred in the case of a good emitter.[33] It is noteworthy that strong-field enhancement is unlikely to be present in other configurations used for IETS measurements such as crossed-wire[10] or microsphere[24] junctions.

In summary, single-molecule identification has been achieved by using IETS. Vibrational spectroscopy of single molecules using IETS can be used as a sensitive probe of conformational dynamics and local environment around the single molecule. We have been able to quantify the local electric field on specific single bonds of single molecules. This demonstrates that the IETS analysis can be extended into the fascinating domain of single-molecule study, where the single molecule acts as a probe of its local environment with unprecedented sensitivity. The ability to probe the effect of the local electric field quantitatively is very valuable as understanding the role of local electric field in a tunnel junction is one of the key elements of understanding charge transport in single-molecule junctions.

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