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Electrical conduction and structure of copper atomic junctions in the presence of water molecules

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We have investigated Cu atomic contacts in the presence of H_2O both experimentally and theoretically. The conductance measurements showed the formation of H_2O/Cu junctions with a fixed conductance value around 0.1 G_0 (G_0=2e^2/h). These structures were found to be stable and could be stretched over 0.5 nm, indicating the formation of an atomic or molecular chain. In agreement with the experimental findings, theoretical calculations revealed that the conductance of H_2O/Cu junctions decreases in stages as the junction is stretched, with the formation of a H_2O/Cu atomic chain with a conductance ca. 0.1 G_0 prior to junction rupture. Conversly,in the absence of H_2O, the conductance of the Cu junction remains close to 1 G_0 prior to junction rupture and abrupt conductance drop.

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Introduction

Nanoscale electronic devices in which a single atom, atomic chain or molecule is suspended between metal electrodes have been extensively studied both experimentally and theoretically due to their fundamental interest and potential application in nanoelectronics. [1] The aim is to miniaturize electronic devices by using a single molecule as an active electronic component. [2-4] The electronic properties of these nanostructures depend strongly on the atomic species involved and the contact geometries. In order to study the nature of atomic and molecular contacts and to advance in our understanding of atomic scale quantum transport, there have been numerous studies regarding single-molecule junctions using mechanically controllable break junctions (MCBJ) and scanning tunnelling microscopy (STM). Transistor, diode, and switching behaviours have been reported in recent years for single-molecule junctions. [5-9] However, it is still challenging to determine the detailed atomic structures of the single-molecule junctions, including the metal-molecule contact configuration and the structure of the metal electrode near the contact.[10, 11] This difficulties arise from the technical limitations regarding the characterization of single-molecule junctions with spectroscopic techniques.

Single-molecule junctions with simple and small molecules are the systems best suited for the investigation of the junction atomic structure, enabling the study of the relationship between the physical properties (*e.g.* conductance) and the atomic structure, because various advanced techniques can be applied to them. The H_2/Pt junction has been the most extensively studied system of this kind. [12-15] It was revealed that a single hydrogen molecule forms a bridge between Pt electrodes with its molecular long axis parallel to the junction axis, and its conductance is 1 G_0 (2e^2/h). The length analysis revealed that the single H_2/Pt junction can be stretched over 0.5 nm, forming an atomic chain. The formation of an atomic chain indicates that the single-molecule junction is highly stable in the presence of H_2 molecules. The stabilization of nano-junctions in the presence of molecules has also been reported for other systems, namely: H_2/Co, Ni, Pd; and O_2/Ag junctions. [16-21]

Single-molecule junctions of uncomplicated homonuclear diatomic molecules are becoming increasingly well understood. The next logic step is the study of small heteronuclear molecules. Here we focus on H_2O molecules. The H_2O molecule while still being a relatively small molecule, it plays an important role in many fields, such as: catalysis; corrosion; electrolysis; photosynthesis; and hydrogen fuel cells. To the best of our knowledge, H_2O single-molecule junctions have been studied only for Pt electrodes. [22] Tal *et al.* reported the crossover between enhancement and reduction of the conductance due to the electron-vibration interaction by measuring the H_2O/Pt junction with point contact spectroscopy (PCS) and inelastic tunnelling spectroscopy (IETS) at 4 K. [22] However, in that work the conductance histogram did

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not present a clear peak, and the atomic structure of the H_2O/Pt junction remains unclear. Fabrication of single-molecule junctions with a fixed conductance value is of outmost importance for development reliable single-molecule electronic devices. One of the possible reasons for the absence of a well-defined H_2O/Pt junction is a strong molecule-metal interaction. Various atomic configurations are possible for single-molecule junctions with strong molecule-metal interaction, leading to various conductance values. We have already reported that a moderate molecule-metal interaction is necessary to obtain single-molecule junctions with reproducible conductance values. [23]

In the present study, we investigated the less reactive Cu. While H_2O/Cu junctions have not been studied previously, the H_2O/Cu system is of great relevance due to the catalytic role of Cu in the water-gas-shift reaction, hydrolysis reaction, and other useful catalytic reactions. [22] The dissociation reaction and proton relay reaction were reported on Cu (110) surfaces studied with STM and first-principles calculations.[25,26] The dissociation reaction has been reported on Cu nano-particles and Cu single crystal surface at elevated temperature (> 600 K). [27, 28, 29] The H_2O dissociation does not proceed at low temperature. [30] Here we report experimental and theoretical studies of H_2O/Cu junctions. The experimental results obtained using MCBJ at l0 K reveal the formation of H_2O/Cu junctions with a stable conductance value around 0.1 G_0. The length analysis of the conductance-distance traces showed the formation of the atomic or molecular chain. Theoretical studies reveal that stretching of the Cu junction in the presence of H_2O results in the formation of a continuous Cu atomic chain bridging the junction with a H_2O molecule adsorbed to a bridging Cu atom. Prior to the formation of the chain the calculated conductance of the junction initially decreases gradually and then, as the chain begins to form, it drops abruptly to near 0.1 G_0. This behaviour closely resembles that experimentally observed for the H_2O/Cu junction. We therefore propose that the observed 0.1 G_0 conductance feature is due to the formation of a Cu atomic chain with an adsorbed H_2O molecule that backscatters electrons travelling along the chain, reducing the observed conductance of the H_2O/Cu chain to 0.1 G_0.

Experimental

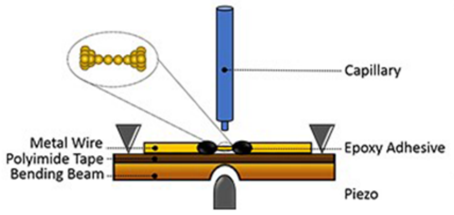

Fig. 1 Schematic image of the MCBJ setup.

Experiments were performed using a MCBJ technique at about 10 K in an ultrahigh vacuum (UHV) as in our previously reported study (Fig. 1). [16] A notched Cu wire (0.10 mm in diameter) was glued on the top of a phosphor bronze substrate covered with a polyimide tape. The substrate was mounted in a three-point bending configuration inside a custom-made vacuum chamber. After the chamber was evacuated, it was cooled down in a dewar filled with liquid helium. The notched part of the Cu wire was repeatedly broken by bending the substrate using piezo-controlled elements. Ultra-pure H_2O was placed in a glass container and it was purified by repeated cycles of freezing, pumping, and thawing. The H_2O molecules were introduced into the junction through a heated capillary during the breaking process. The DC two-point voltage-biased conductance measurements were performed by applying a bias voltage of 100 mV. The experiments were performed on 8 independent samples with Cu electrodes.

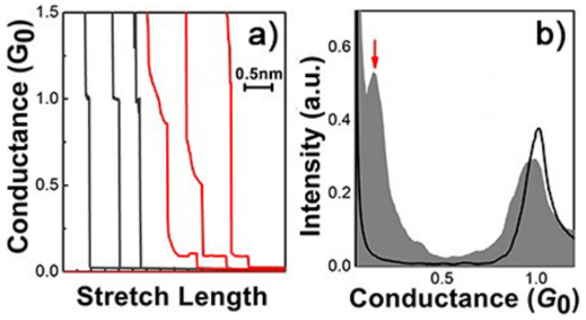

Fig. 2 (a) Typical conductance traces for Cu contacts before (black) and after (red) introduction of H_2O. (b) Conductance histograms for Cu contacts before (black solid line) and after introduction of H_2O (grey) introduction of water. The number of conductance traces was 1024 (before introduction of water), and 1078 (after introduction of water). The histograms were normalized to the number of traces. The bin size is 0.004 G_0.

Fig. 2(a) shows typical conductance traces obtained during the junction breaking process before and after the introduction of H_2O. The stretch length is defined as the displacement between the glued stems of the Cu electrodes. Before the introduction of H_2O, conductance plateaus appeared ca. 1 G_0, corresponding to the Cu atomic contact. [3] The length of the 1 G_0 plateau (<0.1 nm) was found to be shorter than that of the Cu-Cu interatomic distance (0.3 nm). This result confirms the previously reported inability of Cu to form atomic chains. [31, 32] After introduction of H_2O, additional conductance plateaus appeared around 0.1 G_0. It is noted that this 0.1 G_0 plateau could be extended over 0.3 nm. Since the Cu-Cu distance is 0.26 nm for bulk Cu, the present results indicate the formation of the atomic or molecular chain. Fig. 2(b) shows the conductance histogram constructed from more than 1000 conductance traces. The conductance histograms were normalized to the number of the conductance traces. Before the introduction of H_2O, a prominent peak appeared at 1 G_0, corresponding to a single Cu atomic contact. After the introduction of H_2O, an additional peak appeared ca. 0.1 G_0. Since the conductance of the contact depends on its atomic configuration, the appearance of this new peak indicates the formation of an atomic-scale contact with a well-defined atomic configuration. In addition, the 1 G_0 peak shifted to slightly lower conductance values compared to that of clean Cu contacts.

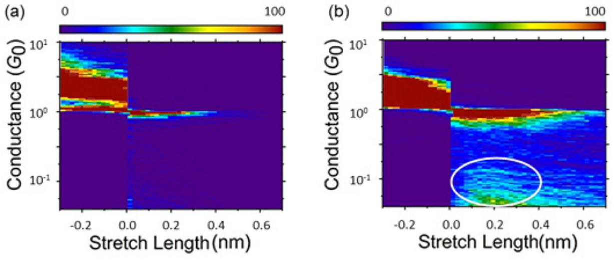

Fig. 3 The 2D conductance histograms for Cu contacts before (a) and after (b) introduction of H_2O. The histograms were constructed from 2020 (before introduction of H_2O) and 3179 traces (after introduction of H_2O).

Fig. 3 shows the two-dimensional conductance histograms constructed from more than two thousand conductance traces for Cu contacts before and after introduction of H_2O. These histograms were constructed by taking the first data point with a value of conductance lower than 1.2 G_0 as a relative zero distance z = 0, for each individual trace. Large counts were observed around 1 G_0 for both cases. After the introduction of H_2O, a surge in the number of counts was observed in the 0.1 G_0 region. The plateau in 0.1 G_0 region extended to about 0.3 nm, which is consistent with the previously discussed conductance trace (Fig. 2a).

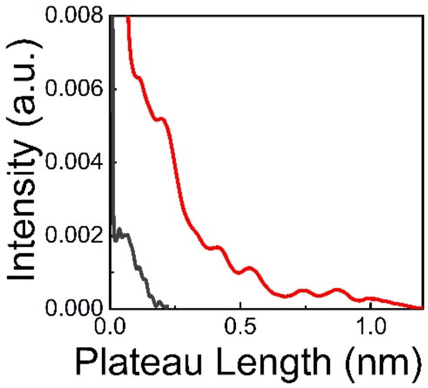

Fig. 4 The plateau length histogram for Cu junction in low conductance regime (0.4-0.04 G_0) before (black) and after (red) introduction of H_2O. The histograms were constructed from 2020 (before introduction of H_2O) and 3179 traces (after introduction of H_2O). The histograms were normalized to the number of traces. The bin size is 0.0012nm.

In order to evaluate the stability of the observed atomic chain at 0.1 G_0, the length of the conductance plateau was investigated for more than 2000 conductance traces (Fig. 4). The plateau length was defined as the distance between the points at which the conductance dropped below 0.4 G_0 and 0.04 G_0. Before exposition to H_2O, the contacts broke within 0.2 nm, with an average plateau length of 0.05 ± 0.01 nm. After the introduction of H_2O, the contact was extended over 0.5 nm with an increased average plateau length of 0.27 ± 0.01 nm. These results quantitatively indicate the formation of the atomic or molecular chain.

Here, we comment on the possibility of the dissociation of H_2O molecule on Cu atomic contacts. As previously discussed in the introductory part of this article, dissociation of H_2O on the surface of Cu occurs at elevated temperatures. The reactivity of a metal increases with a decrease in the coordination number. However, we consider that H_2O does not dissociate in the present experimental condition. Upon dissociation of H_2O on the surface of the Cu atomic contact, hydrogen and oxygen are present in the vicinity the contact. The conductance response of the Cu atomic contact in the presence of hydrogen has been studied at low temperatures (10 K). The conductance histogram shows a peak at 0.3 G_0.[33,] While our experimental findings are explained very well by the mechanism described above, we cannot completely rule out the possibility of an alternate mechanism in which copper oxide resulting from a chemical reaction between copper and water plays a role.

Theoretical studies

The experimental findings are explained below with using *ab initio* calculations [34] of the low energy geometries of atomic junctions consisting of two Cu clusters in the presence of H_2O molecules. A semi-empirical extended Hückel model of quantum chemistry [1,35] for the electronic structure that includes electrostatic potentials obtained from density functional theory (DFT), and Landauer theory-based transport calculations. [1]

Experimentally, single metal atom or atomic chain are formed by stretching a metallic junction close to its rupture point.[36-38] In order to simulate the stretching of the Cu junctions in our experiments, we carried out *ab initio* calculations to study the evolution of the structure as the junction was elongated by increasing the distance between the outer ends of two Cu clusters that were initially in direct contact with each other. Optimization of the stretched structures, formed from this fully relaxed initial structure, was carried out by systematically moving the leftmost and the rightmost Cu atoms further apart, freezing them and relaxing the positions of all the other atoms. We repeated this to obtain junction geometries with different distances between the outermost Cu atoms. All of the relaxations were carried out with the GAUSSIAN'09 package and the minimum energy configurations of the systems were found at the PBE1PBE functional and Lanl2DZ pseudopotentials and basis sets level.[34, 35, 39]

Since the behaviour of the electrical conductance, *G*, for atomic and molecular junctions under tensile stress can give a quantitative understanding of the system and clarify whether or not the junction breaks, we use the Landauer formula [1]

$$G(E_F) = G_0 \sum_{\alpha,\beta} |t_{\alpha\beta}(E_F)|^2 \frac{v_\alpha}{v_\beta} \qquad (1),$$

to calculate the zero bias conductance at the Fermi energy, E_F. Here $t_{\alpha\beta}$ is the electron transmission amplitude through the junction, β is the electronic state of a carrier that is coming from the left lead, and α is the electronic state of a carrier that is transmitted to the right lead. v_α and v_β are the velocities of the carriers in the right and left leads at the Fermi level.

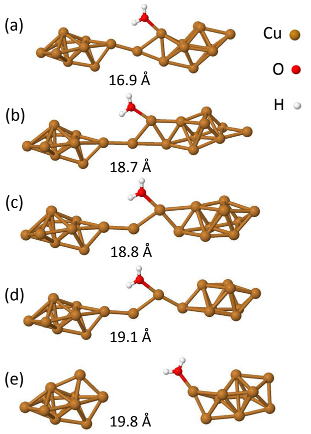

Fig. 5 Relaxed structures of a Cu junction with an adsorbed H_2O molecule for various distances between the outermost atoms of the Cu clusters. As the junction is stretched starting from structure (a), Cu-Cu bonds break in succession and a Cu atomic chain with an adsorbed H_2O molecule forms, as in (c) and (d). Upon further stretching, the Cu chain breaks, as in (e).

As in our previous work, [10,11,38,40-51] we couple the outer parts of the two Cu clusters to a large number of semi-infinite quasi-one-dimensional ideal leads that represent the macroscopic electron source and drain in the transport measurements. The transmission amplitudes $t_{\alpha\beta}$ are found by solving the Lippmann-Schwinger equation

$$|\psi^i\rangle = |\phi_0^i\rangle + g_0(E_F)W|\psi^i\rangle \qquad (2),$$

where $|\phi_0^i\rangle$ is an electron eigenstate of the i^{th} ideal semi-infinite one-dimensional left lead that is decoupled from the "extended molecule" that consists of the two Cu clusters and the H_2O molecule, $g_0(E_F)$ is the Green's function of the decoupled system of the ideal leads and the extended molecule, W is the coupling between the extended molecule and the ideal leads, and $|\psi^i\rangle$ is the scattering eigenstate of the complete coupled system associated with the incident electron state $|\phi_0^i\rangle$. The semi-empirical extended Hückel model [1] with the parameters of Ammeter *et al.* [35] which we have improved [43-45] by inclusion of atomic electrostatic potentials obtained from DFT calculations for each extended molecular structure was used to evaluate the Hamiltonian matrix elements and the atomic valence orbital overlaps that enter the Green's function in Eq. (2). Note that this methodology involves no fitting to any experimental data relating to transport in molecular junctions, as has been discussed in Refs. 1, 41 and 42. It is known to yield low bias conductance values in reasonably good agreement with experiments on Au atomic junctions and for a variety of molecules bridging Au electrodes [1,10,11,41,42,52-55] as well as molecules with silicon and tungsten electrodes. [43-45]

Some of the calculated geometries of our model Cu junction with an adsorbed H_2O molecule under tensile stress are shown in Fig. 5. In the present model, two 10-atom Cu clusters are initially bonded to each other with a H_2O molecule adsorbed to one of the clusters as the starting optimized geometry, shown in Fig. 5(a). We find stretching the junction to result in gradual deformation of its structure, punctuated by successive Cu-Cu bond breaking events. Representative calculated geometries at different stages of the stretching process are shown in Fig. 5 (b)-(e).

The behaviour shown in Fig. 5 differs qualitatively from that of Pt junctions stretched in the presence of H_2 molecules [12-15] and of Au junctions stretched in the presence of alkanedithiolate (ADT) molecules.[1] Specifically after the metal point contact in a stretched Pt/H_2 or Au/ADT junction has ruptured, a molecule is often suspended between the two electrodes. By contrast, when the Cu/H_2O junction is stretched, our calculations (see Fig. 6) do not exhibit evidence of a H_2O molecule bridging the Cu electrodes after the Cu chain between the Cu clusters has ruptured. Instead, our results indicate that the observed decrease in conductance is due to the bonding between a H_2O molecule and the metallic atomic chain bridging the two Cu electrodes, as shown in Fig. 5 (d). When the Cu atomic chain breaks, the H_2O molecule does not bridge the junction but bonds to only one of the Cu electrodes, as shown in Fig. 5(e).

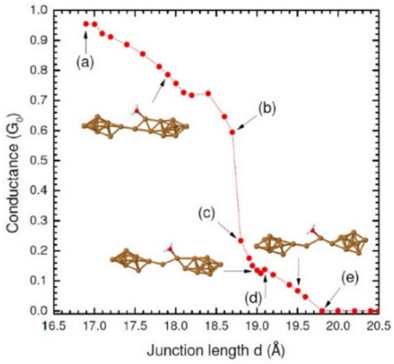

Fig. 6 Calculated conductance values at zero temperature of a Cu molecular junction with a H_2O molecule for different junction lengths. Red circles marked (a)-(e) show the conductance values of the structures in Figs. 5(a)-(e), respectively. The conductance values of intermediate structures obtained by stretching the junction starting from the geometry in Fig. 5(a) until the junction breaks (and beyond) are also shown.

Based on the formalism outlined above, the calculated conductance for each relaxed structure versus the junction length d is plotted in Fig. 6. When the molecular junction with an adsorbed H_2O molecule is stretched from d= 16.9 Å (Fig. 5(a)) to 18.7 Å (Fig. 5(b)), no bond breaking happens in the Cu clusters and the electrical conductance during this elongation, marked by (a) and (b) in Fig. 6, shows a gradual decline from 1 G_0 to 0.6 G_0. This is similar to the behaviour observed experimentally in some cases for Cu junctions exposed to H_2O; see the two leftmost red curves in Fig. 2(a). At d= 18.8 Å (Fig. 5(c)) a Cu-Cu bond breaks between the Cu atom at the tip of the right Cu cluster and one of its neighbours. This results in the junction's conductance drop by ~ 0.36 G_0 from (b) to (c) in Fig. 6. Very similar abrupt conductance drops were observed in our experiments as seen in the two leftmost red curves of Fig. 2(a). The conductance decreases somewhat on further stretching and G approaches ~ 0.12 G_0 at the 19.05 Å distance in Fig. 6. At d= 19.1 Å, shown in Fig. 5(d) and labelled (d) in Fig. 6, one more Cu-Cu bond breaks, the Cu atomic chain with the adsorbed H_2O molecule is fully formed, and, counterintuitively, the conductance increases slightly. This conductance increase may be attributed to the reorientation of the Cu atomic chain (Fig. 5(d)) between the two Cu clusters with the H_2O molecule located at the centre of the chain.

It is worth noting that although the conductance increase is small, this small conductance increase is in agreement with our previous work on Au-propanedithiolate-Au molecular junctions [31] which showed the conductance increase of that molecular wire under tensile stress to be due to changing bond angles at the molecule-electrode interfaces and structural changes in the Au electrodes. Similar small conductance increases at the ~ 0.1 G_0 plateau were observed in our experiments in some cases; see, for example, the leftmost red curve in Fig. 2a.

Upon further stretching of the junction from d= 19.1 to 19.6 Å, the conductance again decreases, while no Cu-Cu bond breaking happens. This conductance reduction happens due to the elongation of the junction and a slight increase in the O-Cu-Cu bond angle as a result. Lengthening of Cu-Cu bonds which weakens the orbital overlap between the two neighbouring Cu atoms in the vicinity of oxygen atom also contributes to the reduction of the conductance. At junction length d= 19.8 Å, the junction eventually breaks down resulting in the structure shown in Fig. 5(e). The adsorbed H_2O molecule is pulled back to its nearest Cu cluster and the conductance value becomes extremely small as labelled (e) in Fig. 6.

Based on the above, a possible explanation of the Cu junction experiments in the presence and absence of the H_2O is as follows: Initially there is no H_2O attached directly to the atomic Cu junction and the conductance is 1 G_0. When a H_2O molecule attaches, forming a structure such as that in Fig. 5(a) or 5(b), a gradual decline in the conductance from ~ 1 G_0 to a plateau around ~ 0.7 G_0 occurs in Fig. 6. The corresponding plateau in our experiment is located above ~ 0.5 G_0. Upon further stretching the structure changes (Fig. 5 (c)) and there is an abrupt conductance drop to the plateau at 0.1 G_0. Thus both our experimental and theoretical results show a sequence of plateaus: first, at 1 G_0; second, at an intermediate conductance value; and third, at 0.1 G_0. In some cases, our experiments signal another possibility where the H_2O molecule attaches directly to the Cu junction in a structure similar to Fig. 5(c) or 5(d), without going through the intermediate steps (Fig. 5(a) or 5(b)); therefore the conductance goes directly from 1 G_0 to values close to 0.1 G_0 as in the rightmost curve in Fig. 2(a).

As well as the Cu junctions with an adsorbed H_2O molecule that we have discussed above, we have also studied other related junctions theoretically. For Cu clusters not linked by a Cu atom or Cu atomic chain but instead bridged by a H_2O molecule, hydroxyl group or oxygen atom chemically bonded to both Cu clusters, we found very small junction conductance values, up to a few times 0.001 G_0. We therefore conclude that such molecular junctions are not relevant to the present experiments where the observed conductance values prior to rupture of the junction were larger by 2 orders of magnitude.

Here, we propose a possible reason why only one preferred structure was formed for the H_2O/Cu system in contrast to the H_2O/Pt system. [22] The interaction between the H_2O molecule and Pt is stronger than for Cu, which is supported by the binding energy of H_2O to Cu (111) and Pt (111) surfaces. [56] When the interaction between a molecule and metal contact is strong, various kind of contacts with different atomic configurations can be formed. Since the conductance of the contact depends on its atomic structure, the contact would show various conductance values. By contrast, when the interaction between a molecule and metal contact is weak, only the most energetically stable structure could be formed, which leads to formation of the contact showing a fixed conductance value. Other meta-stable structures would immediately break. Next, we discuss the stabilization mechanism of the H_2O/Cu junctions. Through our experimental and theoretical studies, it is revealed that the hydrated Cu junctions showing a conductance value of 0.1 G_0 were highly stabilized and an atomic chain was formed. This stabilization could be explained by the reduction of the surface energy. The H_2O molecules should adsorb on the chain and the stem part of the Cu electrodes. The adsorbed molecules reduce the surface energy of the metal contacts, leading to the stabilization of the contact. [57, 58] The adsorbed H_2O molecules would also act as scattering centres of the conduction electrons in the Cu atomic contact. Therefore, the conductance of the 1 G_0 peak was decreased by the adsorbed H_2O molecules, as shown in Fig. 2(b).

Conclusions

We have studied the effects of mechanical stretching on the conductance of Cu nano-junctions in the presence H_2O molecules both experimentally and theoretically. The conductance of Cu nano-junctions was found to decrease in stages from near 1G_0 upon elongation, exhibiting a stable conductance plateau near 0.1 G_0 before the junction rupture. Based on *ab initio* density functional theory and a semi-empirical methods, we have demonstrated theoretically that the adsorption of a single H_2O molecule on the junction and ultimately to a Cu atomic chain bridging nano-junction can account for the observed behaviour. Our results demonstrate that the conductance values of molecular junctions using Cu electrodes are sensitive to the presence of an aqueous environment. This behaviour may be of relevance in the development of Cu based mechanical nano-switches.

Acknowledgements

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