

# Atomic probes: a search for conduction through a single molecule\*

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**Abstract.** We present a novel approach in an effort to perform electrical measurements at the level of a single molecule. A mechanical controllable break junction is utilized in combination with a molecular deposition technique in fluid to obtain the system: metal-molecule-metal. The  $I-V$  curve of this system shows pronounced features over a large voltage scale.

Small is beautiful. This is not a meaningless phrase in contemporary solid state physics. When macroscopic meets microscopic interesting new physics is expected to be revealed. Here, by macroscopic we mean a structure which is connected to the outside world, i.e. the measurement equipment. The microscopic can be a molecule or even a single atom. It is a structure provided by nature which forms a well defined building block, which shape does not suffer from small atomic size irreproducibilities as encountered in macroscopic structures. By macroscopic we usually think of structures that are fabricated in high tech laboratories using e-beam lithography or advanced etching techniques. However, also belonging to this class are the STM or two atomically sharp electrodes positioned opposite to each other with an adjustable gap in between. In order for the macroscopic to meet the microscopic it should be fabricated in such a way as to allow for a microscopic building block to fit in. An adjustable gap between two electrodes may prove advantageous, since in this case the macroscopic structure can be adjusted to fit the microscopic building block.

In this paper we address the difficulties associated with the experiment of how to connect two electrodes to a single molecule. In relation with this we describe the mechanically controllable break (MCB) junction, which is used in an effort to obtain conduction through a single phenyl ring.

The term molecular electronics has been used in the past decades for numerous ill defined topics. Without underestimating the importance of bulk molecular

properties such as dopants in between molecular chains, interchain hopping and light emissions from molecular systems, nowadays molecular electronics is often associated with the conducting properties at the level of a single molecule. Although tunnel conduction through single atoms and molecules has been measured [1] this is not conduction in the sense that the molecules are bound to both electrodes. The reason for the difficulties in the experimental situation is that no general technique is available allowing the fabrication of a long term stable gap with a tolerance of the order of one Ångström, where the microscopic building block fits in. Suppose we evaporate two electrodes separated by a small gap ( $\sim 100$  Å) extending over the entire width. From a macroscopic viewpoint this gap may look isotropic over the width of the electrode. From a microscopic viewpoint, however, the electrodes are rough on the atomic scale and somewhere along the width there are two well defined atoms on opposite electrodes which are nearest. The distance between these two atoms constitutes the smallest gap distance. With e-beam lithography it is possible to fabricate gaps as small as 100 Å [2] with a tolerance at best of tens of Ångströms. It is certainly possible to produce molecules as long as 100 Å [3], but since the tolerance of the gap is relatively large, the smallest gap distance between the electrodes will either be larger than 100 Å which prohibits spanning by a molecule, or it will be smaller resulting in a number of molecules spanning the gap. This example shows the necessity of making gaps where the smallest gap size is *exactly* the size of the molecule if one wants to perform measurements on a single molecule.

It seems logical to perform the experiment with a STM. The STM has the advantage over fixed electrode structures that the gap between two electrodes can be adjusted. Just

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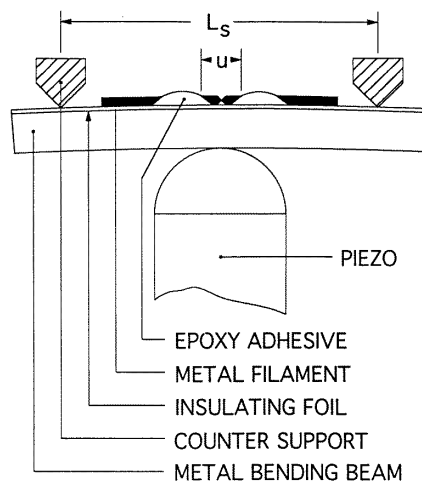
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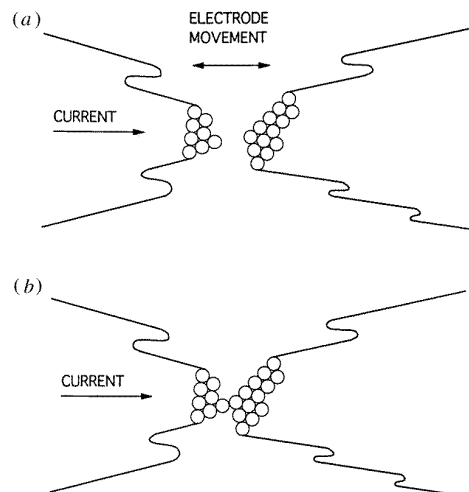
as in the above mentioned case the STM consists of two electrodes separated by a gap. Due to the exponential dependence of the tunnel current on the gap distance, the majority of tunneling takes place between two nearest atoms on opposite electrodes, which is the reason of the atomic resolution of the microscope. However, a STM is designed to operate in a feedback loop. It can be used to obtain  $I-V$  curves after switching off the feedback loop but this is usually done in a short time period because the electrodes become susceptible to temperature drift and vibrations (especially in ambient conditions).

A complementary technique to the STM, which could be used to obtain a stable metal-molecule-metal structure, is the MCB technique [4]. Part of the research program at Yale is focused on the use of an inherently stable MCB junction to provide the stable electrodes and the adjustable gap capability. The MCB junction is schematically indicated in figure 1. A metal wire is glued on a bending beam in such a way that the central notched part remains unglued. By means of a coarse adjustment (using an electromotor) a piezo is directed towards the bending beam. This results in a strain in the bending beam and consequently in an elongation of the unglued section  $u$ . This elongation is concentrated at the notched part, and will at some point result in the fracture of the metal filament. Once this is achieved the motor direction is reversed until a contact is re-established. From this point onward a voltage on the piezo is used for fine adjustment of the coupling between the two freshly broken electrodes. Due to the sample geometry the mechanical stability of the electrodes is guaranteed. There is a reduction factor imposed by the sample geometry; a piezo length change results in an electrode displacement of approximately 100–1000 times smaller. This large reduction factor and the small loop (the total length of electrode-glass contact-bending beam-glass contact-electrode path) results in two electrodes which are inherently stable with respect to each other. The reduction factor is also the reason that the MCB junction is less susceptible to temperature drift and vibrations since these amplitudes are also reduced. With the use of the piezo a long term stable gap of arbitrary size between two atoms can be adjusted, schematically drawn in figure 2(a), which again is due to the roughness of the electrodes on an atomic scale. This roughness is also responsible for the possibility of obtaining a long term stable single atom point contact, see figure 2(b), which is already established experimentally [5]. In a sense the single atom contact is the ultimate device where macroscopic meets microscopic, since two (macroscopic) electrodes are connected to a single (microscopic) atom. The atoms of the electrodes are the same as the microscopic building block but nevertheless it has been shown that electrical experiments can be performed on a single atom and that a pressure or tensile force can be applied on this atom by using the piezo element [6]. Our research goal is simply to replace the single atom in figure 2(b) by a molecule. In order to obtain conduction through this molecule it should be strongly chemically bound to each of the two electrodes.

The molecule used in the experiments, 1, 4-phenyldithiol, is shown in figure 3. The parathiol endgroups

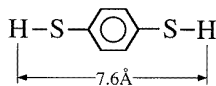


**Figure 1.** The sample mounting in a three point bending configuration. The bending beam consists of flexible phosphorus bronze covered with an insulating layer of capton. The junction is formed by breaking the electrode material. This is achieved by bending the beam, the elongation of the unglued section,  $u$ , is concentrated on the notch and will result in a fracture of the material. A voltage on the piezo element is used for fine adjustment of the coupling between the two electrodes. The distance between the counter supports,  $L_s$ , measures 20 mm.

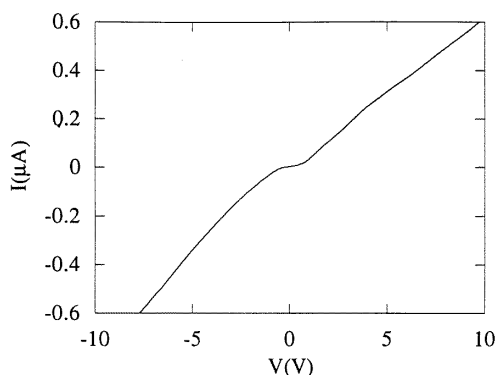


**Figure 2.** (a) the MCB junction in the tunnel regime. Tunneling will occur between two nearest atoms on opposite electrodes. Because the electrodes are rough on an atomic scale, there exists only one single point where tunneling occurs. (b) when the electrodes are moved closer together, at some point they will form a stable single atom point contact (this is already experimentally established [5, 6]).

on the phenyl ring are known to adhere selectively to gold surfaces and furthermore, aromatic thiols are known to be unstable in an oxygen environment. In order to perform the molecular deposition on the freshly broken electrodes a liquid MCB cell has been designed. It consists of the sample mounting shown in figure 1 with a small glass tube glued vertically, centered with one opening around the notched unglued section, on top of the bending beam. With this set-up the deposition can be performed inside the tube



**Figure 3.** 1, 4-phenyldithiol, the molecule which we have used in the molecular deposition experiments.

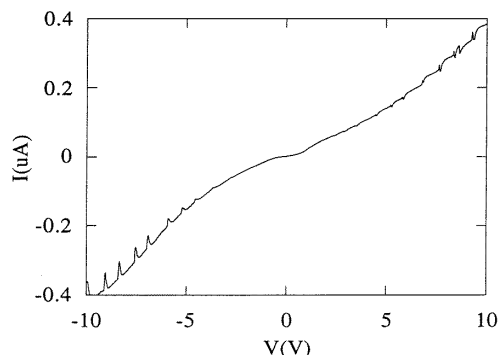


**Figure 4.** The  $I-V$  curve obtained with the electrodes far apart and immersed in the solution.

containing a solvent, tetra-hydro-furane (THF), in which the molecules are dissolved. The electrodes are formed within this solution and since the thiol groups adhere strongly to gold all gold surfaces inside the tube, including the freshly broken areas, will be covered with molecules.

In figure 4 an  $I-V$  curve is shown of the junction in the liquid cell, where deposition has taken place and the electrodes are still in solution, spaced far apart. The shape and also the scale of the  $I-V$  curve are approximately the same for different samples as well as for various distances between the electrodes in the liquid. We expect that some kind of ionic conduction process is responsible for this conduction since it is independent of electrode separation. After this deposition the electrodes are brought closer together until a metallic contact (figure 2(b)) is formed. Although we lack the exponential dependence of the conductance on the electrode distance (so we do not know how far the electrodes are apart) there exists a clear transition point when a single atom contact is reached. In general a one atom point contact has a resistance of approximately  $h/2e^2 \simeq 13 \text{ k}\Omega$  [5, 6]. This resistance value can be reached in the fluid cell, however, after breaking a one atom contact in the solution, curves similar to the one in figure 4 are always measured.

After the initial formation of the electrodes in the fluid cell the junction was fine adjusted by carefully increasing the piezo voltage, thus, going from metallic contact to separated electrodes. When the jump from the  $\simeq 13 \text{ k}\Omega$  point contact to separated electrodes occurs the piezo voltage is fixed and the solution is evaporated. Over a 15 min period we were able to measure  $I-V$  curves like the one presented in figure 5. The curve was recorded by sweeping the voltage from  $-10 \text{ V}$  to  $10 \text{ V}$  in 5 min. Pronounced features appear in the  $I-V$  curve at voltage values which differ a small amount from curve to curve. We believe that this  $I-V$  curve reveals the conduction through a single molecule and that the features find their origin in the phenyl ring system and the strength of the



**Figure 5.** An  $I-V$  curve after carefully adjusting the electrodes and evaporating the solvent. Regularly spaced features appear in the characteristic. We believe that this  $I-V$  curve reveals conduction through one single molecule, which is connected via its opposite endgroups to the gold electrodes. Note that the resistance in this case is higher than the resistance of the separated junction in figure 4.

coupling of the ring to the electrodes [7]. The curve is not perfectly symmetric around zero, in addition the number of features differs for positive and negative bias. Also the features have different shapes for positive and negative bias. Nevertheless, we think that these ‘imperfections’ can be accounted for by a different coupling to the molecule, which may occur due to drift and/or changes in the chemical environment of the electrodes in the vicinity of the bridged junction.

In conclusion, we have used the MCB junction at ambient conditions as a tool to search for conduction through one phenyl ring coupled to two electrodes. We observed pronounced oscillations in the resistance as a function of voltage, which are tentatively attributed to quantum interference effects in the phenyl ring and its coupling to the electrodes.

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