Contacting individual molecules using mechanically controllable break junctions

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Abstract. Among the experimental techniques employed in contacting individual molecules Mechanically Controllable Break Junctions are being frequently used. Some of the advantages are (1) straight-forward preparation of clean surfaces for anchoring the molecule; (2) the possibility to produce many different single-molecule junctions in one experiment, allowing obtaining statistical averages; (3) adapting the electrode gap to the molecules' length; (4) control over the mechanical stress of the molecule. We briefly review results obtained on organic molecules anchored to gold electrodes by thiol groups, both at room temperature and at cryogenic temperatures, and experiments on simple molecules chemisorbed to platinum electrodes.

1. Introduction

For studying the electronic transport through individual molecules, several experimental techniques, including scanning tunnelling microscopy (STM) [1], conducting atomic force microscopy (CAFM) [2] or microfabricated electrodes provided by different schemes have been considered [3, 4, 5]. Here we will focus on experiments employing Mechanically Controllable Break Junctions (MCBJ), which have a number of attractive features compared to the other methods used.

In STM and CAFM a certain quantity of the molecular compound under investigation is deposited onto a conducting surface. By varying the substrate material the interaction strength between the molecule and the surface can be tailored, which has been shown to be crucial for the interpretation of the electronic properties of the system [6, 7]. However, for a given substrate, the configuration of the molecule cannot be altered in a controlled manner. Since in those measurements the scanning probe is usually kept at a distance to the molecules, no chemical bond is formed between the molecule and the tip, giving rise to a strongly asymmetric configuration of the electrochemical potentials of the system. When the amount of the deposited molecule is varied, interaction and self organization effects between the molecules can be studied [8, 9]. With high-speed

STM the diffusion of molecules on surfaces was investigated even in real time [9, 10]. However, these methods usually require intensive cleaning procedures and ultrahigh vacuum techniques (UHV) in order to obtain reproducible conditions. Furthermore, scanning tunnelling spectroscopy at room temperature has a limited energy resolution in the range of 100 mV and changing external parameters as e.g. temperature or magnetic field give rise to position drifts that hamper the systematic study of an individual molecule. One of the main advantages of is the fact that the actual configuration can be manipulated atom by atom or molecule by molecule [11] and monitored with atomic or even subatomic resolution [12]. Recently, a STM arranged logical device, consisting of about 300 CO molecules on a copper surface has been demonstrated [13]. The relatively complicated and expensive setup can be regarded, however, as a crucial drawback of STM and CAFM. Therefore, for defining devices for a possible use in nanoelectronics, direct and scalable electrodes that are separated by the typical size of the object under study are desirable.

With standard electron-beam lithography, electrode pairs with spacings below approximately 20 nm are difficult to define reproducibly. Therefore, several alternative methods, including electromigration methods [3] or electro-deposition [14], have been proposed and used successfully for special applications. For the study of the electronic properties of small ensembles of molecules, different techniques using self assembled monolayers and shadow evaporated, electron-beam defined electrodes have been used [15]. However, the success rate for these methods is usually rather low and the deposition of metal on top of a layer of molecules risks inducing uncontrolled chemical modifications. Another drawback of using electrodes that are fixed on a substrate is the lack of flexibility, concerning the contact configuration once the molecule or molecules of interest have been contacted.

A gap-width in the order of nanometers between two metal electrodes is easily adjusted mechanically by exploiting the MCBJ technique, which will be discussed in more detail below. It relies on mechanically breaking a metal wire, thus exposing clean fracture surfaces. This circumvents the problem of UHV surface preparation necessary in STM-type of experiments. The two wire ends are mounted on a bendable substrate at close proximity, so that the distance can be repeatedly adjusted by mechanically controlling the bending of the substrate and the junction is rather insensitive to the influence of external vibrations since both wire ends are fixed to the same substrate. The fresh fracture surfaces can then be exposed to the molecules of interest and the junction can be repeatedly opened and closed to search for characteristic conductance levels associated with a molecular bridge.

Once a molecular junction has been established, this junction may be stressed or deformed mechanically, resulting in different configurations and thus different electronic properties. Due to the small dimensions of the experimental device, the stability of the molecular junction is sufficient to allow investigating the same junction on a time scale that permits the systematic variation of control parameters such as temperature or magnetic field. Contacts can be opened and closed to large contacts repeatedly in the

Figure 1. (a) Schematic top and side view of the mounting of a MCBJ, having a notched wire (1), two fixed counter supports (2), a bending beam (3), two drops of epoxy adhesive (4), and a pushing rod consisting of stacked piezo element (5). (b) Electron micrograph of a lithographically fabricated MCBJ made of Co with a metal thickness of 150 nm.

presence of the molecules of interest, thus allowing to gather statistical information on a certain molecular species. When necessary, by applying high voltage pulses to the electrodes they can even be cleaned and can be re-used for the same study without replacing the device. On the other hand, obvious drawbacks of the existing techniques are the lack of information of the atomic scale configuration of the junction and the fact that both electrodes are necessarily made of the same metal. Although in principle lithographically fabricated MCBJ devices can be incorporated into more complex electronic circuits, the mechanical control setup is rather large and does not easily allow the independent control of more than one junction. Thus, the MCBJ technique, although very useful for investigating fundamental properties of the electronic transport on the molecular scale, might be less appropriate for the fabrication of highly integrated molecular electronics devices. For the realization of molecular field effect transistors a third electrode controlling the electrostatic potential of the molecule is required, and has recently been achieved with MCBJ in combination with breaking by electromigration [16].

2. Experimental techniques

2.1. Fabrication of the electrodes

In a seminal experiment by Reed *et al* [17], it has been demonstrated that molecules can be contacted by MCBJ [18, 19, 20]. Since then, different variations of MCBJ have been developed and used for this purpose [21, 22, 23, 24, 25]. The MCBJ technique was first proposed by Moreland and Ekin [18] for the fabrication of tunable tunnel junctions. Later the method has been refined and used for the investigation of stable single-atom contacts [19]. The principle of a MCBJ is shown in Fig. 1a. It consists of a wire with a manually fabricated constriction having a cross section of the order a few tens of

micrometers. The wire is glued on both sides of the constriction to a flexible substrate, which is mounted on a three-point bending mechanism consisting of a pushing rod and two counter supports. By bending of the substrate with the help of a piezo drive, the wire is elongated such that the mechanical stress is concentrated in the constriction area. In the last stages of the elongation the lateral size of the constriction is gradually reduced to the size of a few atoms until it eventually breaks forming two separated electrodes. By controllably relaxing the bending of the substrate, the contact between them can be re-established. As a result of the chosen geometry the setup itself acts as a reduction gear for the motion of the pushing rod with respect to the resulting relative displacement of the two electrodes. The reduction ratio is given by

$$r = \frac{\delta u}{\delta x} = \frac{6tu}{l^2} \quad (1)$$

where δu denotes the change of the electrode separation u when moving the pushing rod by δx (vertically in Fig. 1a). Since the substrate thickness t and the distance L of the counter supports cannot be easily varied over a wide range, the separation u between the anchor points of the bridge arms (i.e. the distance of the glue drops) controls the reduction ratio r . As this distance has a lower bound of a few tens of micrometers with the technique just described, a microfabricated version of the MCBJ technique has been put forward [20, 26]. An electron micrograph of such a lithographic MCBJ is given in Fig. 1b. By electron beam lithography a metallic nanowire is patterned, having a width of about 100 nm and a similar thickness, onto a flexible metallic substrate covered with an insulating sacrificial layer. The sacrificial layer is then partially removed by dry etching in order to suspend the nanobridge over a length of approximately 2 μm . By virtue of the small length of the bridge the displacement ratio is of order 10^{-4} . In general, the displacement of the pushing rod that can be achieved with a piezo element corresponds to an electrode gap variation of ≈ 0.1 nm, in particular in low-temperature applications. The adjustment of the contact is therefore achieved by a purely mechanical drive. The stability of the atomic-sized contacts or molecular junctions formed with these devices has a higher stability than with the conventional MCBJ because external mechanical perturbations are reduced by the same displacement ratio. The main drawbacks of the use of a mechanical drive lie in the fact that mechanical systems have a larger backlash (hysteresis), are slower, and their motion may lead to some heat generation. Furthermore, a mechanical drive rod needs to be installed that may give rise to additional heat load on low-temperature measurements. Nevertheless, the lithographic MCBJs have shown to be very useful for the formation and investigation of molecular junctions since they allow to fabricate particularly stable electrodes. The long-time stability can be estimated by recording the resistance of a clean metallic bridge when it is broken to form a tunnel junction. Taking the bulk value for the work function Φ of the metal and using the relation

$$R_T \propto \exp\left[\frac{2}{\hbar}\sqrt{2m^*\Phi} \cdot d\right] \quad (2)$$

for the tunnelling resistance R_T , where m^* is the electron effective mass, a value for the increment in the distance d between the electrodes can be obtained from a measurement of the change in resistance. We find that the stability at ambient conditions has a typical value of 250 pm (standard deviation averaged over 24 h) and achieves values of less than 1 pm at low temperature.

Thus, the MCBJ technique provides a simple method to prepare atomically spaced, clean and tunable pairs of electrodes. By controlling the distance of the electrodes they can be adapted to different sizes of molecules. Since both electrodes are of the same material and dimensions, symmetric contacting of the molecule is possible. By suitable choice of the electrode material and molecule, strong chemical bonds without extrinsic tunnel barriers are obtained. Depending on the nature of the molecule of interest, different techniques are used to deposit the molecules and to establish the contact between the electrodes and the molecules.

2.2. Deposition of molecules

For the investigation of the transport through small molecules such as hydrogen, acetylene, carbon monoxide, or others presented in section 3, a standard "notched-wire" MCBJ is broken at low temperature, i.e. under cryogenic UHV conditions. Platinum is chosen as electrode material for several reasons. First, it strongly chemisorbs some interesting small molecules. Secondly, due to its electronic properties, it is possible to detect unambiguously the presence of the molecules (see below.) A small amount of the gaseous molecules, which is controlled by controlling the pressure in a small reservoir, is then inserted into the vacuum of the sample space. Only hydrogen has a finite vapor pressure at the desired measuring temperature that, for reasons of stability, spectroscopic resolution, and vacuum conditions, is kept at 4.2 K. For other substances the gasses were admitted through a capillary that can be temporarily heated by a resistive wire running all the way down its interior. Because of the large temperature gradient between the gas inlet at room temperature and the electrodes at low temperature, the amount of deposited gas molecules arriving on the electrodes is difficult to quantify. However, an amount of $\approx 5 \mu\text{mole}$ has been shown to be suitable for the experiments described below. After the addition of the molecules the system is allowed to equilibrate for about one hour before the electronic measurements are started.

For the investigation of larger conjugated molecules, usually gold electrodes are employed because the molecules can be terminated by thiol groups that allow to establish a strong chemical bond to gold. This requires some wet chemistry at room temperatures. The first series of experiments were limited to room temperature [17, 21, 22], but procedures for low-temperature experiments have recently been established [27]. Once the MCBJ has been mounted onto the mechanical bending gear and measuring leads have been attached to the two ends of the junction, the electrodes are broken under ambient conditions to a distance of about 5 nm. A droplet of a solution containing a distinct concentration of the molecules is deposited onto an opened lithographic

MCBJ. After a certain reaction time the molecules that did not establish a chemical bond are washed away by the addition of the pure solvent and a subsequent cleaning and drying procedure. After these steps the device is brought into high vacuum and room-temperature measurements can be performed immediately. For low-temperature measurements, particular care has to be taken to avoid insulating barriers e.g. due to ice formation. Furthermore, a single-molecule junction adjusted at room temperature cannot be held fixed during the cool-down procedure due to the difference in thermal contraction of the various construction materials used in the setup. In order to prevent the molecular bridge from contaminating, the MCBJ junction is closed thoroughly and opened again repeatedly before cool-down. Since the chemical bond between the thiol endgroups and the gold atoms of the electrodes is stronger than the gold-gold bonds within the outermost planes of the electrodes, the junction is expected to break within the electrodes themselves upon elongation. The result is that the molecules are attached with one thiol end to one of the electrodes, while the other thiol end is capped by a small gold cluster. After these preparations, the setup is cooled down to the desired measuring temperature that is usually about 30 K, or below. The gold electrodes and clusters are expected to remain fairly clean and a cold weld of the cluster cap to the other electrode can be made by bringing the electrodes closer together.

It is also possible to deposit molecules by thermal evaporation, as was recently done for fullerene molecules (C_{60}) [24]. A lithographic gold break junction (electrically connected to the measuring circuit) is broken at room temperature under high vacuum conditions $p \simeq 10^{-8}$ mbar to a distance of approximately 2-3 nm. The fullerenes are evaporated from a tungsten boat and the deposition is controlled by a quartz crystal. When half a monolayer is deposited, the evaporation is stopped and the bridge is closed. The fullerene molecules, which presumably land at the surface, are attracted into the gap both by diffusion and by dielectrophoresis, when a voltage is applied to the electrodes.

2.3. Measurement techniques

One of the main advantages of the MCBJ technique is the possibility to manipulate the molecular junctions and to modify the measuring configuration. Depending on the system under study, different characterization procedures for the electrodes and for the junctions are performed that are described in sections 3 and 4, respectively. Here, we mention briefly the electronics for the setups.

The typical resistances of molecular junctions range from a few $k\Omega$ up to several $G\Omega$. Since most organic molecules present a large gap between filled and empty molecular orbitals, the current-voltage characteristics (IV) are often nonlinear, with differential resistances up to $T\Omega$ at low bias. In this resistance range it is advantageous to source a voltage and to measure the resulting current. This is either performed by a commercial automatic source-measure unit that allows to apply bias voltages from a few μV up to 10 V and to record currents from a few fA up to mA. The differential conductance can then be calculated numerically from the IV. However, for detecting small variations of

the differential conductance as described in section 3 it is advantageous to measure directly the differential conductance dI/dV by a lock-in technique. The absolute accuracy of the determination of the linear resistance is of the order of 1%, while relative changes down to 10^{-5} can be detected. However, two problems should be mentioned: First, usually this precision is not achieved at room temperature due to fluctuations of the junctions. Second, such measurements are slow compared to the relatively fast IV recording and may exceed the lifetime of the junction. In particular at high bias voltage ($V \sim 1V$) and at room temperature, the junction may be altered during the measurement.

When measurements of the conductance as a function of the inter-electrode distance are performed, e.g. for the recording of conductance histograms or the study of individual so-called opening or closing curves, a constant dc-bias voltage is applied, the current is recorded and the position of the electrodes is controlled by ramping the piezo voltage or running the motor linearly with a certain turning speed.

3. Simple molecules

The early experiments aimed at probing the electronic transport properties of individual organic molecules have shown that it is difficult to identify the number of molecules actually contacted and that the characteristics observed vary widely between experiments. Under such conditions it is not surprising that there is also very little agreement with calculations. This situation forms a strong motivation to study simple systems, that by themselves will not be useful as molecular devices, but that may provide a more viable test system to identify the problems in experiment and theory. The simplest molecule is dihydrogen, which has been shown can be contacted between platinum electrodes [23]. The discussion of the hydrogen experiments will occupy most of this section. Towards the end experiments on slightly more complex molecules will be presented briefly.

Smit *et al* [23] obtained molecular junctions of a hydrogen molecule between platinum leads by the method outlined in the previous section. The inset to Fig. 2 shows a conductance curve for clean Pt (black) at 4.2 K, before admitting H_2 gas into the system. About 10,000 similar curves were used to build the conductance histogram shown in the main panel (black, normalized by the area). After introducing hydrogen gas the conductance curves were observed to change qualitatively as illustrated by the gray curve in the inset. The dramatic change is most clearly brought out by the conductance histogram (gray, hatched).

Clean Pt contacts show a typical conductance of $1.5 \pm 0.2 G_0$ for a single-atom contact[‡], as can be inferred from the position and width of the first peak in the Pt conductance histogram. Below $1 G_0$ very few data points are recorded, since Pt contacts tend to show an abrupt jump from the one-atom contact value into the tunnelling regime towards tunnel conductance values well below $0.1 G_0$. In contrast, after admitting

[‡] $G_0 = 2e^2/h$ is the quantum unit of conductance

Figure 2. Conductance curves and histograms for clean Pt, and Pt in a H₂ atmosphere. The curves for Pt in the inset and the histogram in the main panel were measured at a bias of 10 mV. The curve for Pt with H₂ in the inset was measured at 100 mV, and the histogram was obtained at 140 mV. All data were taken at 4.2 K under cryogenic vacuum. From Ref. [23]

hydrogen gas a lot of structure is found in the entire range below $1.5 G_0$, including a pronounced peak in the histogram near $1 G_0$. The research to date on this system has been focussed on the molecular arrangement responsible for this sharp peak. Clearly, many other junction configurations can be at the origin of the large density of data points at a lower conductance, but they have not yet been studied in detail.

The interpretation of the peak at $1 G_0$ was obtained from combination of measurements, including vibration spectroscopy and the analysis of conductance fluctuations, and Density Functional Theory (DFT) calculations. Experimentally, the vibration modes of the molecular structure were investigated by exploiting the principle of point contact spectroscopy for contacts adjusted to sit on a plateau in the conductance near $1 G_0$. The principle of point contact spectroscopy is similar to inelastic tunnelling spectroscopy (IETS, cf. chapter 10), but differs somewhat in a few important details. As for IETS, the differential conductance is measured using a small modulation superimposed on a dc bias that is slowly swept over a wide voltage range. When the bias increases from 0 and crosses a voltage corresponding to the energy of a vibration mode in the contact, $eV = \hbar\omega$, a new channel for electron scattering opens. For an ideal one-channel contact the only option is backscattering since all forward propagating states are occupied. Thus, in contrast to IETS, to first approximation scattering by vibration modes leads to a drop in the conductance.

Figure 3 shows examples for Pt-H₂ and Pt-D₂ junctions at a plateau near $1 G_0$. The conductance is seen to drop by about 1 or 2%, symmetrically at positive and negative bias, as expected for electron-phonon scattering. The energies are in the range 50–60 meV, well above the Debye energy of ~ 20 meV for Pt metal. A high energy for a vibration mode implies that a light element is involved, since the frequency is given by

Figure 3. Differential conductance curve for a molecule of D_2 contacted by Pt leads. The dI/dV curve (top) was recorded over 1 minute, using a standard lock-in technique with a voltage bias modulation of 1 meV at a frequency of 700Hz. The lower curve shows the numerically obtained derivative. The spectrum for H_2 in the inset shows two phonon energies, at 48 and 62 meV. All spectra show some, usually weak, anomalies near zero bias that can be partly due to excitation of modes in the Pt leads, partly due to two-level systems near the contact. From Ref. [28].

$\omega = \sqrt{\kappa/M}$ with κ an effective spring constant and M the mass of the vibrating object. The proof that the spectral features are indeed associated with hydrogen vibration modes comes from further experiments where H_2 was substituted by the heavier isotopes D_2 and HD . The positions of the peaks in the spectra of d^2I/dV^2 vary within some range between measurements on different junctions, which can be attributed to variations in the atomic geometry of the leads to which the molecules bind. Figure 4 shows histograms for the vibration modes observed in a large number of spectra for each of the three isotopes.

Two pronounced peaks are observed in each of the distributions, that scale approximately as the square root of the mass of the molecules, as expected. The two modes can often be observed together, as in the inset to Fig. 3. For D_2 an additional mode appears near 90 meV. This mode cannot easily be observed for the other two isotopes, since the lighter HD and H_2 mass shifts the mode above 100 meV where the junctions become very unstable. For a given junction with spectra as in Fig. 3 it is often possible to stretch the contact and follow the evolution of the vibration modes. The frequencies for the two lower modes were seen to increase with stretching, while the high mode for D_2 is seen to shift downward. This unambiguously identifies the lower two modes as transverse modes and the higher one as a longitudinal mode for the molecule. This interpretation agrees nearly quantitatively with DFT calculations for a configuration of a Pt-H-H-Pt bridge in between Pt pyramidally shaped leads [28, 29]. The conductance obtained in the DFT calculations [23, 28, 29] also reproduces the value of nearly $1 G_0$ for this configuration. The number of conduction channels found in the

Figure 4. Distribution of vibration mode energies observed for H_2 , HD, and D_2 between Pt electrodes, with a bin size of 2 meV. The peaks in the distribution for H_2 are marked by arrows and their widths by error margins. These positions and widths were scaled by the expected isotope shifts, $\sqrt{2/3}$ for HD and $\sqrt{1/2}$ for D_2 , from which the arrows and margins in the upper two panels have been obtained. From Ref. [28].

calculations is one, which agrees with the analysis of conductance fluctuations in the experiment of Refs. [23, 30]. The fact that the conductance is carried by a single channel demonstrates that there is indeed just a single molecule involved.

Several other DFT calculations have been performed, see e.g. Refs. [31, 32], where the agreement is only partial. Although Cuevas *et al* [32] find a similar high value for the conductance, the molecular orbitals responsible for the transport are the bonding orbitals, while Refs. [23, 28, 29] attribute the transport almost entirely to the antibonding orbitals. This difference implies that the sign of the charge transfer between the molecule and the metal leads differs between the two groups of calculations. Using a slightly different approach Garcia *et al* [31] agree with Cuevas *et al* on the bonding orbitals as the transport channel, but they obtain a conductance well below $1 G_0$. They propose an alternative atomic arrangement to explain the high conductance for the Pt-H bridge, consisting of a Pt-Pt-bridge with two H atoms bonded to the sides. However, this configuration gives rise to three conductance channels, which is excluded based on the analysis of the conductance fluctuations as discussed above. The rather strong disagreement between various approaches in DFT calculations for this simple molecule

Figure 5. Differential conductance gray-scale plot for a C_{60} molecule in a gold junction, obtained by electromigration breaking. High levels of dI/dV are shown in black and low levels white and these are plotted as a function of the gate voltage (ordinate) and the source-drain voltage (abscissa). Arrows mark the energy levels with an energy of 35 meV that are attributed to the excitation of the internal vibration mode illustrated in the inset. From Ref. [35].

show that there is a need for a reliable set of experimental data against which the various methods can be tested. The hydrogen metal-molecule-metal bridge may provide a good starting point since it is the simplest and it can be compared in detail by virtue of the many parameters that have been obtained experimentally.

Conductance histograms recorded using Fe, Co or Ni electrodes in the presence of hydrogen also show a pronounced peak near $1 G_0$ [33], indicating that many transition metals may form similar single-molecule junctions. Also Pd seemed a good candidate, but Csonka *et al* [30] did not observe the same suppression of conductance fluctuations as for Pt. There is an additional peak at $0.5 G_0$ in the conductance histogram, and it was argued that hydrogen is incorporated into the bulk of the Pd metal electrodes.

Going beyond the simplest molecule using similar techniques much work is still in progress. Preliminary results have been obtained for CO and for C_2H_2 between Pt electrodes [33, 34]. By its high symmetry buckminster fullerene, C_{60} , also forms an excellent system to start with, and we will end this section by briefly reviewing the recent results.

Single-molecule junctions for C_{60} were first obtained by Park *et al* [35], using pairs of gold electrodes broken by electromigration. The molecule in this case is weakly coupled to the electrodes, presumably by van der Waals forces and the low-bias conductance is extremely low (below 1 nS). However, the molecular levels can be shifted into resonance with the Fermi levels of the electrodes, either by increasing the source-drain bias voltage, or by use of a gate voltage, see Fig. 5. The gold electrodes for this device have been fabricated onto SiO_2 layer on top of a doped silicon wafer, that was exploited as a back-

Figure 6. Room temperature experiments on contacting C_{60} molecules in a lithographically fabricated MCBJ device. The left panel shows a typical trace of conductance vs. distance of the pushing rod while closing the contact after evaporation of the fullerene molecules. One often observes a plateau near $0.1 G_0$. For some contacts a spontaneous fluctuation is observed (right panel, inset) that is dominantly between two conductance levels of about 0.1 and $0.2 G_0$ as shown by the histogram. From Ref. [36].

gate. The molecular levels were observed to behave just as expected for the levels in a weakly coupled quantum dot. However, new features appeared as weak additional current jumps with energies of about 5 meV and 35 meV above threshold. They fit very well to the energies expected for a center-of-mass bouncing mode of the molecule as a whole, and an internal mode (Fig. 5, inset), respectively.

More recently Champagne *et al* [16] combined the electromigration break technique and back gate with a mechanical adjustment of the junction by bending of the substrate, as mentioned above. Although they did not resolve the vibration modes they could manipulate the position of the energy levels for a C_{60} molecule *and* the strength of the coupling to the electrodes by controlling the gate voltage and the mechanical bending of the substrate, respectively. This will be an important tool for further investigations of single-molecule junctions. Again, the low-bias conductance in these experiments is very low which leads to sharply defined molecular levels.

Room temperature measurements [24, 36] on the system C_{60} between gold electrodes reveal the possibility to establish low-resistance contacts between the metal and the molecules. Using a lithographically fabricated MCBJ device and evaporation of the molecules as described in section 2.2, the bridge was opened slowly and the conductance was monitored. A typical trace is shown in Fig. 6 (left). In contrast to the measurements on the pure gold electrodes before deposition of the molecules, one often observes a conductance plateau close to $0.1 G_0$. When further closing the contact and then stopping the motion of the pushing rod, fluctuations as a function of time between two or three preferred conductance values may occur. An example is given in Fig. 6 (right), showing a histogram of such two-level fluctuations in the main panel and the corresponding conductance trace in the inset. The conductance fluctuates between $0.1 G_0$ and $0.2 G_0$,

suggesting that a molecular junction is established by one fullerene molecule or two, respectively. The conductance plateau at $0.1G_0$ is also regularly observed when opening the bridge. It is therefore interpreted as the preferred conductance of a single C_{60} molecule between metallically clean gold electrodes. This value is one to two orders of magnitude larger than that reported when contacting the molecules by other techniques [35, 16] which usually require the exposition of the electrodes to ambient conditions. and more experiments at low temperatures are needed to investigate this further.

4. Molecules bonded by thiol groups to gold

For conductance measurements on single, or few, organic molecules under controlled local environment, MCB's, but also an electrochemical STM can be used [37]. The STM of the Tao group was equipped with a gold covered tip and was repeatedly brought in contact with a gold surface such that gold filaments were formed and then retracted. These measurements were performed at room temperature in an ultrapure electrolyte. The phenomena observed are rather similar to the MCBJ experiments in the previous section: conductance plateaus at multiples of $G_0 = 2e^2/h$ occurred immediately before the disruption, which was analyzed by histogram techniques very similar to Fig. 2. Then an organic molecule was added to the electrolyte, for example a 4,4'-bipyridine which forms relatively stable bonds between the nitrogen atoms at both ends of the molecule and the Au surfaces. It turns out that the conductance plateaus close to $1 G_0$ were more or less unaffected by the presence of the molecules, but in the histograms an additional peak at $\approx 0.01G_0$ and integer multiples thereof appeared. This was attributed to a single-molecule junction which temporarily was formed when the tip distance was such that a molecule fitted between the STM tip and the surface. In principle, the electrochemical setup is advantageous because it allows for an additional tuning parameter: the electrical potential within the electrolyte. For larger objects, this may be regarded as a gate electrode [38]. Here, the consequences of the reference voltage is mainly to stabilize or destabilize the nitrogen-gold bond. Experiments similar to those performed in Tao's group with STM in a wet cell, can also be done with a MCBJ approach, as demonstrated in Ref. [39].

The small molecules mentioned in section 3 above are investigated at low temperatures and under clean conditions. There is an advantage in studying organic molecules which are designed to form stable covalent bonds to both electrodes. When the combination thiol endgroup (of the molecule) and gold electrode is chosen, the bonds are strong enough to form metal-molecule-metal contacts, which are stable even when one slightly pulls the electrodes apart. For example it has been measured with AFM techniques that the disruption force of thiol-ended molecules on gold is in the nano-Newton regime [40], and it has been calculated that when one pulls slightly at the molecules, a small atomically sharp tip forms, and finally (if one pulls further) some gold is pulled off the surface [41]. This has two consequences: First, these properties are favorable when *single*-molecule junctions are desired, because a broader contact will be

Figure 7. Thiol-ended molecules **1** and **2**: a spatially symmetric (9,10-Bis((2'-para-mercaptophenyl)-ethynyl)-anthracene) and an asymmetric molecule (1,4-Bis((2'-para-mercaptophenyl)ethynyl)-2-acetyl-amino-5-nitro-benzene) in between two gold electrodes.

reduced in diameter during pulling at the contact. Second, the strong thiol-gold bonds turn out to be strong enough to withstand relatively high currents and voltages even at room temperature. This is, of course, important for nanoelectronic applications.

As mentioned before, the first measurements have been performed by Reed and coworkers, who used the MCBJ technique to investigate 1,4-benzenedithiol [17]. The molecules were self assembled on the gold surface from solution and then the bridge was broken. Stable junctions were formed and stable, reproducible IVs were recorded, which were clearly nonlinear. One of the final conclusions was “*The reproducibility of the minimum conductance at a consistent value implies that the number of active molecules could be as few as one*” [17]. This work stimulated a large number of theoretical calculations of the charge transport, the majority of which, however, overestimated the conductance by orders of magnitude compared to the experimental results.

Two years later, Kergueris *et al* published results from a similar experiment with a different molecule, based on thiophene units in the molecular backbone [21]. One important finding was that two stable configurations were observed, namely a symmetric one, but also one which was asymmetric in shape, a fact that could only be explained by an asymmetric geometrical realization of the metal-molecule-metal junction.

At this stage, many open question arose. Whereas the results obtained with molecules were clearly differing from blind experiments without molecules, no clear information was available on the number of molecules or how the molecules were arranged in the junction. Neither the experiment nor the theory was able to clarify the geometry.

Further insight was obtained from comparative studies with different molecules. As an example, Reichert *et al* used an MCBJ device with molecules that were specially designed for this purpose [22, 27]. In a first step, two molecular ‘rods’ were synthesized of

Figure 8. Current voltage characteristics, reproducibly recorded for a stable junction in a MCBJ (red) and their numerical derivative dI/dU (blue). a) with molecule **1** at room temperature, b) with molecule **2** at room temperature, c) with molecule **2** at $T = 30$ K

comparable length with a conjugated inner part. The main difference is their symmetry, see Fig. 7: Molecule **1** has a mirror symmetry with the mirror plane between the electrodes and therefore both current directions are equivalent. This symmetry is absent in Molecule **2** due to two different side groups in the central unit. Consequently one could expect a different behavior for the two possible current directions and, consequently, an asymmetric IV.

The junctions were formed by a continuous opening and closing procedure, which results frequently in stable junctions before the contact disrupts (observed as a sudden decrease of the current), where nearly identical IVs could be detected subsequently several times. Fig. 8 displays data thus obtained, both the IVs as well as its numerical derivative (blue). The junction is stable up to $V \approx 1.1$ V, allowing to trace the same IV several times. The current level ranges up to $1\mu\text{A}$. The IV curve is clearly nonlinear, having a broad step-like feature at $V = \pm 0.35\text{V}$, which presumably corresponds to

the onset of conductance when the first molecular orbital comes in resonance with the electrochemical potential of the electrodes. The blue curve is the differential conductance dI/dV , obtained by numerical differentiation of $I(V)$. It displays two peaks and the overall structure is to a good approximation symmetric. The corresponding curve for the asymmetric molecules is shown in Fig. 8b, it is clearly asymmetric. There are two important conclusions that can be drawn from this comparison: (i) the fact that the symmetric molecule gives symmetric IVs and the asymmetric molecule gives asymmetric IVs proves that indeed the molecule is forming the contact (and not water or dust or anything else). (ii) the number of molecules is very small, perhaps even a single one: a large ensemble of molecules, being randomly oriented during the deposition on both electrodes, would result in a symmetric IV. These findings, together with additional observations described in [22] do not unambiguously prove, but indicate strongly that indeed a single molecule or at most a few molecules form the junction.

The data shown in Figs. 8a and 8b are typical examples of IV curves. When the measurement is repeated, the shapes of the IVs change: The peak position may shift up and down by 100 mV or it may appear at the opposite voltage sign, the overall conductance may vary within a factor of 10 as well as the peak height and peak width vary within a certain range. For the symmetric molecule **1**, sometimes also asymmetric IVs occur, which can be attributed to strongly asymmetric contacts, whereas for **2** the asymmetry is always observed. These sample to sample fluctuations are an intrinsic feature of *single* molecule junctions: The wave function of the molecule is sensitive to the molecules' local environment, which differs from junction to junction. This effect, which is the origin also for sample-to-sample fluctuations in optical experiments [42] will also affect the electronic transport properties. For single-molecule contacts, an additional effect comes into play: the sulphur can bond to different sites of the gold electrode tip because they are not well-defined on the atomic scale. Upon contact, however, this bond has become one part of the molecules' wave function. It has been shown theoretically that different atomic geometries in the contacts lead to a different charging of the molecules and in the peak shifts, similar to the phenomena observed in the experiment [43, 44]

One important finding is that the conductance of this type of molecule is significantly lower than for the short molecules discussed in section 3. There are several factors that may play a role in explaining the difference. For a high transmission probability of the electrons, and therefore a high conductance, there should be at least one electronic orbital on the molecule that extends all the way across to the two ends. In addition, this orbital needs to hybridize strongly with the metallic states near the Fermi level in the leads. The sulphur atom, which accumulates some charge upon contact with the electrodes due to its high electronegativity forms an effective tunnel barrier, which reduces the transparency of the junction. The important role of the details of the molecular structure and, in particular, the role of the sulphur atom on the conductance properties has been demonstrated in [45, 46]. It is noteworthy that the spatial structure of a molecular junction is inhomogeneous, which plays an important

role for the transport process. In particular for thiol-ended conjugated molecules, the conjugated part can be considered as an island, which is electronically decoupled from the electrodes by the sulphur atoms.

4.1. Low Temperatures

There are important advantages in taking the experiment to lower temperatures. Electronic excitations and in particular vibrational degrees of freedom are expected to be frozen out, giving rise to much sharper spectroscopic features. For the formation of the molecule-electrode bond, on the other hand, room-temperature conditions are required to enable the diffusion of the reaction products and to provide sufficient activation energy (other combinations than acetyl-protected thiol vs. gold might be suitable under different conditions, but have not yet been tested). The two requirements can be met by using the following procedure: Once a molecular junction is established at room temperature, it is reopened because it is difficult to control the electrode distance during the cool-down process. After cooling down to cryogenic temperatures the junction is closed again until stable IVs are observed. A detailed description of the experimental protocol can be found in [27]. The data thus obtained with molecules **2** are displayed in Fig. 8c). By comparing with Fig. 8b) one notes, as an example, that the broad minimum observed at room temperature develops at low temperature towards a blockade of the current around zero bias. Looking at the shoulder-like structure around -0.5 V in Fig. 8b), the features have a peak width of several hundred millivolts. In contrast, the peaks are much better resolved at low temperature. The molecule is indeed oscillating very fast at room temperature and the measurement thus averages over many configurations. The increase in stability can also be inferred from the larger accessible stable bias window, which spans from -1.5V to 1.5V at low temperature. In addition, the noise, which is intrinsic to the nanocontact and not due to experimental limitations, is substantially reduced.

Hence, molecules are soft objects and at finite temperature and at finite current they may tremble! This is clearly a qualitative difference to purely electronic phenomena in semiconductor quantum dots and may also be of certain interest for applications: mechanical degrees of freedom may be exploited as resistance switches and the oscillations observed with molecule **2** can be regarded as a precursor to such a switching event.

A chemically defined switching of the conductance between high and low states may be controlled by light, as demonstrated by Dulić *et al* [47]. They used a photochromic molecule that can be switched from a high-conductance state to a low-conductance state under the influence of visible light and back under near UV irradiation. The two states had been investigated before in detail in solution. Dulić *et al* used a lithographically fabricated MCBJ device to contact individual molecules of this kind, modified to have thiol-anchoring groups. They observed switching of the conductance of a molecule from the high-conductance state to the low-conductance state, but the reverse step was not

obtained. They present evidence that the reverse step is suppressed as a result of the interaction of the UV light with surface plasmons in the gold electrodes.

5. Conclusions and prospects

Although the field of molecular electronics has seen several false starts, we are now seeing some experiments that may provide a reliable basis for further development. The mechanically controllable break junction technique is likely to play an important role in these developments. However, in all cases the information obtained in the experiments is limited to whatever can be learned through current and voltage measurement and control. Imaging is still not possible, and the interpretation of the data is seldom straightforward or unique. It is important to maintain a critical attitude towards the data and the interpretations, but there is good reason for optimism. It will be important to extend the collection of available experimental tools, e.g. by combining gate electrodes and force sensors, and by measuring shot noise, conductance fluctuations, interaction with light, and more. There is a lot that remains to be done, but we have a start.

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