Electronic properties of organic single-molecule junctions

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1. Introduction

1.1 Molecular Electronics

According to the predictions of Gordon Moore in 1965, the number of transistors per square centimeter of silicon doubles every 18 months [1]. Since the 1965s, devices have been shrinking at a steady speed, while improving the performance in terms of efficiency, speed and capacity. However, this downscaling is now rapidly approaching the atomic limit. As the conductor gets smaller than the mean free path of the charge carriers, electron transport does not follow Ohm's law anymore. When a conductor becomes smaller than the mean free path, the electron transport is not a diffusive process anymore and the charge carriers experience no scattering within the conductor. Nevertheless it reveals an electrical resistance that originates from the quantum nature of the electrons. Another important reason, which makes the electronic transport in nanoscale conductors different compared to macroscopic conductors, is the quantized energy spectrum (particle in a box). In that case, the contact between macroscopic electrodes and the nanoscale conductor strongly affects the overall conductance.

Molecules are the smallest objects in nature that can perform a specific function such as photosynthesis or signal transduction. On the other hand (more than chemical properties that determine the functionality) they could be the basis of future electronic devices because of several advantages like being inexpensive, functional and atomically precise. Molecules can be produced reproducibly in large numbers by chemical reactions. Organic chemistry can generate different molecules which can be integrated for larger scale electronic circuits. Molecular recognition can then be used to build these circuits in a process called self-assembly. However, molecules also have some disadvantages such as instabilities at high temperatures, but the advantages are enough to motivate the scientists to explore this field which offers manifold possibilities for technological development such as diodes [2,3], transistors [4,5], switches [6,7] and memories [8].

1.2 This thesis

In this thesis the charge transport properties through single-molecule junctions are investigated to answer four questions:

1. What is the preferred current path through a tripodal single 9,9'-spirobifluorene molecule in contact with gold electrodes?

2. How many conduction channels contribute to the current through a single 1,4benzenedithiol molecule in contact with gold electrodes?

3. What is the influence of vibration modes on the shot noise of gold single-atom contacts?

4. What are the influences of an unpaired electron on the charge transport through single oligo (p-phenyleneethynylene) (OPE)-based radical molecular junctions?

To answer these questions, we used the mechanically controllable break-junction (MCBJ) technique to fabricate atomic or single-molecule junctions. We performed all experiments

at helium temperature (4.2 K) to have advantages of low thermal noise and highly stable contacts with the ability of sub-Ångstrom mechanical manipulation of the atomic and/or molecular junctions. The characteristic conductance of each molecule was determined by repeated opening and closing of the molecular junctions. To obtain a deeper understanding of the observed conductance characteristics, the current-voltage (*I-V*) characteristics, differential conductance (dI/dV-V), and IETS (d^2I/dV^2-V) were measured. In addition, to be able to answer the questions 2 and 3, we also performed shot noise measurements. Finally, we examined the impact of magnetic fields (up to 5 T) on electron transport in single oligo (p-phenyleneethynylene) (OPE)-based radical molecular junctions. Chapter 2 gives a brief overview over the experimental methods to address single-molecule electron transport. The focus of this chapter is on the scanning tunneling microscope (STM) method, MCBJ technique and the electromigration technique.

In chapter 3, we review the study of charge transport through mesoscopic systems and single molecule junctions including current-voltage characteristics, inelastic electron spectroscopy, point contact spectroscopy, current noise and molecular spintronics. The nano-fabrication process of the MCBJ and the experimental setup including the electronic measurement methods and the mechanical control is presented in detail in chapter 4.

In chapter 5, the charge transport measurements for a new tripodal platform based on a rigid 9,9'-spirobifluorene is presented. By study the elastic and inelastic charge transport (experimentally and theoretically) the preferred binding geometry is revealed and it showed that despite the length of the current path, the conductive molecular wire on the platform features a well-defined and relatively high condcutance. A perpendicular molecular wire with respect to the surface is desirable to separate the π -system from the substrate and can be used to incorporate functional units like switches. The shot noise measurements on single-molecule Au-1,4-benzenedithiol (BDT)-Au junctions in a wide range of conductance values are presented in chapter 6. By help of a simple setup which includes a current-amplifier and a spectrum analyzer we found that the current is carried by a single conduction channel throughout the whole conductance range for BDT single moleculecontacts. The results are supported by quantum transport calculations using density functional theory (DFT). The agreement between the experimental observations and theoretical calculations demonstrate the formation of a stable high-conductance Au-BDT-Au junction with one channel. Chapter 7 addresses the role of unpaired electrons for the electron transport at the single molecule level for radical molecules. We investigated the impact of magnetic fields on the electron transport in single radical molecular junctions. We observed huge positive magnetoresistances (MRs) which were one order of magnitude larger than those of the analogous non-radical molecule. Our findings with the help of DFT calculations suggested that the large MR for the single radical molecules can be ascribed to decoherence in the charge transport under a magnetic field.

Finally, we present the influence of electron-phonon scattering on shot noise of single-atom gold contacts in chapter 8. We confirmed the previous experiments and obtained the same conductance threshold for sign change of inelastic noise. This thesis is completed by a summary in chapter 9.

2. Experimental methods to address single-molecule electron transport

2.1 Introduction

The first single-molecule electronic device was proposed in 1974 [9]. However, it was not until the late 1990s that the first electronic measurements could be performed on single molecules [10-13]. The challenge lies in coupling macroscopic electrodes to a nanometersized molecule. In order to achieve this coupling, a nanometer-sized gap, or nanogap, needs to be formed between the two electrodes, in which a molecule is then deposited. It is for this reason that numerous ways of forming molecular junctions have been and are still being developed such as the scanning tunneling microscope (STM) [10], the mechanically controllable break junction (MCBJ) [12], atomic force microscopy (AFM) [14], electromigration [15], gold nanoparticles [16], nanopores [17], crossed wire technique [18]. In this chapter the focus is on STM method, MCBJ technique and electromigrated nanojunction technique. These three methods are the most popular and reliable approaches for single-molecule conductance measurements. Figure 2.1 shows a relatively simple scheme for three techniques. A molecule is contacted by two macroscopic metal electrodes. These electrodes are connected to external equipment for measuring the current and voltage. To measure the conductance, one applies a bias voltage (V) between the electrodes and then measures the current (I) flowing through the device.



Figure 2.1. Schematic of a conductance measurement of a single-molecule contact. A bias is applied between the electrodes while the current flowing through the molecule is measured. The circle with blue shadow represents the sulfur atom.

2.2 Scanning Tunneling Microscope

The scanning tunneling microscope was developed in 1982 by Gerd Binnig and Heinrich Rohrer at IBM [19]. The physical phenomenon behind the STM technique is the tunneling effect, in this case electrons overcome a potential barrier that is forbidden in classical physics. Figure 2.2 shows a schematic view of the STM. When a metal tip is brought near a

conducting surface, electrons can tunnel from the tip to the surface or vice-versa. A small bias is applied to the tip and when the tip is within a few Ångstroms of the surface, a tunneling current will flow. The tip is attached to a piezoelectric tube with electrodes. Applying a high voltage across opposite piezo electrodes causes a small distortion of the piezoelectric tube and thus effects the in-plane (x-y) or out of plane (z direction) motion of the tip.



Figure 2.2. STM schematic view. The tip is attached to a piezoelectric tube with electrodes.

The STM allows to repeatedly open and close the contacts (between tip and substrate) and form a 'new' junction in every cycle, and also the high resolution imaging with extension of spatially resolved current sensing spectroscopy, scanning tunneling spectroscopy (STS), make this instrument suitable for exploring the electric phenomena at the molecular scale.



Figure 2.3. Schematic representation of the STM-type contact junction approach. (a) approach, (b) formation of atomic junction, (c) retraction and formation of single molecule junction and (d) breaking of the molecular contact.

Gimzewski and Möller used the STM for exploring the transition from the tunneling regime to the point contact [20]. The feasibility of building and characterizing the charge transport in the single molecule with the help of STM was presented in 1995 by Joachim and Gimzewski for a C_{60} molecule [10]. As such, one can measure charge transport through hundreds of junctions and statistically address the variability in junction formation [2,21-26]. Figure 2.3 shows a schematic view of a formation of a molecule junction with STM.

2.3 Mechanically Controllable Break Junction

The Mechanically Controllable Break Junction is another important tool for fabrication of atomic contacts, tunable tunnel contacts and single molecule contacts. This method was developed from initial inventions by Yanson et al. in 1981 [27] with needle-anvil technique and Moreland et al. with squeezable tunneling junctions [28,29]. Moreland's break junction technique was pursued further by Muller et al. in 1992 in order to obtain clean and stable contacts [30,31].

The working principle is depicted in Figure 2.4. This technique consists of a lithographically defined, suspended metallic bridge on an insulating (polymer or oxide) layer or a notched wire, fixed on the top of a bendable substrate. A three-point bending mechanism consisting of a pushing rod and two counter-supports enables the substrate to bend and elongate the metallic wire until finally the metallic constriction breaks and two fresh electrode surfaces are created. The position of the pushing rod relative to the counter supports is controlled by a motor or piezo drive or combinations of both. The broken atom contact then can come to contact again by pulling back the pushing rod and by reducing the curvature of the substrate.



Figure 2.4. Working principle of the MCBJ consisting of pushing rod and two counter supports and the dimensions which are used for calculating the reduction ratio.

The important advantage of the MCBJ technique is the enhanced stability due to transformation of the motion of the pushing rod into a much reduced motion of the electrodes perpendicular to it. The interelectrode distance change (Δs) is estimated from the displacement of the pushing rod (Δz) via an attenuation factor (*r*):

$$\Delta s = r \Delta z \tag{2.1}$$

Where
$$r = \xi \frac{6tu}{L^2}$$
 (2.2)

Here, *t* is the thickness of the substrate, *u* is the length of the free standing bridge, *L* is the distance of the counter supports, and ζ is a correction factor which has a value varying from 2 to 4 depending on details of the sample [32]. *r* can be determined experimentally from conductance-vs-distance curves in the tunneling regime, when the work function of the electrode is known. The effective reduction ratio has a typical value of 10^{-6} to 10^{-4} for the thin-film MCBJs. In principle with this technique one can manipulate the distance between the electrodes with sub-Ångstrom accuracy. The high stability of the junction and the sub Ångstrom control of the junction make the MCBJ technique a very good tool for studying the single-molecule junctions [12,33-40]. The target molecule can assemble on two electrode surfaces. The molecular junctions are then formed during the opening/closing of the nanogap between the two electrodes (see figure (2.5)).



Figure 2.5. Scenario of the evolution of a molecular junction during elongating the metallic wire from atomic contact to establish a single-molecule junction.

MCBJ techniques have been developed for different environments including very low temperatures [41] or liquid solutions [42], ambient conditions and vacuum. The first experiment with MCBJ technique for single- molecule junctions was done by Reed et al. in 1997 [12]. In this study, with a self-assembled monolayer (SAM) of 1,4-benzenedithiol (BDT) on gold wire, the gold wire then was covered with BDT molecules. These molecules were able to bind to the gold electrodes through thiol groups. The solvent was evaporated and by opening and closing the junction the molecule can bridge between the gold electrodes. Figure 2.6 shows a schematic view for this experiment. The advantage of MCBJs as compared to STM techniques are high stability (reduction factor) and clean conditions (the atomic contacts are only formed during the measurement by breaking the bulk of the electrodes while in STM setups clean contacts can only be guaranteed when working in good vacuum conditions). The drawback of the MCBJ technique is the low speed and the fact that the surrounding area of the contact cannot be scanned (blind measurements).



Figure 2.6. (a) Schematic of the single-molecule junction formation. A: The gold wire before formation of the tip electrode. B: Deposition of 1,4-benzenedithiol (BDT) solved in tetrahydrofuran (THF) with self-assembled monolayer (SAM). C: Production of two opposing gold contacts covered with BDT molecules. D: After the evaporation of the solvent, the onset of conductance is achieved by gentle movement of the gold electrodes toward each other. Steps (C) and (D) (without solution) can be repeated several times for reproducibility. (b) A schematic of a 1,4-benzenedithiol SAM between gold electrodes. Reproduced from Ref. [12].

2.4 Electromigration technique

The electromigration technique is a very useful tool to form a nanometer (\sim 1-3 nm) scale gap for studying molecular electronics and atomic contacts. This technique has been introduced by Park et al. in 1999 [15]. The fabrication of nanometer gap size was based on the fact that atoms in a metallic wire can migrate when they are subject to a large current

density. This idea came from the observation of failure in microelectronic circuits because of large current density [43]. Park et al. exploited this phenomenon advantageously to break gold nanowires in a controllable and self-limiting fashion. They were able to produce two metallic electrodes whose typical separation is about 1 nm. Although the control of nano gaps is still difficult, one can obtain more control of the electromigration process by minimizing the series resistance of the leads (reduce the temperature of leads) [44] and by limiting the power dissipation by a cycling process [45,46].



Figure 2.7. Field-emission scanning electron micrographs of a representative gold nanowire (a) before and (b) after the breaking procedure. The nanowire consists of thin (~10 nm) and thick (~ 90 nm) gold regions. In the images, diffuse white lines separate these two regions. Representative conductance trace obtained during a nanowire breaking procedure. The conductance is measured in a four-probe configuration schematically shown in the inset. The nanowire is broken by ramping a bias voltage through a 100 Ω series resistor at a rate of 30 mV/s. Reproduced from Ref. [15].

Since the electrodes are not suspended in this method, the contact is more stable compared to MCBJ technique. The major drawback of the electromigration technique is that once the metallic wire burns it cannot be closed again. A combination of electromigration with the lithographic MCBJ technique overcomes this problem [47].

Figure 2.7 (a) shows field-emission scanning electron micrographs of a representative gold nanowire before the breaking procedure which was fabricated with electron-beam lithography and shadow evaporation on a SiO_2 substrate [15].

By using the four probe configuration the voltage drop across a nanowire was monitored during the breaking process. Figure 2.7 (c) shows a representative conductance trace during the breaking process. The voltage drop reaches 300–500 mV while the current increases and the conductance start to change. Upon further enhancement of the current, finally the nanowire breaks. A representative SEM image of a broken wire is shown in Fig. 2.7(b). Similar to other methods (STM and MCBJ) the single molecule then can bridge between the nanogaps of the electrodes. The electromigration technique is also widely used in single-molecule transistors because of the higher gate efficiency compared to the MCBJ technique [48,49].

3. Theoretical aspects and background

3.1 Introduction

This chapter review several theoretical concepts and background including: mesoscopic conductors, charge transport through single-molecule contacts, current noise and molecular spintronics. We present important experiments and techniques and for analyzing these experiments, we introduce the theoretical concepts. In the beginning we introduce the ballistic conductor, transport channels, chemical potentials and Landauer formula and present systems such as an atomic-sized constriction and constriction in a two- dimensional electron gas with a quantized conductance.

After that two important aspects of single molecule junctions electronic characterization including the characteristic conductance and the interaction of the electronic and the vibrational degrees of freedom for a single metal-molecule-metal junction is presented. By help of the single-level model and inelastic tunneling spectroscopy (or point contact spectroscopy) one can understand the role of molecular energy levels, metal-molecule coupling, and electron-phonon interaction.

Following these methods and techniques, the current noise including shot noise and thermal noise is presented which can give valuable information about the system. For example by shot noise measurements, the number of quantum conductance channels and their transmission probabilities can be determined which is not possible by other normal conductance measurements. After that we present an overview on the field of molecular spintronics and influence of unpaired electrons in radical molecule on the conductance. Finally we discussed the influence of electron-phonon interaction on the shot noise. We discuss here that how such diverse measurement techniques and theoretical concepts can help us to understand the physics behind our observations.

3.2 Ballistic conductors

In a macroscopic system the conductance value *G* is described by Ohm's law:

$$G = \frac{\sigma A}{L} = \frac{1}{R}.$$
(3.1)

With cross-section area *A*, length *L*, conductivity σ , and resistance *R*.

According to this relation one expects vanishing resistance, perfect conductor, for a conductor with small length. This is not the case, however for conductors with *L* between microscopic and macroscopic scale. *G* is bounded on one side by the mean free path of the electrons (l_e) , and on the other, by the length scales for various scattering mechanisms that destroy the electron's phase coherence or momentum. For a diffusive conductor $(l_e << L)$, the electron motion can be viewed as a random motion caused by scattering from the impurities. On the other hand, for some mesoscopic conductors, such as carbon nanotubes or point contacts in two-dimensional electron gas (2DEG), the mean free path l_e is getting

larger than the conductor length and we reach the ballistic regime, in which the electron's momentum can be assumed to be constant and only limited by scattering with the boundaries of the sample. If the phase coherence length (l_{φ}) is also longer than the device dimensions, then the transport is clearly coherent. Figure 3.1 shows schematically a ballistic conductor which is connected with two electrodes, 1 and 2. We assume that these two electron reservoirs have different chemical potentials μ_1 and μ_2 [50].

Because of the confinement of electronic states in the direction perpendicular to the current flow, there are several energy subbands:

$$E_{N,k} = \frac{\hbar^2 k^2}{2m} + \varepsilon_N \,. \tag{3.2}$$

Here a parabolic potential is assumed in which *m* is the effective mass of the electron, \hbar is Planck's constant, *N* is the mode number and $\varepsilon_N = E$ (*N*,*k* = 0) is the lower cut-off energy given by the confinement to the width *W*. The subbands are also called channels. Thus the total current is given by the sum of the microscopic currents of all the subbands.



Figure 3.1 (a) A ballistic conductor with length *L* and width *W* is connected to two electrodes 1 and 2 with different chemical potentials μ_1 and μ_2 . (b) Energy dispersion relation for a ballistic conductor for three channels or subbands.

The number of channels is a function of energy, which is denoted by M(E). If M(E) is constant over the energy range (μ_1 - μ_2) then the conductance of a ballistic conductor is given by [50]:

$$G_C = \frac{2e^2M}{h}.$$
(3.3)

 $G_{\rm C}$ is the contact conductance and $G_0 = 2e^2/h = 1/12906$ (Ω^{-1}) is the conductance quantum. Although the ballistic conductor should have zero resistance a contact resistance arises from the mismatch of the few numbers of conduction channels in the ballistic conductor with many conduction channels in the macroscopic leads.

If one considers an imperfect ballistic conductor (it means that there is scattering inside the conductor and the transmission probability is not one) according to Landauer's formula [51] the conductance of this conductor is equal to:

$$G = \frac{2e^2}{h} \tau(E). \tag{3.4}$$

 τ (E) is the total transmission probability of all modes M:

$$\tau(E) = \sum_{n=1}^{M} \tau_n.$$
(3.5)

with the required demand $0 \le \tau_n \le 1$. The τ_n are the transmission probabilities of the individual modes or channels. If the transmission probability is unity, we recover the conductance of a ballistic conductor.



Figure 3.2 (a) Point-contact resistance as a function of gate voltage at 0.6 K. Inset: Point-contact layout. (b) Point-contact conductance as a function of gate voltage. The conductance shows plateaus at multiples of $2e^2/h$. Reproduced from Ref. [52].

Quantized conductance in ballistic conductors was first observed experimentally in 1988 by B. J. van Wees et al. [52]. In this experiment ballistic point contacts were defined in the two-dimensional electron gas of a GaAs-AlGaAs heterostructure, and the width of the point contact was varied smoothly from 0 to ~360 nm using a gate on top of the heterojunction, the measurements were performed at 0.6 K. As the width was increased, it was observed that the conductance did not increase linearly but rather in quantized steps of $2e^2/h$ (see figure 3.2).

To date, many nanoscale systems have been investigated, including single-atom contacts [53-57] as well as chemical nanostructures such as carbon nanotubes [58-60] or single-molecule contacts [10-13,21,34,61]. Figure 3.3 shows a conductance trace for a gold atomic contact and force measurements during the elongation of the atomic-sized constriction. Rubio et al. simultaneously measured the conductance and force during the formation and rupture of an atomic-sized gold contact at room temperature [62]. The steps in the conductance trace represent the quantization of conductance.



Figure 3.3. Simultaneous recording of the measured (a) conductance and (b) force during the elongation of an atomic-sized constriction at 300 K. The inset shows a schematic view of the experimental setup. Reproduced from Ref. [62].

For single-atom contacts the number of modes or transport channels is determined by the number of valence orbitals (see figure 3.4) [63]. Scheer et al. found that for s-metals for example Au, which has only one valence orbital (6s), a single atom has a single channel that can achieve almost perfect transmission (the last step of conductance in figure 3.3 (a)). For sp-metals like Al and Pb, three channels contribute to the current and transition metals, for example Nb, have five conduction channels (s and d-orbitals).

Charge transport through single molecules is more complicated than that through atomic junctions for several reasons. For example the molecules consist of different atoms (more complicated electronic structure), the influence of coupling between a molecule and electrodes and the impact of internal degrees of freedom (vibration modes) need to be considered while studying the single-molecule junctions. Further discussion will be presented in section 3.4.



Figure 3.4. Conductance traces for Au, Nb, Al and Pb as a function of electrode distance. The number of channels for each material (indicated in the figure) is determined for each point in the curve by fitting of the current-voltage to the superconductor subgap structure theory. Reproduced from Ref. [63].

3.3 Molecular orbital

According to valence-bond theory, for atomic orbitals the bonds are formed between valence electrons on an atom. However, the valence-bond model is not able to explain some of the molecules (for example some molecules with two equivalent bonds with a bond order between that of a single bond and a double bond). The best this theory can do is to suggest that these molecules are hybrids, or combination of the two Lewis structures for these molecules. To study the structure of molecules more in depth, the molecular orbital (MO) theory was developed [64].

The position of the electron cannot be accurately determined, but it is possible to calculate the probability of finding the electron at any point around the nucleus. The electron has a fixed energy and a fixed spatial distribution called an orbital. Similar to waves which can be added or subtracted from each other, for atomic orbitals the solutions of the Schrödinger equation, which can be considered as wavefunctions, can also be added or subtracted which is called molecular orbitals. This quantum superposition of atomic orbitals and a technique for calculating molecular orbitals is called linear combination of atomic orbitals (LCAO) [65].

For example, the individual hydrogen atoms exist at very high temperature, but the diatomic hydrogen molecules are formed at ordinary temperatures and pressures. According to the molecular orbital theory, the H_2 molecule can be formed with linear combination of the 1s wave functions of the two H atoms.

Figure 3.5 (a) shows two molecular orbitals (the bonding and antibonding molecular orbitals) for hydrogen molecules. For the bonding molecular orbital the electron density between the two nuclei is greater and the energy is lower than two 1s separated atomic orbitals of hydrogen atoms. Therefore this molecular orbital is more stable than the atomic orbitals of the hydrogen atom. For the antibonding molecular orbital there is a node in the electronic wave function and the electron density is low between the two positively charged nuclei.

In this case the energy is higher and it is unstable. Electrons are filled to the molecular orbitals (bonding and antibonding) using the same rules that are used for adding electrons to atomic orbitals which are: The aufbau principle (lowest energy MOs fill first), The Pauli exclusion principle (maximum of two electrons with opposite spin per orbitals) and Hund's rule (when there are equal energy or "degenerate" orbitals, these fill one electron at a time before pairing begins). From all the possible molecular orbitals in one system, two are so special that they have their own names. One is the highest occupied molecular orbital (HOMO). The other is the lowest unoccupied molecular orbital (LUMO). To reveal whenever a system exists, one can check the bond order according to the molecular orbitals:

bond order =
$$\frac{(\text{electrons in bonding MO}) - (\text{electrons in antibonding MO})}{2}$$
(3.6)

For example the dihelium molecule He_2 (unknown molecule) the bond order is zero but for dilithium which is known in the gas phase it is one. See figure 3.5 (b) and (c).



Figure 3.5. Molecular orbitals schematics representing bonding and antibonding orbitals for (a) hydrogen molecules (b) dihelium molecules (c) dilithium molecules. Redesigned from Ref. [66].

A common method for the determination of the molecular electronic structure is density functional theory (DFT). In this method, the eigenvectors (molecular wave functions) and eigenvalues (molecular orbital energies) will be calculated after diagonalizing the Hamiltonian. Figure 3.6 shows the energy spectrum of a 1,4-benzenedithiol molecule in the gas phase and in the absence of interaction with the environment.



Figure 3.6. DFT calculations for molecular orbitals of 1,4-benzenedithiol in the gas phase and in the absence of interaction with the environment. In the right panel, the black lines represent the occupied orbitals and the gray lines indicate the unoccupied orbitals. Reproduced from Ref. [49].

3.4 Charge transport through single-molecule junctions

In this section we focus on two important aspects of single-molecule junction electronic characterization. The first is the conductance of a single metal-molecule-metal junction which depends not only on the chemical nature of the molecule (such as anchoring groups or molecular conjugation) but also on its conformation, the second is the interaction of the electronic and the vibrational degrees of freedom of the molecular bridge. The first one can be addressed by dc conductance measurements and building a conductance histograms. In this case one can determine the characteristic conductance value related to metal-molecule-metal junctions. In the second scope which can be addressed by studying the current-voltage characteristics and inelastic tunneling spectroscopy (or point contact spectroscopy), we can understand the role of molecular energy levels, metal-molecule coupling and electron-phonon interaction. These diverse measurement techniques and analysis methods are of crucial importance in understanding the basic ingredients of charge transport of a single-molecule junction.

3.4.1 Conductance traces and histogram

According to different atomic configurations of each contact, each conductance trace is different but there are features which are reproducible in most of the traces. For example, figure 3.7 shows conductance traces and histograms for atomic gold contacts with 4,4' bipyridine molecules. The measurement performed with the help of a gold STM tip and a

gold substrate. As the tip is pulled away from the substrate the conductance decreases in steps near multiples of G_0 (= $2e^2/h$) [26]. Each contact configuration is different for each opening and closing cycle. Therefore each conductance trace is unique (figure 3.7 (c)). In this case, it is useful to construct conductance histograms from a large set of these conductance traces (figure 3.7 (b and d)). The peaks in the histogram correspond to conductance values that are preferred by the atomic contact or single-molecule junction and are common in most of the conductance traces [67]. From figure 3.7 (a and c) it is also clear that often the plateaus are not at exactly integer quantum values. For gold atomic contacts the last plateau (one atom contact chains) can be stretched to values below 1 G_0 (0.6 $G_0 \le G \le 1 G_0$).



Figure 3.7. Conductance traces for (a) gold atomic contacts (c) 4,4' bipyridine molecules (e) In absence of molecules (pure tunneling). Corresponding conductance histogram constructed from 1000 conductance curves for (b) gold atom contacts (d) 4,4' bipyridine molecules (f) In absence of molecules. The histogram for gold atomic contacts shows pronounced peaks near 1 G_0 , 2 G_0 , and 3 G_0 due to conductance quantization and the histogram for the 4,4' bipyridine molecules shows integer values of 0.01 G_0 (1,2 and 3) demonstrating the one, two, and three molecules contacted in parallel with gold electrodes. Reproduced from Ref. [26].

3.4.2 Current-voltage characteristics

The metal electrodes have continuous density of states and the electronic eigenfunctions are plane waves. On the other hand, the small size of the molecule causes spatial confinement of the charge carriers and the formation of a discrete energy spectrum. Calculation of the combined system when they are brought together is a complex task and very difficult to solve analytically. In this case several approximate models such as the Simmons model [68] or the single-level model [69] have been developed.

In the Simmons model, the tunneling of electrons through a potential barrier (molecules) is calculated with the WKB approximation and the current-voltage relation when the applied bias is less than the barrier height is equal to:

$$I = \frac{qA}{4\hbar\pi^2 d^2} \left\{ \left(\varphi - \frac{qV}{2}\right) \exp\left(-\frac{2d\sqrt{2m_e}}{\hbar}\sqrt{\varphi - \frac{qV}{2}}\right) - \left(\varphi + \frac{qV}{2}\right) \exp\left(-\frac{2d\sqrt{2m_e}}{\hbar}\sqrt{\varphi + \frac{qV}{2}}\right) \right\}.$$
(3.7)

Where A is the junction area, m_e is the electron effective mass, q is the electronic charge, d is the barrier width and φ is the barrier height. In two different limits, the equation (3.7) reduces to:

$$I \sim V \exp\left(-\frac{2d\sqrt{2m_e\varphi}}{\hbar}\right) \quad \text{for } eV \sim 0$$
 (3.8)

$$I \sim V^2 \exp\left(-\frac{4d\sqrt{2m_e\varphi^3}}{3\hbar qV}\right) \text{ for } eV > \varphi$$
 (3.9)

When applying a voltage to the junction the rectangular barrier (eV=0) is inclined, finally when the bias is larger than the work function ($eV > \varphi$), the charge carriers tunnel through a triangular barrier. This latter regime is called Fowler-Nordheim (F-N) tunneling [70]. For the high-voltage regime, it is useful to rescale Eq. (3.9):

$$\ln\left(\frac{l}{V^2}\right) \sim -\frac{4d\sqrt{2m_e\varphi^3}}{3\hbar qV} \left(\frac{1}{V}\right) \qquad \text{for } eV > \varphi \tag{3.10}$$

The plot of $\ln(I/V^2)$ against 1/V will yield a line. The slope of this line depends on the barrier height. Because field emission experiments generally involve barriers with both substantial width and height, no measurable current flows before the onset of field emission. Therefore, only for small barrier height and width, such as metal-molecule-metal junctions, the transition from direct tunneling to field emission would be possible. From the current-voltage characteristics of metal-molecule-metal systems, the transition/inflection voltage (V_{infl}) between the direct tunneling to the Fowler-Nordheim (F-N) tunneling is deduced, indicating the position of the molecular level (see figure 3.8).

This model is widely used, although the nature of a molecule is not taken into account when assuming a molecule as a tunneling barrier. Moreover inadequacies of the Simmons model are mentioned in conjunction with unreasonable fitting parameters [71]. It is possible to refine the barrier models, but in reality the nature of the molecule and its characteristics should be considered in the model from the beginning.



Figure 3.8. Schematic of the conventional model to qualitatively explain the inflection of the F-N curve. $E_{\rm F}^{\rm L}$ and $E_{\rm F}^{\rm R}$ are the Fermi energies of both electrodes and $V_{\rm infl}$ is the voltage at which the inflection takes place. The red area (triangle, trapezoidal, or rectangle) in the upper panel represents the tunneling barrier. Reproduced from Ref. [72].

Therefore in the following sections the focus will be in introducing such a model. The metal electrodes in the vicinity of the molecules act as reservoirs with a chemical potential, which at 0 K is equal to the Fermi energy (E_F). For T > 0 K, the energy distribution of the electrons in the electrodes is smeared out by thermal broadening and is given by the Fermi-Dirac distribution function:

$$f_{\alpha}(E) = \frac{1}{1 + \exp(\frac{E - \mu_{\alpha}}{k_B T})}.$$
(3.11)

Where *E* is the electron energy, $k_{\rm B}$ the Boltzmann constant, μ the chemical potential of reservoir α (α is either the left (L) or the right (R)) and *T* is the temperature. In equilibrium, no current flows because the chemical potential of both electrodes is equal (see Fig. 3.9 (a)). By symmetrically applying a bias voltage *V*, the chemical potential of the electrodes is shifted accordingly:

$$\mu_L = E_F + \frac{eV}{2}.\tag{3.12}$$

$$\mu_R = E_F - \frac{eV}{2}.\tag{3.13}$$

This results in occupied states in the left and empty states in the right electrode (see Fig. 3.9 (c)).

In the resonant tunneling model (single-level model) which was introduced recently [69], it assumed that the current is carried by one single molecular orbital coupled to the Fermi seas of the electrodes in the generic situation, in spite of the fact that the molecule may provide a multitude of electronic states (see Fig. 3.9 (a)).



Figure 3.9. (a) A molecule provides a multitude of electronic states. (b) In the single-level model, it is assumed that the current is carried by one single molecular orbital coupled to the Fermi seas of the electrodes. This level can be either the HOMO or the LUMO, depending on the position which is closest to the Fermi energy. (c) By symmetrically applying a bias voltage V, the chemical potential of the electrodes is shifted. As the chemical potential of one of the electrodes is aligned with the molecular level, the current flows.

This level can be either the HOMO or the LUMO, depending on the position which is closest to the Fermi energy (see Fig. 3.9 (b)). The presence of the electrodes has another influence which is hybridization of the molecular states with the states of the metal. Electrons can therefore tunnel from and towards the molecule with a finite probability. According to Heisenberg's uncertainty principle, their finite residence time on the molecule allows for a finite window of electron energies to tunnel, effectively resulting in a broadening of the molecular levels. The electron transfer rate from the left electrode to the molecule ($\Gamma_{\rm L}$) and from the molecule to the right electrode ($\Gamma_{\rm R}$) depends on the overlap of the wave function of the molecule and those of the electrodes, and defines the level broadening. The total coupling ($\Gamma = \Gamma_L + \Gamma_R$) is a measure for the overall hybridization, and determines the amount of current through the molecule. One can define three different transport regimes based on the ratio of Γ , Δ , Ec and $k_{\rm B}T$ [69,73]. The three regimes are, weak coupling regime ($\Gamma \ll \Delta$, E_c , k_BT), intermediate coupling regime (Γ , $k_BT \le E_c$, Δ), and strong coupling regime (Γ , $k_{\rm B}T > E_{\rm c}$, Δ). Here the Δ is the confinement energy which is due to the small size of the molecule and spatial confinement of the charge carriers (Δ = $\hbar^2/(2m_eL) \sim 0.4$ eV for L = 1 nm, L is the length of molecule), E_c is charging energy which is due to the Coulomb interactions between the charge carriers ($E_c = e^2/2C \sim 100$ meV, C is the capacitance of the molecule to the environment) and $k_{\rm B}T$ is the thermal energy. The weak coupling mostly occurs for physisorbed molecules which are weakly bound to the electrodes and the level broadening can be neglected. The density of states on these molecules are given by a series of discrete levels represented by Dirac delta functions and only integer charges are allowed to tunnel. Charge transport is also incoherent because the electrons stay on the molecule for a long time and causes the electrons to lose information about their phase. On the other hand, in the strong coupling regime the electronic states of the molecule and the electrodes are hybridized and by quantum fluctuations of the molecular charge, the blockade effects are vanising. As for a strong coupling because of a

significant overlap between the wave functions of the molecule and the electrodes, this regime is mainly relevant in the case of small molecules. For a more detailed description of this regime, see reference [73].

In the intermediate coupling regime which is the case for most of the situation, molecules are covalently bonded to the electrodes, and the level broadening has to be taken into account. In this regime, transport occurs through off-resonant tunneling (single level model), which is a first-order process. In addition, transport is coherent, and effects involving the phase of the electrons (for example quantum interference) can be observed. Following the Landauer approach, the current through the molecule can be computed from the following expression [69,74]:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE \,\tau(E, V) [f(E - eV/2) - f(E + eV/2)].$$
(3.14)

Where the f(E) is the Fermi function and $\tau(E,V)$ is the transmission coefficient that is dependent on energy and voltage and given by the Breit-Wigner formula:

$$\tau(E,V) = \frac{4\Gamma_L \Gamma_R}{[E - E_0(V)]^2 + [\Gamma_L + \Gamma_R]^2}.$$
(3.15)

$$E_0(V) = E_0 + \left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R}\right) \frac{eV}{2}.$$
(3.16)

In the low temperature

limit where $k_BT \ll \Gamma$, the analytical Eq. 3.17 can be derived from Eq. 3.14 for symmetric coupling ($\Gamma_L = \Gamma_R$) and Eq. 3.18 for asymmetric coupling (($\Gamma_L \neq \Gamma_R$).

$$I(V) = \frac{2e}{h}\Gamma\left[\arctan\left(\frac{\frac{eV}{2} - E_0}{\Gamma}\right) + \arctan\left(\frac{\frac{eV}{2} + E_0}{\Gamma}\right)\right].$$
(3.17)

$$I(V) = \frac{2e}{h} \frac{4\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \left[\arctan\left(\frac{eV\Gamma_R - E_0(\Gamma_L + \Gamma_R)}{(\Gamma_L + \Gamma_R)^2}\right) + \arctan\left(\frac{eV\Gamma_L + E_0(\Gamma_L + \Gamma_R)}{(\Gamma_L + \Gamma_R)^2}\right) \right].$$
(3.18)

Figure 3.10 (a) presents *I-Vs* for various E_0 for fixed $\Gamma_{L,R}$.



Figure 3.10. (a) Current-voltage characteristics for various values of E_0 and a fixed $\Gamma_{L,R} = 0.02 \text{ eV}$. (b) Current-voltage characteristics for various values of $\Gamma_{L,R}$ and a fixed $E_0 = 0.4 \text{ eV}$.

As a result of the symmetric voltage drop across the two barriers, the position of the step shifts according to $V_{\text{step}} = 2E_0/E$. For decreasing E_0 , the low bias current increases also. The sharpness of the step and the current after the steps are the same for all the curves because of the fixed $\Gamma_{\text{L,R}}$. Figure 3.10 (b) shows *I-V*s for fixed E_0 and different $\Gamma_{\text{L,R}}$. The situation is now different. In this situation the location of the step remains the same for all curves, but its maximum current increases for increasing Γ and the sharpness of the step decreases.



Figure 3.11. Experimental *I-V* of an Au-BDT-Au junction with a conductance of 0.244 G_0 (black symbols) fitted with the single-level model (solid red line). The single-level fit to the *I-V* yields an energy level of E_0 = 0.32 eV and the coupling constants of Γ_R = 0.099 eV and Γ_L = 0.088 eV (corresponding to a slight asymmetry $\alpha = \Gamma_L/\Gamma_R \sim 0.89$).

Figure 3.11 shows an experimental *I-V* of an Au-BDT-Au junction with a conductance of 0.24 G_0 (black symbols) measured with MCBJ technique at 4.2K. The data is fitted with the single-level model (solid red line). The single-level fit to the *I-V* yields an energy level of $E_0 = 0.32$ eV and the coupling constants of $\Gamma_R = 0.099$ eV and $\Gamma_L = 0.088$ eV (corresponding to a slight asymmetry $\alpha = \Gamma_L/\Gamma_R \sim 0.89$).

3.4.3 Inelastic electron tunneling spectroscopy

In 1966, Jaklevic and Lambe discovered inelastic electron tunneling spectroscopy (IETS) [75], which is a crucial tool to detect the vibrational features of molecules buried in the interface of a metal-insulator metal (MIM) device. When a metal-molecule-metal sandwich is formed, electrons can tunnel from metal to metal through the molecule. These molecules can affect the tunneling via the excitation of vibrational states. Figure 3.12 shows the energy-band diagrams of a tunnel junction and the corresponding I(V), dI/dV and d^2I/dV^2 [76]. When a negative bias is applied to the left electrode (figure 3.12 (a)) an electron can tunnel from occupied states (left electrode) to an empty state (right electrode). This is an elastic process and the energy is conserved (process a). During the elastic process the current increases linearly with small applied bias (figure 3.12 (b)). However when the applied bias (eV) exceeds the excitation energy ($\hbar\omega$) of a vibrational mode such that $eV \ge \hbar\omega$, the electron can lose a quantum of energy, $\hbar\omega$, to excite the vibration mode and tunnel into another empty state (process b) [77].



Figure 3.12. (a) Energy band diagram of a tunnel junction with a vibrational mode of frequency ω localized inside. Here "a" is the elastic tunneling process and "b" is the inelastic tunneling process. (b) Corresponding *I-V*, d*I*/d*V*, and d²*I*/d*V*² characteristics. Reproduced from Ref. [76].

Therefore the total current after $eV = \hbar \omega$ is a combination of elastic and inelastic current and the overall current increases. The total tunneling current has a kink and this kink becomes a step in the differential conductance (dI/dV) plot and a peak in the d^2I/dV^2 plot (figure 3.11 (b)). In fact a very small fraction of electrons can tunnel inelastically because the cross-section for such an excitation is very small and the electron traversal time is much smaller than the oscillator period.

The peak in the d^2I/dV^2 can be determined theoretically by the numerical derivatives of the measured I(V) characteristics [78]. However, due to noise and low signal-to-noise ratios this method is not practical. In practice, with a phase-sensitive "lock-in" detection technique, it is possible to directly measure the peaks of the second derivative of I(V). In this method a small sinusoidal signal is applied (modulation voltage) and the response of the current through the device to the applied signal is studied. A Taylor expansion of the current around the applied bias can be expressed as [79,80]:

$$I(V_{a} + V_{AC}\cos(\omega t)) = I(V_{a}) + \frac{dI}{dV}\Big|_{V_{a}}V_{AC}\cos(\omega t) + \frac{1}{2}\frac{d^{2}I}{dV^{2}}\Big|_{V_{a}}V_{AC}^{2}\cos^{2}(\omega t) + \dots = I(V_{a}) + \frac{dI}{dV}\Big|_{V_{a}}V_{AC}\cos(\omega t) + \frac{1}{4}\frac{d^{2}I}{dV^{2}}\Big|_{V_{a}}V_{AC}^{2}(1 + \cos(2\omega t)) + \dots$$
(3.19)

Where V_a is the applied bias, V_{AC} is the AC modulation voltage, and ω is the modulation frequency. The scaled values of first and second derivatives of I(V) can be detected from the first (ω) and second (2ω) harmonic signals, respectively. In order to examine the validity of IETS, the broadening, the symmetry of IETS (see figure 3.13 (b)) can be checked. For measurement setup with low noise and good signal to noise ratio a comparison between the numerical derivative of the measured dI/dV and the measured d^2I/dV^2 is also possible (see figure 3.13 (a)).

The IETS spectra are broadened by intrinsic linewidth, thermal broadening, and ac modulation broadening [81,82]. The assignment of each molecular vibration can be done by comparing Raman or Infra-red (IR) spectroscopy with the IETS. However, because of their rigorous selection rules some particular vibrational modes can be silent in Raman or IR investigations. With the help of IETS measurements it is possible to detect all modes, although the amplitudes of some modes may be small due to the "propensity rules" effect [83,84]. In molecular junctions, vibrational modes can vary when molecular orientation, conformation, or contact geometry change for each different contact. Therefore IETS is also useful to investigate the molecular conformation, contact geometry, chemical bonding [76,82,83,85] but at the other hand, for the assignment of vibration modes it is not easy to compare with other experimental IETS or theoretical calculations, because the vibrational mode position and their intensity may change or for complex molecules several modes may appear together at a same vibrational energy. However, in many cases the position of modes does not shift significantly and drops in a certain range of the energy window. Figure 3.13 (a) shows an experimental IETS (black curve) for an Au-1,4-benzenedithiol (BDT)-Au junction with conductance of 0.244 G_0 obtained by MCBJ technique at 4.2 K with its numerical derivative of the dI/dV (green curve). The red curve in figure 3.13 (b) is a symmetrized curve with respect to the bias polarity obtained by the simple formula y =(f(x) - f(-x))/2) which applies for the symmetrization of point-symmetric functions.



Figure 3.13. (a) Experimental IETS (black curve) and the numerical derivative of the dI/dV (green curve) for an Au-1,4-benzenedithiol (BDT)-Au junction with conductance of 0.244 G_0 obtained by MCBJ technique in 4.2 K. (b) IET spectrum (black) shown together with a symmetrized curve (red) with respect to the bias polarity. (For negative bias polarity the sign of d^2I/dV^2 has been inverted for better illustrating the symmetry.) (c) Comparison of symmetrized experimental (red lines) and theoretical (blue line) IET spectra. The vibrational mode assignment and details about the theoretical calculations are presented in chapter 6.

Here for negative polarity the sign of d^2I/dV^2 has been inverted for better illustrating the symmetry. To compensate the change of conductance, the IETS should be normalized as $(d^2I/dV^2)/(dI/dV)$ [81,83]. Figure 3.13 (c) shows the experimental (black) IET spectrum for the same junction and DFT calculations. Figure 3.14 shows the different IET spectra while stretching for an oligo(phenylene ethynylene)dithiol (OPE3) single-molecule junction with MCBJ technique at 4.2K.



Figure 3.14. (a) Low-bias conductance trace recorded during the stretching of an Oligo(pphenyleneethynylene) (OPE3) single-molecule junction (top) and color-map representing the IETS signal upon stretching (bottom). (b) Extracted IETS master-curves at the positions indicated by the arrows in (a). Note that not all peaks/steps are visible in the color-map for this choice of contrast. Reproduced from Ref. [85].

3.4.4 Point contact spectroscopy

The point contact spectroscopy (PCS) is a similar measurement method as the IETS for conductive junctions with $G > 0.5 G_0$ [34,86-91]. When the transmission (τ) exceeds the so called crossover transmission ($\tau_{crossover}$), which is given by half the value of the maximum transmission (τ_{max}) of a junction [89,91,92].



Figure 3.15. (a) Energy band diagram of a tunnel junction with a vibrational mode of frequency ω localized inside. Here "a" is the elastic tunneling process and "b" is the inelastic tunneling process. (b) Corresponding *I-V*, d*I*/d*V*, and d²*I*/d*V*² characteristics.

In this range of higher transmission, because of a momentum transfer to the excited mode, the electron backscattering increases (see figure 3.15 (a)) and this leads to a negative contribution (or reduction) of the transmission probability, reduced differential conductance and a dip in the second harmonics (d^2I/dV^2) (see figure 3.15 (b)). For example, the vibration modes phonons of the gold atomic contacts [86,87] can attain values between about 10 mV and 20 mV, which vary due to softening of the bonds with the strain in the atomic wire. These longitudinal phonon modes shift to low energy by the decrease of the elastic constant of the atomic chain (see figure 3.16).

Another interesting system is the 1,4-benzenedithiol (BDT) molecule, which has variable conductance value ranging from ~ $10^{-4} G_0$ to ~ 0.6 G_0 . For this system it was observed that the sign of the second harmonics changed from peaks (IETS) to dips (PCS) while increasing the conductance [88]. Such large variation occurs because the BDT molecules may adopt several configurations in the junction including tilting of the ring plane with respect to the electrodes or bonding to different sites on the metal atoms (i.e., top or hollow) when the molecular junction is stretched or compressed [88,93-95].



Figure 3.16. (a) Short and long atomic wire, 4 Å long and 22 Å long, respectively. At the point of rupture, the atomic wire collapses and the conductance, which is negligible in the scale of this figure, corresponds to the tunneling regime. To reestablish contact, the electrodes must reapproach by a distance of the order of the chain length. Panels (b), (c), and (d) show the differential conductance and its derivative at points S, M, and L, respectively, marked by the arrows. The various curves in (b), (c), and (d) were acquired at intervals of 0.3, 0.3, and 0.5 Å, respectively. Note that the vertical scales are identical in these panels (Reproduced from Ref. [87]).

Figure 3.17 shows differential conductance (dI/dV) and the IETS measurements for various transmission regimes ($\tau = 0.56$, 0.01, and 0.002) for Au-BDT-Au junctions. For a contact with $\tau = 0.56$ the conductance is reduced (figure 3.17 (a)) while the IETS shows dips at the same transmission (figure 3.17 (b)).

However, at $\tau = 0.01$ and 0.002, the dI/dV and IETS are stepwise enhanced and show peaks, rather than dips. High transmission with 0.56 could be achieved via the contributions of several molecules in parallel or by direct Au-Au contacts. However, larger contacts with contributions from several molecules in parallel summing up to a total transmission of 0.56 should show peaks in the IETS as expected for low-transmission junctions. On the other hand, metallic Au-Au contacts would not excite the molecular vibrational modes [88].



Figure 3.17. (a) The differential conductance (dI/dV) curves are obtained as a function of bias voltage for a contact with $\tau = 0.56$ (top panel), 0.01 (mid panel) and 0.002 (bottom panel). The conductance steps downward at $\tau > \sim 0.5$, whereas it steps upward for $\tau < \sim 0.5$. (b) Normalized IETSs measured for the contact with $\tau = 0.56$ (top panel), 0.01 (mid panel) and 0.002 (bottom panel) is presented. Likewise the IETS spectra change their sign from dips to peaks. The vibrational modes of Au-BDT-Au junctions are assigned: I: gold-sulfur stretching (v (Au-S)), II: C-S stretching (v (C-S)), III: C-C-C bending (γ (C-C-C)), IV: C-H in-plain stretching (v (C-H)), V: C-H in-plain bending (γ (C-H)), VI: C=C stretching (v (C=C)). The vertical dashes indicate the maximum dip or peak of each vibrational mode (Reproduced from Ref. [88]).

3.5 Current noise

Intrinsic noise, random and uncorrelated fluctuations of signals, is a fundamental ingredient in any measuring process. The fundamental of intrinsic current noise in electrical conductors had been known for some time but for the first time in 1918, the German physicist Walter Schottky formulated a theory of "tube noise" [96]. Schottky reported that in ideal vacuum tubes where all sources of artificial noise have been eliminated there are two types of noise, described by him as the "Wärmeeffekt" and the "Schroteffekt". The first of these is now known as Johnson-Nyquist or thermal noise, which is caused by the thermal agitation of the electrons and occurs in any conductor that has a resistance (R). The second is the shot noise which originates from the discrete nature of electric charge.

Electronic current noise is dynamical fluctuations of the electrical current around its time averaged mean value:

$$\Delta I(t) = I(t) - \langle I \rangle. \tag{3.20}$$

Here, the brackets indicate an ensemble average for a random system. A detailed description of current noise in the time domain is given by the correlation function:

$$f_{\rm I}(t) = \left\langle \Delta I(t+t_0) \Delta I(t_0) \right\rangle. \tag{3.21}$$

Equivalently noise can be characterized by its power spectral density $S_I(\omega)$, which is the Fourier transform at a certain frequency ω of the current-current correlation function:

$$S_{\rm I}(\omega) = 2 \int_{-\infty}^{\infty} dt \ e^{i\omega t} \ f_{\rm I}(t). \tag{3.22}$$

In the last decade, it has become clear that by studying the current noise, one can obtain more information on the electron transport mechanism in one system which cannot be obtained from resistance measurements.

3.5.1 Thermal noise

Thermal noise is caused by the electron's mobility within a conductor's lattice and is an electrical analogy of Brownian motion and also known as Johnson-Nyquist noise because it was first reported experimentally by J. B. Johnson [97,98] and analyzed theoretically by H. Nyquist [99] in 1928. Johnson found that the electric charges in a conductor are in a state of thermal agitation, in thermodynamic equilibrium with the heat motion of the atoms of the conductor. The manifestation of the phenomenon is a fluctuation of potential difference between the terminals of the conductor which can be measured. Johnson also found that the mean-squared voltage fluctuation across the ends of the conductor was directly proportional to the resistance of the conductor.

The Nyquist relation can be derived from a simple classical model of a short-circuit consisting of a resistor *R* in parallel with a capacitor *C* [100]. In equilibrium, an average energy of $\frac{C\langle V^2 \rangle}{2} = \frac{k_B T}{2}$ is stored in the capacitor. Therefore, the current in the resistor fluctuates due to the decay of voltage with a characteristic RC time:

$$I(t) = \frac{V}{R} e^{\frac{-(t-t_0)}{RC}}, \quad t > t_0.$$
(3.23)

Substituting this I(t) behavior into Eq. 3.22 yields:

$$S(\omega) = 4 \int_0^\infty dt \ e^{i\omega t} \ \frac{V^2}{R^2} \ e^{\frac{-t}{RC}}.$$
 (3.24)

Since $V^2 = k_B T/C$, we get:

$$S_I(\omega) = \frac{4k_B T}{R} \frac{1}{1 - i\omega RC} \,. \tag{3.25}$$

In the low frequency limit, $\omega \ll (RC)^{-1}$, we obtain for the thermal noise of a resistor *R*:

$$S_I = \frac{4k_B T}{R} \,. \tag{3.26}$$

Thermal noise is useful for calibrating the experiment setup to extract correct data and beyond that the conductance measurement is enough to determine the resistance of the system [100]. As it is clear from Eq. 3.26, the spectral density of a thermal noise is independent of frequency, therefore such a spectrum is called white. However, in the electronic devices one should consider two more important regions, in which the noise spectrum is not white. First, the low frequency regime which is due to Flicker noise or 1/f noise and second is the high frequency regime which is due to the cut-off frequency of the system (see figure 3.18). Generally the noise spectrum can be decomposed into different parts:

$$S_I(f) \propto A + \sum_{\alpha=0}^{2} \frac{1}{f^{\alpha}}$$
 (3.27)

Here *f* is the frequency, $0 < \alpha < 2$ and *A* is constant, however the most important terms of the noise spectrum which are common in almost every electronic devices, are f^0 (white noise) and f^{-1} (1/f noise). 1/f noise has been studied in several systems including nanoelectronic devices [101] quantum point contacts [102], quasiballistic and ballistic nanowires [103-106], tunneling contacts [107,108], and single molecule junctions [109-111]. The origin of 1/f noise is unknown, however, it can be attributed to the motion of the defects in the leads for nano junctions. The noise spectra show a roll-off at higher frequencies due to the low-pass transfer characteristics of the electronic circuit. An ideal low-pass filter completely eliminates all frequencies above the cut-off frequency while passing those below unchanged. The cut-off frequency is defined as the frequency, at which the (output /input) ratio of the signal has a magnitude of $1/\sqrt{2}$. The combination of resistance (*R*) and capacitance (*C*) gives the time constant of the circuit ($\tau = RC$). The cut-off frequency is determined by the time constant of the electronic circuit $f_C = 1/2\pi\tau$.


Figure 3.18. Typical current noise spectrum with 1/f noise, white noise and roll off parts.

3.5.2 Shot noise

Shot noise in an electrical conductor is a non-equilibrium phenomenon, which is a consequence of the quantization of the charge. One can derive Schottky's formula, S = 2e < I>, for a mesoscopic tunnel junction with a high barrier of the interface. Assume there are *n* charge quanta *q* incident on the barrier per unit time with the transmission probability τ . The distribution of the number of transmitted particles n_{τ} can be described as a simple classical statistics (bimodal distribution):

$$P_n(n_{\tau}) = \binom{n}{n_{\tau}} \tau^{n_{\tau}} (1-\tau)^{n-n_{\tau}}.$$
 (3.28)

The average of the transmitted particles $\langle n_{\tau} \rangle$ equals to $n \cdot \tau$ and the variance is given by:

$$\langle \Delta n_{\tau}^{2} \rangle \equiv \langle n_{\tau}^{2} \rangle - \langle n_{\tau} \rangle^{2} = n\tau \ (1 - \tau) = \langle n_{\tau} \rangle \ (1 - \tau). \tag{3.29}$$

Since $I = qn_{\tau}/t$, the variance of the total current is then equal to $\langle \Delta I^2 \rangle = q \langle \Delta I \rangle (1 - \tau)/t$. using the Eq. 3.22 for $\omega \ll t^{-1}$, the frequency independent shot noise power is:

$$S_I = 2q \langle I \rangle (1 - \tau). \tag{3.30}$$

In the limit of low transmission ($\tau \ll 1$), the binominal distribution can be approximated by the poisson distribution. In this case the shot noise can be given by the well known Schottky formula [96]:

$$S_I = S_{Poisson} = 2q \langle I \rangle. \tag{3.31}$$

The Poisson noise is valid, in general, for a 'dilute stream of uncorrelated particles' which are carrying a charge quantum q. The correlations among the charge carriers, for example the Pauli exclusion principle in Fermionic statistics or Coulomb interaction, suppress the shot noise value below S_{Poisson} . To characterize the suppression of shot noise compared to the Poisson value at zero temperature, one defines the Fano factor:

$$F \equiv \frac{S_I}{S_{Poisson}} \,. \tag{3.32}$$

According to Landauer's formula [51] for coherent transport in a mesoscopic conductor with length *L* and width *W* which is connected to two electrodes with different chemical potentials (see figure 3.1 (a)) and has *N* conduction channels with the transmission probabilities τ_n at finite temperature *T*, the total current noise power can be expressed as [112,113]:

$$S_{I} = 2eVG_{0} \operatorname{coth}\left(\frac{eV}{2k_{B}T}\right) \sum_{n=1}^{N} \tau_{n} \left(1 - \tau_{n}\right) + 4k_{B}TG_{0} \sum_{n=1}^{N} \tau_{n}^{2}.$$
 (3.33)

Here V is the applied bias potential, and k_BT is the thermal energy. One should consider that the total current noise expression is not a simple superposition of thermal and shot noise. Eq. 3.33 reduces to shot noise (for $k_BT \ll eV$) or thermal noise (for $k_BT \gg eV$):

$$S_I = 2eVG_0 \sum_{n=1}^{N} \tau_n (1 - \tau_n), \qquad k_B T \ll eV$$
 (3.34)

$$S_I = 4k_B T G_0 \sum_{n=1}^{N} \tau_n , \qquad k_B T \gg eV \qquad (3.35)$$

From Eq. 3.34 it is obvious that the shot noise for a system is suppressed for completely opened eigen-channels (for which $\tau_n = 1$) or completely closed ones ($\tau_n = 0$) whereas $\tau_n = 1/2$ yields the maximum value. In the limit of low transparency $\tau_n \ll 1$, for all n, the shot noise is given by the Poisson form:

$$S_I = 2eVG_0 \sum_{n=1}^N \tau_n = 2e\langle I \rangle. \qquad \tau_n \ll 1$$
(3.36)

In terms of the transmission probabilities, the Fano factor then is equal to:

$$F = \frac{\sum_{n=1}^{N} \tau_n \left(1 - \tau_n\right)}{\sum_{n=1}^{N} \tau_n}.$$
(3.37)

In this case the Fano factor varies from zero (all channels are fully open) to one (Poissonian limit). Several experiments on atomic-scale junctions showed the suppression of shot noise for almost fully open channels [114-120].

For example, van den Brom et al. [114] measured shot noise power for 27 gold atomic junctions by MCBJ technique at 4.2 K (see figure 3.19). To visualize the effect of contributions of different modes to the conductance, they used a model which is described in the inset of figure 3.19. In this model the conductance between $(n-1) G_0$ and nG_0 is built up as $G = (n-2) G_0 + (\tau_{n-1} + \tau_n + \tau_{n+1}) G_0$, where the three partially open channels have transmissions which increase linearly, and the sum of $(1 - \tau_{n-1})$ and (τ_{n+1}) is a constant fraction *x*. A sharp suppression of shot noise at 1 G_0 in this experiment shows that in the

monovalent metal gold, the current through a single atom is indeed almost exclusively carried by one single conductance channel.



Figure 3.19. Measured excess noise (is the subtraction of thermal noise from the total noise) values for 27 gold contacts at 4.2 K with a bias current of 0.9 μ A. Comparison is made with calculations in the case of one single partially transmitted mode (full curve) and for various amounts of contributions of other modes according to the model described in the inset (dashed curves). In the limit of zero conductance, these curves all converge to full shot noise. Inset: transmission of modes in the case of *x*-10% contribution from neighboring modes. Reproduced from Ref. [114].

In general, for different systems the Fano factor (Eq. 3.37) can be universal in the sense that it is insensitive to microscopic properties of the device. An overview over different universal Fano factors for various mesoscopic systems is given in Tab.3.1.

| F | physical system | $	au_n$ | references |
|-----|--------------------------|---------|-----------------------|
| 0 | ballistic conductor | 1 | [114,115,119,121,122] |
| 1/4 | chaotic cavity | bimodal | [123,124] |
| 1/3 | diffusive wire | bimodal | [125-127] |
| 1/2 | symmetric double-barrier | bimodal | [101,128] |
| 1 | single tunnel-barrier | « 1 | [96] |

Table 3.1. Overview over different universal Fano factors ($F \equiv S/S_{Poisson}$) observed in mesoscopic devices.

These universal values have been derived for generic cases but sometimes the variances from these universal values can occur because of the electron-electron interaction. For example *F* can increase to ~ 0.43 for a diffusive wire [129]. For normal conducting systems

the Fano factor is in the range of 0 < F < 1, but for some systems such as normalmetal/superconductor hybrid structures, the Fano factor can be larger than 1, meaning that the shot noise can be enhanced due to multiple Andreev reflection [130-133]. Fano factor bigger than 1 was also reported for the highly correlated regime of the fractional quantum Hall (FQHE) [134].



Figure 3.20. (a) Total noise spectra for a gold contact with the conductance of 1.53 G_0 at 4.2 K, without correction for the electronic transfer of the setup. The lowest curve shows the thermal noise, a few percent higher than the theoretical value, which is due to the preamplifier noise. The upper curves are the total measured noise for increasing current, I = 0.1- 0.9 μ A. (b) Excess noise, calculated from the data in (a) and corrected according to electronic transfer function of the system. (c) Measured excess noise values for a gold contact at 4.2 K with $G = 1.02 G_0$, as a function of bias current. For comparison the calculated excess noise according to Eq. 3.33 is also plotted: full shot noise, 2*eI*, one single partially transmitted wave (i.e., $\tau_1 = 1$ and $\tau_2 = 0.02$) and two equally transmitted waves ($\tau_1 = \tau_2 = 0.51$). A good description of the data is obtained with $\tau_1 = 0.99$ and $\tau_2 = 0.03$. Reproduced form Ref. [114].

Shot noise measurements can provide important information about the charge transport in mesoscopic systems which cannot be obtained from conventional resistance. For example, one can determine the fraction of the charge 'q' of the current carrying quasi-particles in the fractional quantum Hall regime [135-137] or multiple charge quanta for an atomic point contact between two superconducting electrodes [133]. Another important information, which can be achieved is the determination of the quantum mechanical transport channels and their transmission probabilities of atomic contacts [114,115,119,138] as well as to single-molecule junctions [91,139-141].

For example figure 3.20 shows how sensitive the noise power is to the number and transmission probabilities of the transport channels for gold atomic contacts at 4.2 K [114]. Figure 3.20 (a) shows a total noise spectrum as a function of bias current for a contact with conductance of $G = 1.53 G_0$. The 1/f noise and roll-off of the spectra is visible in the total noise spectra and sharp peaks are due to electromagnetic pickups. After the subtraction of the thermal noise, I = 0, (plus the background noise of the setup) the excess noise is white in a window of the frequencies between 10 to 40 kHz (see figure 3.20 (b)). Averaging over the white frequencies window for each applied bias current can give the related shot noise (see figure 3.20 (c) for different contacts with conductance of $G = 1.02 G_0$).

3.5.3 Inelastic shot noise

The interaction between conducting electrons and local vibrations are presented in section 3.4.3 and 3.4.4. In these sections we mentioned that there is a conductance variation crossover from an increase to a decrease when a total transmission τ changes from zero to one. The same behavior is also predicted by several theoretical calculations for shot noise [142-151] and have been observed in several measurements of molecular junctions and atomic contacts [86,91,152-154]. Similar to elastic noise which can give information about the system such as number of transmission channels and their probability, studying the inelastic noise can provide useful information about the lattice temperature or local phonon population of a nanoscale system. To understand the crossover from increase to suppression of shot noise due to electronic vibrational coupling in a nanoscale systems, the single-level model with a single vibrating scatterer has been investigated theoretically [86,145,147,148,151].

In this model a single resonant molecular level E_0 couples to the left and right electrodes with coupling constants of Γ_L and Γ_R . Here one can consider a localized vibration mode with frequency ω_0 which interact with the single molecular level with a coupling constant of λ . Figure 3.21 shows a schematic view of this model for the regime $\Gamma_{L,R} \gg \omega_0$. The inelastic correction (to second order in λ) to the noise when the energy dependence of the transmission can be neglected, $\tau(E) = \tau(0)$, is given by [86,145]:

$$\delta S_I \cong \frac{e^2}{h} \left(\frac{\lambda}{\Gamma}\right)^2 \tau^2 \left\{2(1-\tau)(1-2\tau)eV + (8\tau^2 - 8\tau + 1)(eV - \hbar\omega_0)\,\theta(eV - \hbar\omega_0)\right\}.$$
(3.38)

Here the transmission probability τ is given by Eq. 3.15. According to equation 3.38, there are two limits that indicate the crossover form positive to negative correction in shot noise, $\tau = 2 \pm \sqrt{2}/4$ ($\tau \sim 0.86$ and $\tau \sim 0.15$). Up to now, few experimental efforts for investigating this model have been published [86,154].



Figure 3.21. Schematic representation of single-level model with interaction localized vibration mode characterized by frequency ω_0 and electron-vibration coupling constant λ . The top part illustrates the atomic chain configuration and the vibration mode involved in the scattering. The lower part sketches an example of a two-electron process giving rise to reduction of the Fano factor: two electrons injected from the left lead at different energies tend to compete for the same outgoing state after the emission of a phonon. Reproduced from Ref. [86].

Kumar et al. [86] measured the phonon signals in the conductance and the noise power on Au nanowires at 4.2 K with the MCBJ technique. Figure 3.21 (a) shows a dip in a positive range of the bias voltage in the derivative of the differential conductance (black curve) of an Au contact with zero-bias conductance of $G = 0.98 G_0$. This dip shows the excitation of the longitudinal vibration mode which can attain values between about 10 mV and 20 mV [87]. Figure 3.22 (b) shows a measurement of the noise power for the same contact as in Figure 3.22 (a). They observed a kink at 20 mV in the noise signal which matches the energy of the vibration mode. The red curve in figure 3.22 (b) is a fit to Eq. 3.33 and gives a Fano factor of $F_1 = 0.02 \pm 0.002$ and slope of the green curve gives the modified Fano factor F_2 . The relative Fano factor is then calculated as $\delta F/F_1 = (F_2-F_1)/F_1 = + 0.9$. To simplify the fitting, two dimensionless, voltage-dependent parameters are introduced:

$$Y(V) = \frac{S_I(V) - S_I(0)}{S_I(0)}$$
(3.39)

$$X(V) = \frac{eV}{2k_{\rm B}T} \coth\left(\frac{eV}{2k_{\rm B}T}\right)$$
(3.40)

Using these definitions, expression (3.33) reduces to a linear relationship:

$$Y(V) = [X(V) - 1]F$$
(3.41)



Figure 2.22. (a) Symmetric part of the differential conductance (left axis) and its derivative (right axis) for a Au atomic chain. The signal was measured with 2 mV modulation amplitude at 3.33 kHz; the second derivative was computed numerically. The peak at 20.0 \pm 0.4 mV signals the onset of scattering by a vibration mode. (b) Shot noise as a function of bias for the same atomic contact as in (a). The red curve is a fit to Eq. (3.33) up to 20 mV. The Fano factor $F_1 = 0.02 \pm 0.002$ agrees with the conductance of $G = 0.98 G_0$ in (a). The broken red curve is an extrapolation of the fit. The green line is a linear fit to the data above 20 mV. Reproduced from Ref. [86].

Figure 3.23(a) shows data for seven different chain configurations, plotted as *Y* vs *X*. The authors found a positive correction above the kink for conductance close to $1G_0$ and negative correction for $G < 0.95G_0$.



Figure 3.23. (a) Reduced noise *Y*, Eq. (3.39), plotted as a function of the variable *X*, defined in Eq. (3.40). (b) Distribution of the observed change in the Fano factor at the kink, plotted as a function of the conductance. The points are obtained for different realizations of Au atomic chains. For conductance (i.e., transmission) close to 1 we find exclusively positive values for $\delta F/F$. Below a cross-over regime near $G = 0.95G_0$ only negative values are observed. The curves are obtained from the theory of Ref. [145], for fixed values of the inelastic scattering strength λ . Reproduced from Ref. [86].

The relative change in the Fano factor for a set of about 120 measurements has been measured and is shown in figure 3.23 (b). The crossover in their data to negative values ($\tau \sim 0.95$) is higher than the calculated value of ($\tau \sim 0.854$) [148,149]. This discrepancy was attributed to the occurrence of conductance fluctuations [86]. We performed an equivalent measurement on Au atomic contacts with a different setup and observed the same threshold of 0.95 G_0 for the sign change in the relative Fano factor. Further discussion about the results and possible reasons for this discrepancy between the theory and experiment can be found in chapter 8.

3.5 Molecular spintronics

In the last decades, the increasing demands in computational power and storage capacity direct much attention to spintronics [155]. Spintronics aims at the enhancement of the properties of electronic devices by usage of the spin degree of freedom. This additional degree of freedom in transport is expected to enhance the storage capacity and speed of the electronic devices. Reaching the quantum limit in the electronics devices, on the other hand, can open the door to quantum computation. Compared to classical computers, large-scale quantum computers should be able to solve problems much quicker according to the superposition principle (qubits). By downscaling the devices and by improvement of the energy efficiency processes, molecules attracted considerable attention [156-159]. Molecular magnets also possess low spin-orbit coupling (higher relaxation times) which can overcome one of the greatest challenges in this field of quantum computing which is controlling or reducing quantum decoherence [160-162]. This research field attained its own scientific name: "Molecular Spintronics". The final goal of molecular spintronics is to manipulate the spin and charge on the single molecule level. In this section, we review seminal works on molecular spin-transistors and molecular spin-valves.

3.6.1 Molecular spin-transistors

Molecular spin-transistors are essentially single-electron transistors with nonmagnetic electrodes and a magnetic molecule as the island [5,48,163]. Figure 3.24 (a) shows a side view for a single-molecule magnet, the Mn_{12} derivative $Mn_{12}O_{12}$ ($O_2C-C_6H_4$ -SAc)₁₆ (H₂O)₄. The schematic view for the three-terminal device including a single M_{12} molecule is also presented in figure 3.24 (b) [163]. The electrons can flow from source to drain through the magnetic molecule and charge transport can be tuned with the gate voltage (V_g). One can define three regimes, named weak-coupling, intermediate-coupling and strong-coupling by the coupling between molecule and electrodes [164].

Molecules are considered to be weakly or strongly coupled to the electrodes depending on the coupling constant (Γ) and charging energy E_C of the molecule. If $\Gamma \ll E_C$, the molecule is weakly coupled to the leads, whereas for $\Gamma \gg E_C$ strong coupling is obtained (see section 3.4.2 also). Between the weak coupling and strong coupling regime one can identify a third regime which we shall refer to as the intermediate coupling regime. In the weak coupling regime, for low temperature, the electron transport can be blocked (Coulomb blockade) and by tuning the gate voltage V_g , the molecular level can be in resonance with the Fermi energy [164,165]. In the first Coulomb blockade measurements [163,166], it was found that the differential conductance can be negative because of the presence of the single-molecule magnet.

The observations in the magnetic field also demonstrated that the degeneracy at zero field and the nonlinear behavior of the excitations as a function of field are typical of tunneling via a magnetic molecule [164,166]. Figure 3.25 shows the plots of the differential conductance (dI/dV) as a function of V and V_g for, Mn₁₂O₁₂ (O₂CCH₃)₁₆ (H₂O)₄ (short: Mn₁₂Ac). Jo et al. [166] observed crossed diagonal lines at V = 0 which indicate tunneling transitions between the ground states of adjacent charge states. In Figure 3.25 (a), transition to excited states with energies of ~ 1.1 and 1.34 meV appear astwo additional peaks in dI/dV (marked with green and yellow arrows). Figure 3.25 (b) shows the dI/dV for magnetic field of 8T. In contrast to measurements for nonmagnetic quantum dots [167], in the single-molecule-magnet transistor, neither the ground-state transition nor the excitedstate peaks exhibit simple Zeeman splitting of degenerate spin states.



Figure 3.24. (a) Side view of a Mn_{12} molecule with tailormade ligands containing acetylprotected thiol end groups (*R*-C6H4). Atoms are color labeled: manganese (orange), oxygen (dark red), carbon (gray), sulfur (yellow). The molecule diameter is about 3 nm. (b) Schematic drawing of the Mn_{12} molecule (red circle) trapped between electrodes. A gate changes the electrostatic potential on the molecule enabling energy spectroscopy. (c) Scanning electron microscopy image of the electrodes. The gap is not resolvable. Scale bar corresponds to 200 nm. Reproduced from Ref. [163].

If the coupling strengths increase (intermediate-coupling, $\Gamma \gtrsim E_C$), the molecular wavefunctions are replaced by hybrid states. The LUMO and HOMO (both) can be shifted closer to E_F and broadened due to hybridization. The system of the electrodes and molecule can be presented by an occupancy fraction of the new HOMO and LUMO levels, because of delocalization of the electrons between electrodes and the molecule. When an unpaired electron occupies the HOMO of the molecule, a screening of the spin happening which is known as Kondo effect [5,168-170]. This screening leads to a zero-bias conductance resonance (associated with the entangled state of electrons in the leads and in the molecule) below the Kondo temperature T_K [164]. Liang et al. [48] performed an experiment on single-molecule transistors containing individual divanadium (V₂) molecules ([(N,N',N''trimethyl-1,4,7-triazacyclononane)₂V₂(CN)₄(μ -C₄N₄)] (see figure 3.26 (a)) prepared by depositing a dilute methanol solution of the V₂ molecule onto the gold bridge on an aluminium pad with a ~ 3 nm oxide layer serving as gate electrode.



Figure 3.25. (a and b) dI/dV vs V and Vg for a Mn₁₂Ac transistor at B= 0 and 8 T. Arrows (yellow and green) indicate excited energy states. The insets depict energy diagrams for the transport features. The color scale in both panels varies from deep purple (10 nS) to light pink (200 nS). Reproduced from Ref. [166].

This paramagnetic molecule which contains two magnetic centers, can be tuned, using V_g , into two differently charged states of S = 1/2 (single occupancy) and S = 0 (due to antiferromagnetic coupling between the two magnetic centers) as shown in figure 3.26 (b). Kondo effects are observed only for non-zero spin moment states, as expected [168].



Figure 3.26. (a) Left, the structure of the V₂ molecule as determined by X-ray crystallography; red, grey and blue spheres represent V, C and N atoms respectively. Right, the schematic representation of this molecule. (b) The dI/dV values at T = 300 mK represented by the colour scale, which changes from dark red (0) to bright yellow (1.3 e^2/h). The value of e^2/h is 38.8 µS or (25.8 kΩ)⁻¹. The labels I and II mark two conductance-gap regions, and the diagrams indicate the charge and spin states of the V₂ molecule in each region. Reproduced from Ref. [48].

3.6.1 Molecular spin-valves

The molecular spin-valves (SVs) include a molecule that bridges between two electrodes. This system consists of at least one magnetic component (molecule or electrodes). Several studies on SVs [171-175] demonstrated that the electrical resistance depends on mutual alignments of the magnetizations of the electrodes and of the molecule. Recently, Rakhmilevitch et al. showed that single-molecule junctions based on nickel electrodes and benzene molecules can (ferromagnetic electrodes and non-magnetic molecules) yield a significant anisotropic magnetoresistance of up to 200 % near the conductance quantum G_0 [171].



Figure 3.27. (a) Schematic view of a benzene molecule between two Ni electrodes. (b) Selected magnetoconductance curves for different junction elongations. (c) AMR ratio for the entire stretching sequence, partially shown in (a), as a function of G_m which is the conductance of the molecular junction; the decrease in G_m is due to a monotonic increase in electrode separation. Reproduced from Ref. [171].

Their analysis indicated that due to efficient spin-selective orbital hybridization a maximal anisotropic magnetoresistance (AMR) was achieved for an optimal molecular orientation with respect to the ferromagnetic metal electrodes (see figure 3.27). There are also several studies on neutral radical molecules with gold electrodes which show pronounced Kondo features [176-178]. However up to now very few is known about the magnetoresistance (MR) of such a pure organic systems. In chapter 7, we present a comprehensive study on a single radical molecule which bridges between gold electrodes. Large positive MRs of up to 78 % was observed at 4 T which show that the unpaired electrons can cause the confinement of π -orbitals in the magnetic fields.

4. Experimental setup and fabrication method

4.1 Introduction

In this chapter the fabrication of the MCBJ electrodes, the deposition of molecules, the working principle of MCBJ, the low temperature and the electronical measurement setup are presented. Low temperature measurements have several advantages compared to room temperature. While at room temperature measurements, the metal atoms are very mobile and produce large conductance fluctuations, at low temperature the formation of highly stable metal-molecule-metal contacts that last for several hours can provide a chance for systematically studying the influence of external stimuli, such as contact geometry, change of temperature or conformation. The second important advantage is clean contacts due to the high cryogenic vacuum conditions. Finally the lower thermal noise which can drop by one order of magnitude compared to room temperature. The lower electron thermal agitation is crucial for shot noise measurements and vibronic excitations. Because of these reasons the focus of this thesis is on low temperature measurements.

4.2 Sample fabrication

A softly polished bronze wafer (60 mm in diameter and 270 µm in thickness) is covered by a spincoated layer of polyimide (~2 μ m in thickness), which serves as an electrical insulator and a sacrificial layer in the subsequent etching process. In order to polish the bronze wafer, two different grain sizes of sand papers are used, and then the wafer is polished again using a polishing paste. The spin-coated polyimide is baked at 430 °C for 100 min in vacuum. On top of these prepared wafers, a double layer of electron-beam resists (ER), MMA-MAA / PMMA, is deposited by spin-coating. Prior to performing the electron beam lithography (EBL) process, the wafer is cut into proper dimensions (4x19 mm²). After developing (development is performed in metyl isobutyl ketone (MIBK) and isopropanol (IPA), MIBK : IPA = 1:3 solution), a thin film of gold of about 80 nm is deposited using electron beam evaporation at a pressure of about 10⁻⁸ mbar. The sample is then immersed in acetone over night for the lift-off of the MMA-MAA / PMMA laver. Finally, in order to form a free-standing bridge, the samples are installed into the vacuum chamber of a reactive ion etcher (RIE). Oxygen (O₂) removes about 700 nm of the polyimide layer in microwave plasma of 50 W in oxygen flow of 50 ccm for 30 min (see figure 4.1). Figure 4.2 shows a scanning electron microscope (SEM) image of a free standing Au break-junction. Detailed recipes are listed in the Appendix A at the end of this thesis.



Figure 4.1. The procedure of sample fabrication. (a) Polished bronze wafer (yellow). (b) Polyimide (green) is spin-coated. (c) MMA-MAA (pink) / PMMA (red) layer is spin-coated. (d) The electron beam lithography is performed. (e) Development with MIBK:IPA = 1:3 solution. (f) The Au layer is deposited by thermal evaporation. (g) Lift-off of MMA-MAA / PMMA layer. (h) Dry etching about 700 nm depths of polyimide layer. (This figure was obtained from the data base of the Scheer group).



Figure 4.2. Scanning electron microscope (SEM) image of a nanoscale area of an Au break-junction.

4.3 Molecule deposition

After the etching procedure, a 1 mM dilute solution of molecules is prepared, and then the patterned substrates are immersed in the molecular solution for 12 hours. Each sample is then rinsed with a few milliliters of ethanol and gently blown dry in a stream of nitrogen gas to remove noncovalently-attached molecules from the metal surface. This method is usually applied to form a self-assembled monolayer (SAM), although it cannot be checked

with our methods, whether in fact a single and complete monolayer is formed [179,180]. This method is for chemical adsorption of the endgroup on the metal surface. In this thesis, the SAM method was used for two types of molecules, 1,4-Benzenedithiol ($C_6H_6S_2$) and spirobifluorene ($C_{41}H_{28}S_4O_4$). Figure 4.3 shows the ground geometry for both molecules. For unprotected 1,4-Benzenedithiol (BDT) molecules (chapter 6), the dilute solution of molecules in ethanol is prepared. In the case of spirobifluorene (SBF) molecules (chapter 5) we used tetrahydrofurane (THF) as solvent and then one droplet of ammoniumhydroxide (NH₄OH) is added to the solution to deprotect the acetyle group [181,182]. We received similar results by using triethylamine (ET₃N) for deprotection.



Figure 4.3. Ground geometry of (a) The 1,4-Benzenedithiol molecule. (C6H6S2) (b) The SBF molecule ($C_{41}H_{28}S_4O_4$). The acetyle endgroups are removed with one droplet of ammoniumhydroxide (NH₄OH) or triethylamine (ET₃N).

4.4 Low temperature transport measurement setup

Charge transport measurements through a single molecule were carried out in a custom designed cryogenic vacuum insert equipped with a mechanically controlled break-junction (MCBJ) system. The MCBJ mechanics is presented in figure 2.4 of chapter 2. The devices are mounted into the breaking mechanism inside an inner vacuum chamber which is evacuated to 10^{-6} mbar and then purged with little amount of He gas before being immersed into a liquid He dewar. Helium gas is for heat coupling of the sample to the helium bath. In order to reduce the noise signals, low temperature coaxial cables (stranded, silver-plated copper alloy, AWG 40/7, 100 pF/m, 6 Ω /m) were used which link the sample leads at low temperature to SMA connectors at room temperature. Every ground of the system was carefully designed to avoid ground-loops and electrical noise. All data were collected by Labview software through GPIB cables.

The first step of molecular junction characterization is the determination of preferred conductance values as mentioned in section 3.4.1. This can be done by repeatedly opening and closing the junction. The differential screw limits the maximum number of the turns of the motor to 28. Usually the first breaking occurs after 13 turns of the step motor, but this depends on the junction constriction and sample alignment.

If a molecular junction is formed, the conductance-distance curves may show a series of steps and plateaus while the electrodes are separated with a constant velocity. The plateau values and lengths are characteristic for the metal-molecule combination under study. The

breaking mechanics is controlled by a DC motor with position sensor (Faulhaber, model 22/2, reduction ratio 1:1734) connected with a vacuum feedthrough into the cryostat that drives a rotary axis, see figure 4.4 (b). The rotation of the axis is transformed into a lateral motion of a pushing rod by using a differential screw. The conductance is recorded by an automatic variable-gain source-meter (Keithley, model 6430), as shown in the schematic view of the setup in figure 4.5 (b).



Figure 4.4. (a) Sketch of the MCBJ mechanics consisting of pushing rod and two counter supports. (b) Realization of the MCBJ mechanics using a differential screw connected to a rotary axis, driven by a motor outside the cryostat. The differential screw moves the counter supports upward and downward with respect to the pushing rod, thereby bending the sample.

Technically, the conductance is measured as a function of the motor position. The motor position is then translated into an axial motion of the pushing rod. As mentioned in section 2.3, the interelectrode distance change ($\Delta s = r\Delta z$) is estimated from the displacement of the pushing rod (Δz) via an attenuation factor ($r = 6\xi tu/L^2$). Here, $t \approx 0.25$ mm is the thickness of the substrate, $u \approx 2 \mu m$ is the length of the free-standing bridge, L = 12 mm is the distance of the counter supports, and ξ is a correction factor which has a value varying from 2 to 4 depending on details of the sample. In order to measure the current-voltage (I-V), differential conductance (dI/dV) and IET spectra (d^2I/dV^2), we used a programmable dc source (Yokogawa 7651) and a low-noise current amplifier (Femto DLPCA-200) in combination with one lock-in amplifier (LIA, Stanford Research Systems SR830) followed by digital multi-meters (Keithley 2000), as illustrated in figure 4.4 (c). A DC bias added to an modulation of 5 mV (root-mean square) at a frequency of 1642 Hz was applied to the sample and the response signal then amplified by low noise current amplifier.

The adder has damping factors for DC and for the AC signals:

$$DC_{out_adder} = \frac{DC_{in_adder}}{10}$$
(4.1)

$$AC_{out_adder} = \frac{AC_{in_adder}}{10 \times \sqrt{1 + (\frac{f}{f_0})^2}}$$
(4.2)

For the adder box the the lower cut-off is $f_0 \sim 16.3$ Hz. One can also measure accurately the AC output of the adder (AC_{out_adder}) with a multimeter. We use a battery for the adder to decrease the noise, in this case the batteries need to be checked regularly. The dI/dV and IETS signals then can be calculated according to the lock-in settings and amplifier amplification:

$$\frac{dI}{dV} \left(\frac{A}{V}\right) = \frac{\text{amplifier output } (V)}{\text{amplification}_{\text{amplifier }} (V/A)} \times \frac{\text{sense}_{\text{lock-in}} (V)}{10 \times \text{expand}_{\text{lock-in}} (V)} \times \frac{1}{AC_{\text{out adder}} (V)}$$
(4.3)

$$\frac{d^{2}I}{dV^{2}}\left(\frac{A}{V^{2}}\right) = \frac{4 \times \operatorname{amplifier output}(V)}{\operatorname{amplification_{amplifier}(V/A)}} \times \frac{\operatorname{sense}(V)}{10 \times \operatorname{expand}(V)} \times \frac{1}{\operatorname{AC_{out_adder}^{2}(V)}}$$
(4.4)

The factor 4 in Eq. 4.4 is related to the Taylor expansion (see Eq. 3.19). As mentioned in section 3.4.3, to compensate the change of conductance the IETS should then be normalized as $(d^2I/dV^2)/(dI/dV)$. The wiring and electronics used for these experiments provided a cut-off frequency above 100 kHz.

The cut-off frequency can easily be checked by monitoring the AC amplitude while sweeping the frequency. After identifying a stable contact, we switch to the current noise measurement as shown in figure 4.5 (d). All unnecessary electronic devices are disconnected during noise measurements. The noise signal from the contact is first amplified 10^6 times by a current amplifier (Femto DLPCA-200) and then the noise spectrum between 1 and 100 kHz is recorded by a spectrum analyzer (Stanford Research SR780) and averaged 10,000 times as shown in figure 4.6 (a) for a gold contact with the conductance of 1.19 G_0 . At higher frequency the noise increases weakly, caused by contributions due to the wire capacitances. The wire capacitance is expected to be below 10 pF after the setup optimization, which is done by disconnecting the wire shield.



Figure 4.5. (a) Schematics of the experimental setup for investigating the electronic properties of molecular junctions. (b) DC conductance measurement setup. The conductance is recorded by an automatic variable-gain source-meter (Keithley, model 6430) (c) AC conductance measurement by lock-in technique (d) Shot noise measurement.

The excess noise is then calculated by subtracting the thermal noise $S_{\rm I}$ (V = 0). The subtraction also removes the capacitive noise that is independent of current. After subtraction, the spectra are constant in a frequency range from $f \sim 20$ to 80 kHz as expected for the shot noise (see figure 4.6 (b)). Then subtracted spectra (shot noise) are averaged over a range from 60 to 80 kHz to avoid the 1/f noise and also artifacts due to the roll-off of the wiring.



Figure 4.6. (a) Total noise spectra including the thermal noise and shot noise ranging from 1 to 100 kHz for an Au contact with zero bias conductance of 1.19 G_0 . (b) Excess noise spectra after subtraction of the thermal noise of the system. (c) Shot noise as a function of the bias voltage applied across the gold junction. The red line is the fit to the full expression of noise, Eq. 3.33 which gives two channels with transmission probabilities of $\tau_1 = 1$ and $\tau_2 = 0.19$.

Figure 4.6 (c) shows the shot noise as a function of the bias voltage applied across the junction. The red line is the fit to the full expression of noise, Eq. 3.33 which gives two channels with transmission probabilities of $\tau_1 = 1$ and $\tau_2 = 0.19$. The only correction for the excess noise is a change of noise according to a change in conductance:

$$S_{I \text{ corrected}} = S_{I \text{ excess}} - (G(V)^2 - G(0)^2) \times n_v^2$$
(4.5)

Here $n_v = 4.5 \text{ nV}/\sqrt{\text{Hz}}$ is the amplifier input voltage noise. This correction for a contact with a conductance of 1.19 G_0 is three orders of magnitude smaller than the excess noise at the same voltage. The stability of the contact was checked before and after the noise measurements as shown in figure 4.7.



Figure 4.7. Differential conductance (dI/dV) as a function of bias voltage V, measured by the lock-in technique for the Au atomic contact, discussed in figure 4.6. Black and red curves are conductance traces recorded before and after the noise measurements, respectively.

5. Identification of the Current Path for a Conductive Molecular Wire on a Tripodal Platform

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Author contribution: M. A. K carried out the experiment, analysed the data, and prepared the manuscript.

In this chapter, the charge transport measurements and calculations for a new tripodal platform based on a rigid 9,9'-spirobifluorene equipped with a phenylene-ethynylene wire is presented. The transport experiments are performed with the help of the low-temperature mechanically controlled break junction technique with gold electrodes. By combining experimental and theoretical investigations of elastic and inelastic charge transport, we show that the current proceeds through the designated molecular wire and identify a binding geometry that is compatible with the experimental observations. The conductive molecular wire on the platform features a well-defined and relatively high conductance of the order of 10^{-3} G₀ despite the length of the current path of more than 1.7 nm. Our findings demonstrate that the tripodal platform is suitable to incorporate functional units like molecular switches or sensors.

5.1 Introduction

Intensive studies on single-molecule junctions have been performed to explore the implementation of molecular-scale devices and to understand how the molecules transport charges [69,183]. Rod-like molecules with delocalized π -systems are the ideal model compounds to form wires to be used in electronic applications due to their expected high conductance. However they have the tendency to bind to the substrate, driven by van der Waals interactions. Therefore a more perpendicular arrangement of the wire with respect to the surface is desirable to separate the π -system from the substrate and to establish a connection to another electrode. Only in this way the entire dimension of the molecule can be exploited, e.g. for incorporating functional units like switches. Such a geometric arrangement is the goal behind using multipodal molecules, [184] the electronic properties of which have been studied in recent years mainly by scanning tunnelling microscopy [185-190]. Tripodal molecular platforms (with three "legs"), featuring a rigid molecular wire ("arm") that points almost perpendicular to the surface, appear as ideal candidates to establish a conducting path between two electrodes and have been investigated before [184-197]. However, in practically all cases there is no delocalized electronic system extending entirely from the metal surface over the legs to the arm. In some cases, the arm,

being upright, was not conjugated with the legs [187,190-193,195,197] or the arm, being conjugated with the legs, was lying flat on the surface, making it impossible to form a contact to the counter electrode [186]. To solve this problem, a 9,9'-spirobifluorene (SBF) platform has been introduced that takes into account these aspects [198]. In Ref. [198] scanning tunnelling experiments have been reported which show the good electronic coupling of the spiro platform to the metal substrate while the envisaged full conjugation from the arm to the surface could not be shown. To address the question of the conjugation of the arm, we chose the mechanically controllable break junction (MCBJ) technique that enables to form robust single-molecule junctions at low temperature. We present the first experimental and theoretical electrical transport studies on this spirobifluorene system, where, at variance to Ref. [198], both the legs of the molecular platform and the molecular arm are rigidly coupled to two different electrodes by thiol groups. We demonstrate that the conductance of these junctions is relatively high in view of the extent of the molecule. Furthermore, we reveal the current path and the most-likely bonding geometry by analyzing the inelastic electron tunnelling (IET) spectra as a function of stretching and by comparing with atomistic ab initio simulations.

5.2 Results and discussion

The SBF molecule, featuring three legs and shown in figure 5.1 (a), is designed to be used on planar surfaces as well as on tip-like electrodes. We use the MCBJ technique at 4.2 K as illustrated in figure 5.1(b). As electrode material we use gold and employ the well-studied gold-thiol chemistry for providing the electronic coupling. Further details of the measurement setup, sample fabrication and junction assembly are described in section 4.3 and 4.4 in chapter 4. In order to determine the characteristic conductance values of the Au– SBF–Au junctions, they were repeatedly opened and closed while recording the conductance, as shown in figure 5.1(c).

The conductance histogram in figure 5.1 (d) is compiled from 190 opening traces, recorded on three different samples, without trace selection. It shows a broad peak close to $10^{-3} G_0$ where $G_0 = 2e^2/h$ is the conductance quantum (e = |e|: elementary charge, h: Planck constant). The width of the peak in the histogram is due to the substructure of the plateaus in the conductance-distance traces, i.e. small steps and an overall negative slope of the plateaus (see figure 5.1(c)). The average plateau length is comparable to or larger than the one of the plateaus around $G = 1 G_0$.

The conductance of the molecular junctions generally decreases while stretching, as was observed before for several other complex species [199-203]. In analogy to metallic atomic contacts [204], the small steps presumably indicate rearrangements of the atoms in the electrodes or sliding of the thiol bond along the metal electrodes [83], while the inclination reveals a gradual change of the junction. We performed control experiments on two types of molecules. The first one is a monopodal molecule, displayed in figure 5.2 (a), with the same backbone and length as the SBF. Figure 5.2 (b) and (c) show selected opening traces as well as a conductance histogram. We find similar conductance values as for the full SBF, suggesting that the current path for both is the same.



Figure 5.1. (a) Geometry of the studied SBF molecule introducing the terms "legs", "arm", and "backbone". The hydrogen atoms at the outer ends of the legs and the arm are removed when establishing contact to the metal electrodes. (b) Sketch of the MCBJ setup. The upper part shows a possible junction geometry, where the sulphur atoms at both ends bind to a hollow site of the pyramidal Au electrodes. (c) Conductance-distance traces measured without molecules (black) and with SBF molecules (red). (d) Conductance histogram of Au–SBF–Au molecular junctions.

The preferred conductance value of this backbone molecule is $G_{\text{backbone}} \approx 10^{-3} G_0$, close to those of the SBF molecule. However, the trapping rate is only 8%, i.e. considerably lower than those for SBF, where the trapping rate amounts to 20%, as revealed by the rather small height of the maximum compared to the weight of the single-atom contacts with conductances around 1 G_0 . The plateau length is roughly a factor of 2 larger than those of the last plateaus of the gold contacts, in agreement with the molecule length of 1.7 nm and the fact that gold forms chains with up to 7 atoms in length [204].

The second control molecule features a cyano end group at the arm instead of a thiol, as shown in figure 5.3 (a). Conductance-distance traces and the related conductance histogram are presented in figure 5.3 (b) and (c). For this molecule the trapping rate is 12%, and we find a broad distribution of conductance values between 10^{-6} and $1 G_0$. This finding indicates that the molecules do not favor a particular robust junction geometry, presumably due to the weak physisorption of the cyano end group at low temperature. The weak maximum around $4 \cdot 10^{-2} G_0$ is statistically not significant.



Figure 5.2. (a) Scheme of the monopodal molecule with the same backbone and length as SBF. (b) Conductance traces for SBF monopodal molecules. (c) Conductance histogram for the molecule shown in (a).



Figure 5.3. (a) In this molecule the end group of the arm is given by a cyano. (b) Conductance traces for the cyano-ended molecule. (c) Conductance histogram for the molecule shown in (a) with the cyano end group.

The highly conductive junctions with $G > 10^{-1} G_0$ may correspond to tunnelling between the Au electrodes, eventually through a barrier given by non-specifically absorbed molecules. These control experiments show that a robust binding geometry is necessary to provide well-defined conductance values and highly conductive molecular wires.

The results for the cyano-terminated molecule, that is supposed to bind weakly to one Au electrode via the nitrogenlone pair [205,206], support the expectation that a robust binding of the arm to the gold electrode is necessary to achieve a well-defined conductance of the junction.

To obtain a deeper understanding of the observed conductance characteristics, we performed a theoretical modelling of the system at the atomic scale. For geometrical optimizations we used density functional theory (DFT), while the linear response transport calculations within the Landauer formalism are based on self-energy corrected DFT (DFT+ Σ) and nonequilibrium Green's functions (NEGF) [140,206]. Further technical details are deferred to the appendix B, section B1.



Figure 5.4. (a) The SBF molecular junction on an Au (111) surface contacted by an Au tip. (b) Dominant transmission eigenchannel incoming from the bottom electrode, evaluated at the Fermi energy for the SBF molecule in junction (a). The backbone of the molecule connected to pyramid-shaped electrodes in (c) HH and (d) TT positions. (e) Stretched TT junction, TT'. (f) Computed transmission curves for the SBF molecule and its backbone in HH, TT, and TT' configurations in the DFT+ Σ framework. The vertical dashed black line indicates the Fermi energy $E_{\rm F}$.

The SBF molecule is shown in its relaxed position on an Au(111) surface in figure 5.4 (a). To analyse the electron transport through SBF, we calculated the wave-functions of the dominant transmission eigenchannels. These eigenchannels constitute evanescent waves, decaying along the molecular backbone [207,208]. For SBF we find transmission probabilities $\tau_1 = 1.3 \times 10^{-3}$ and $\tau_2 = 3.8 \times 10^{-7}$ of the first and second eigenchannels at a total transmission of $\tau = 1.3 \times 10^{-3}$ at the Fermi energy. Due to the small contribution of the second and all other transmission channels, we concentrate on the single dominant channel in the following.

As it is shown in figure 5.4 (b), there is basically no weight of the wave-function on those two legs that do not belong to the molecular backbone indicated in figure 5.1(a). This is expected, since these legs are oriented perpendicular to it, decoupling the π -systems of the two spirobifluorenes. Furthermore, they are electronically decoupled through an insulating sp3-hybridized carbon atom that connects them. On tip-like electrodes, as used in MCBJ experiments and suggested in figure 5.1(b), the coupling between the Au electrodes may be provided by only one of the legs. For these reasons we will limit most of our further calculations regarding the electronic transport properties to the molecular backbone to reduce the computing time. There are different possibilities how the molecule can connect to the electrodes [88,206,209].

In addition to the SBF configuration in figure 5.4 (a), we take into account several further possible situations, in which the backbone molecule is bound to the electrodes in the hollow-hollow (HH) or top-top (TT) positions, see figure 5.4 (c) and (d), for the equilibrium configurations. Here, the sulphur atoms bind symmetrically and covalently at both sides either to three Au atoms or to a single Au tip atom. We also calculate the conductance of a stretched TT (TT') junction, shown in figure 5.4 (e), where the molecule is oriented quite parallel to the vertical z direction, comparable to HH. The transmission

curves for SBF, HH, TT, and TT' structures are shown in figure 5.4 (f). We have verified that the obtained configurations HH, TT and its stretching path to TT' are not prohibited by steric hindrance due to the presence of the two electronically uncoupled legs. In all the situations the transport is off-resonant and the highest occupied molecular orbital (HOMO) resonance is closest to the Fermi energy, indicating hole transport. The predicted linear conductance values of SBF, TT, and HH are comparable and amount to $G_{\text{SBF}} = 1.1 \times 10^{-3}$ G_0 , $G_{\text{HH}} = 1.0 \times 10^{-3}$ G_0 , $G_{\text{TT}} = 1.4 \times 10^{-3}$ G_0 , and $G_{\text{TT}'} = 3.0 \times 10^{-4}$ G_0 . They hence agree well with the experimentally observed conductance plateau of around $G_{\text{exp}} \approx 10^{-3}$ G_0 .

Examining the transmission curves in detail, HH exhibits the largest distance between the HOMO-related resonance and the Fermi energy but a relatively large broadening, resulting in a linear conductance comparable to those of SBF and TT. In addition to the HOMO and the lowest unoccupied molecular orbital (LUMO) resonances, a pronounced shoulder develops around $E_F + 1$ eV for the TT configuration, the onset of which contributes to the linear conductance. When elongating this junction to the TT' situation, the conductance decreases, because the HOMO-LUMO gap opens and since the molecular transport resonances narrow. This is expected since, as shown in figure 5.4 (d), the current path is mainly perpendicular to the z direction for the TT geometry. This facilitates electronic overlap of the molecular π -system of the platform with the metal electrodes. If the junction is elongated, this overlap is gradually reduced, resulting in a decaying conductance with distance as observed for TT' and in the experiments in figure 5.1 (c). The transmission curves in figure 5.4 (f) are all obtained within the DFT+ Σ framework. Those of the mere DFT calculations are discussed in section B1 of the appendix B. However, they predict unrealistically high conductance values, since they position the HOMO resonances very close to the Fermi energy.

To clarify which binding geometry is realized in the experiments, the *I-V* characteristics of stable junctions on a conductance plateau were measured using a lock-in technique (see section 4.4). Examples are shown in figure 5.5 (a) for three contacts with conductance values of $2.9 \cdot 10^{-3} G_0$, $1.7 \cdot 10^{-3} G_0$ and $7 \cdot 10^{-4} G_0$ obtained while stretching a particular molecular junction. The *I-V* curves were successfully fitted using the single-level model [69,88,206].

This model assumes a single molecular orbital at energy E_0 , coupled to each lead via the coupling constants Γ_L and Γ_R . This yields a resonance with Lorentzian shape for the transmission (See Eq. 3.15). The current is calculated by integrating over the bias window, using the Landauer formula. From the fitting procedure we obtain the (absolute) value for the energy level E_0 and those of the level broadening ($\Gamma = \Gamma_R + \Gamma_L$) that are displayed in figure 5.5 (b). If the molecule is symmetrically coupled to both electrodes, the two coupling constants are the same ($\Gamma/2 = \Gamma_R = \Gamma_L$) and the *I-V* characteristic is (anti)symmetric (I(V) = -I(-V)). In our case the *I-Vs are usually slightly asymmetric with ratios* $\alpha = \Gamma_R / \Gamma_L$ (or $\alpha = \Gamma_L / \Gamma_R$) ranging from 0.85 to 1. (Note that the ratio is chosen such that the bigger value of the coupling constants is in the denominator). These are typical values for single-molecule junctions, in which the coupling is provided by the same binding motif (here Au-S) at both ends of the molecule. Since the molecular backbone of the SBF molecule is not fully symmetric, we expect slightly asymmetric *I-Vs* [69].



Figure 5.5. (a) *I-V* curves (symbols) of Au-SBF-Au junctions in different transmission regimes. They are fitted using the single-level model (lines) in the voltage range from -0.45 V to 0.45 V. (b) Experimental and theoretical fit parameters for a stretched contact. The best-fit parameters for the experiment are $\Gamma_{\rm R} = 17$ meV, $\Gamma_{\rm L} = 14$ meV, $E_0 = 610$ meV for $G = 2.9 \cdot 10^{-3} G_0$, $\Gamma_{\rm R} = 15$ meV, $\Gamma_{\rm L} = 12$ meV, $E_0 = 670$ meV for $G = 1.7 \cdot 10^{-3} G_0$, $\Gamma_{\rm R} = 12$ meV, $\Gamma_{\rm L} = 9.5$ meV, $E_0 = 770$ meV for $G = 7 \cdot 10^{-4} G_0$, while the Lorentzian fit for the TT and TT' configurations from Fig. 5.4 (d,e) yields $\Gamma_{\rm R} = 17$ meV, $\Gamma_{\rm L} = 14$ meV, $E_0 = 760$ meV for TT and $\Gamma_{\rm R} = 10$ meV, $\Gamma_{\rm L} = 9$ meV, $E_0 = 950$ meV for TT'. (c) The position of the molecular level (E_0 , left axis, black squares) and the level broadenings ($\Gamma_{\rm R}$ and $\Gamma_{\rm L}$, right axis, green and magenta triangles) are obtained by fitting the *I-V* curves in the transmission range of the inclined conductance step.

This finding is also supported by the transmission curves shown in figure 5.4 (f), where the resonances of the HOMO-related transmission peak do not always reach unity. While this observation holds for all the junction configurations, it is most pronounced for SBF. As figure 5.5 (b) shows, upon elongating a particular junction, the transmission decreases (inclined molecular conductance plateau) and E_0 is moving farther away from the Fermi energy while the level broadenings strongly decrease. To examine the experimental observation, we fitted the theoretical transmission curves by a Lorentzian (see section B2 in the appendix B). The theoretical values of E_0 and Γ_L , Γ_R for TT and TT' confirm the experimental trends upon stretching. Figure 5.5 (c) shows the results for E_0 and Γ_L , Γ_R extracted from a set of 30 *I-V*s, obtained for three different samples and thus independently arranged molecular junctions. In this larger ensemble the trend regarding the couplings is

maintained while basically no transmission dependence of E_0 is observed in agreement with reports on other conjugated molecules [88,157,202,206,210]. This analysis reflects on the one hand that the difference in binding configurations gives rise to a broader variation of E_0 than the slight changes caused by stretching a junction. On the other hand stretching an individual junction gives important information regarding the binding geometry of that particular junction realization. In the present case the increase of E_0 was solely observed when stretching from TT to TT', while for HH the equilibrium position was already very elongated and no further stretching was possible. The *I-Vs* remain only slightly asymmetric upon stretching as revealed by the small and almost constant difference of the coupling parameters of 10 to 15%. Since the asymmetry does not increase with decreasing transmission, we argue that it is an intrinsic effect due to the structure of the backbone and not caused for instance by the weakening of the bonds. To further test the electronic path and the binding scheme of the junctions, we study the IET spectra. The vibrational modes of the molecule are detected by their effect on the current-voltage characteristics. In this process the excitation of a molecular vibration by the charge carriers gives rise to a peak at positive bias in the typical off-resonant situation, and a dip at negative bias [82,84]. To date, several IET studies have been performed for testbed molecules such as alkanes and benzene [88,179,211,212] and in smaller functional molecules like the azobenzenes [200]. However, IET measurements on complex tripodal molecules have not been reported so far. Many vibrational modes with similar energy exist and a high resolution of the spectroscopy is required for resolving them.



Figure 5.6. (a) Experimental IET spectrum of a Au-SBF-Au junction (black) with a conductance of $4 \cdot 10^{-3} G_0$ (corresponding to the green curve in panel (b)) shown together with a symmetrized curve (red) with respect to the bias polarity. (For negative bias polarity the sign of d^2I/dV^2 has been inverted for better illustrating the symmetry.) (b) Comparison of experimental (coloured lines) and theoretical (black line, TT position) IET spectra. The arrows show the peak positions in the experimentally and theoretically obtained spectra.

Figure 5.6 (a) shows an experimental IET spectrum of an Au-SBF-Au junction recorded for the conductance value of $4 \cdot 10^{-3} G_0$. More examples are shown in figure B5 in the section B4 of appendix B. The spectrum is highly symmetric, implying that the IET signals

originate indeed from the excitation of molecular vibrations [82,211-214]. At variance to Raman or infrared spectra which consider the coupling of vibrations and electric dipole transitions, the measurements depend on the electron-vibration (EVIB) coupling strength and thus the probability by which the modes can be excited by electron scattering. For the theoretical description of the inelastic corrections in this system, we include the EVIB interaction at the level of the lowest-order expansion (LOE).

| Modes | Description | Theory | Experiment |
|-------------------------|-----------------------------------|--------------------|----------------|
| LOP (Au- | Au-Au longitudinal optical phonon | 0.01-0.02 eV | 0.01-0.016 eV |
| v (Au-S) | Au-S stretching | 0.037 eV, 0.046 eV | 0.038-0.044 eV |
| v (C-S) | C-S stretching | 0.052 eV, 0.075 eV | 0.054-0.068 eV |
| γ _{OP} (C-H) | C-H out of plane bending | 0.094-0.11 eV | 0.097-0.108 eV |
| $\gamma_{\rm IP}$ (C-H) | C-H in plane bending | 0.12 eV, 0.16 eV | 0.144-157 eV |
| v (C=C) | C=C stretching | 0.18-0.2 eV | 0.185-0.193 eV |
| v (C≡C) | C≡C stretching | 0.27 eV | 0.274-0.283 eV |
| v (C-H) | C-H stretching | 0.3-0.38 eV | 0.35 eV |

Table 5.1. Summary of the vibrational mode assignment in the IET spectra for SBF molecular junctions. Peak positions in the spectra are identified by our theoretical IET calculations.

For a detailed discussion of the theory, we refer to Refs. [90,215,216] and the appendix B. In figure 5.6 (b) we show several experimental (coloured lines) IET spectra and a theoretical one (black line). The main character of those modes which are responsible for the peaks in the spectra is indicated. They are identified by the comparison between theory and experiment and are summarized in Table 5.1.

The peak resulting from the v(Au-S) stretching mode shows that the molecule is robustly bound to the Au atomic electrodes. Both experiment and theory show a pronounced peak near 270 to 280 mV, which is related to the C=C stretching mode. In addition we consider the case SBF', where all three legs of the molecule are coupled to one electrode, while the counter electrode couples to the top of the spirobifluorene foot, see figure B1 (b) and figure B2 (b) in the appendix B. In this configuration the mode is shifted to 250 mV and reveals much smaller amplitude, as expected if it is excited indirectly without being part of the current path. Thus the IET spectra give another indication that the current proceeds indeed through the arm of the molecule (figure 5.1 (a)) as conceived when designing the molecule. The comparison between calculated IET spectra for SBF, HH and TT configurations is shown in figure 5.7 as expected, the peak positions are the same for all three configurations, but the amplitudes are varying since they are determined by EVIB couplings that depend on the configuration. Interestingly the C-H stretching mode around 0.37 V is strongly suppressed in the HH configuration and in the SBF as compared to TT. Since in the experiments we do observe pronounced peaks in this voltage range, we conclude that the measured junction is compatible only with the TT configuration.



Figure 5.7. Calculated IET spectra for SBF, HH, and TT configurations. The spectra are offset for better visibility. The inset shows the magnified part of the IET spectrum for HH in the voltage range of 0.34 to 0.39 V, where the peaks have a lower intensity compared to the rest of the peaks and compared to the TT configuration.

5.3 Conclusions

To summarize, we have presented a thorough characterization of the transport properties of single-molecule junctions of 9.9'- spirobifluorene, contacted to mechanically adjustable Au electrodes. The molecule features a tripodal footprint and an arm that is connected in the para position to the foot and that establishes a conjugated conduction path all the way from one of the legs to the end of the arm. When coupling this molecule via thiol end groups to the Au electrodes, a relatively high linear conductance of 10^{-3} G₀ is obtained. In view of the length of the molecular wire of 1.7 nm this implies a current path with a high degree of conjugation that is comparable to the one of the monopodal version of the molecule with a single leg. Our comprehensive data sets reveal that both the conductance values as well as their variation with stretching can be consistently explained by assuming a particular binding geometry, in which the conjugated foot and the arm are coupled to a single Au atom (TT) on either electrode. Besides a higher trapping rate of the tripodal version (20%) compared the monopodal version (8%), both molecules perform comparably well. Our findings also imply that the conductive arm encloses a finite angle with the surface, when deposited on a flat surface as required for scanning tunnelling microscope experiments. This property makes the spirobifluorene platform suitable for hosting functional units like switches, rectifiers or photosensitive moieties.

6. Shot Noise of 1,4-Benzenedithiol Single-Molecule Junctions

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Author contribution: M. A. K carried out the experiment, analyzed the data and prepared the manuscript.

The shot noise on single-molecule Au-1,4-benzenedithiol (BDT)-Au junctions, fabricated with the mechanically controllable break junction (MCBJ) technique at 4.2 K in a wide range of conductance values from 10^{-2} to 0.24 conductance quanta are presented in this chapter. The experimental set is presented in section 4.4. This simple measurement scheme uses a current-amplifier and a spectrum analyzer, and that does not imply special requirements regarding the electrical leads. The experimental findings provide evidence that the current is carried by a single conduction channel throughout the whole conductance range. This observation suggests that the number of channels is limited by the Au-thiol bonds and that contributions due to direct tunneling from the Au to the π system of the aromatic ring are negligible also for high conductance. The results are supported by quantum transport calculations using density functional theory (DFT).

6.1 Introduction

The determination of the quantum mechanical transport channels and their transmission probabilities requires additional information beyond the linear conductance [34,204]. So far, the two best established methods include the analysis of the superconducting subharmonic gap structure [41,63] and the investigation of the shot noise [91,114,115,119,138-141]. While the first one has been mainly used for atomic contacts [204] and for the high-conductance molecule C_{60} [217], the shot noise analysis has been applied to atomic contacts [114,115,119,138] as well as to single-molecule junctions [91,139-141]. However most of the experiments on single molecules concentrate on a rather narrow transmission range or study highly conductive molecules with a conductance very close to 1 G_0 , where $G_0 = 2e^2/h$ is the conductance quantum, e=|e| is the elementary charge and *h* is Planck's constant.

Shot noise results from the discrete nature of the electronic charge. For a system that has N conduction channels with the transmission probabilities τ_n and at finite temperature T, the total current noise power (S₁) can be expressed as Eq. (3.33) and the Fano factor (F) as Eq. (3.37). It is clear that for a perfect transmission of electrons all shot noise is suppressed, because there are no fluctuations in the occupation numbers of left and right moving electrons. Several experiments on atomic-scale junctions showed this suppression at low temperatures [114-118] and also at ambient conditions [119,120].

There is a longstanding puzzle regarding "the" conductance value of an Au-BDT-Au contact, because both, the theoretical predictions as well as the experimental findings are wide spread [93,94,218-221]. In a previous work we suggested that the conductance may vary over three orders of magnitude upon changing the junction geometry [88]. In particular we showed that also the high-conductance state of Au-BDT-Au junctions can be distinguished from mere Au-Au contacts because we clearly detected the vibrational modes of BDT in the IET spectra [88]. From the successful fitting with the single-level model [69,88,206] and the sign of the IET peaks we concluded that these junctions were single-molecule junctions, but unambiguous clarification requires the determination of the number of conduction channels. Therefore we refine here the procedure of Ref. [88].

6.2 Results and Discussion

The measurements of shot noise on Au-1,4-benzenedithiol (BDT)-Au junctions at low ($G \approx 10^{-2} G_0$) and at high ($G > 0.1 G_0$) conductance states, acquired at 4.2 K using a versatile setup, which enables us to determine noise in a broad range of conductance values without the necessity of double wiring and performing cross-correlation [114-118] and without going to high frequency measurements [119,120]. In brief, the measurement scheme relies on careful calibration of all unavoidable noise contributions [222]. The current through the contact is first amplified using a transimpedance amplifier. This signal is fed to a spectrum analyzer that measures the noise spectrum between 1 and 100 kHz. The signal shows contributions of 1/f noise at low frequencies and rolls off above roughly 90 kHz. We limit the frequency range to the white part of the spectrum to determine the shot noise and the thermal noise. We repeat the measurement for different bias voltages. The shot noise is then calculated by subtracting the thermal noise $S_I(V=0)$.

The measurements are performed using the MCBJ technique, by gently breaking an atomic-scale contact between gold wires. After identifying a stable contact, the current-voltage characteristics (*I-V*s), the differential conductance (d*I*/d*V*), the IET spectrum $(d^2I/dV^2/(dI/dV))$, and the shot noise S_I from the contact are measured. The details of the measurement setup are described in section 4.4. The *I-V*s and d*I*/d*V*s are determined before and after the noise measurements to make sure that the contact was stable during the measurement period. We found the highest probability for stable contacts in the high-conductance range of around $G \approx 0.2$ to 0.24 G_0 . In the low conductance range stable contacts were found mostly around $G \approx 0.01 G_0$.

In order to extract the Fano factor from the excess noise, we follow a procedure presented by Kumar et al [86], for or Au atomic contacts. To simplify the fitting, two dimensionless, voltage-dependent parameters Y(V) and X(V) are introduced (see equations 3.39 and 3.41). Using these definitions, expression (3.33) is reduced to the expression (3.41).



Figure 6.1. (a) The excess noise plotted for the reduced parameters X and Y. The red line is the fit to the data and gives a Fano factor of $F = 0.130 \pm 0.001$ for two channels with transmission probabilities of $\tau_1 = 1$ and $\tau_2 = 0.19$. The blue line is the calculated excess noise for $\tau_1 = 0.97$ and $\tau_2 = 0.22$. (b) Fano factor as determined for fifty atomic gold contacts measured for bias voltages below 10 mV (black circles). The solid lines are calculated, assuming a contribution of an additional channel with the indicated percentage to the almost fully open nth channel, before it saturates completely.

The first system, which we investigated, was the well-studied gold contact that serves as a reference system. We found good agreement for it with literature. Figure 6.1 (a) shows a gold contact with a conductance of 1.19 G_0 and a Fano factor of 0.13, as obtained from the slope of the linear fit to expression (3.41). This fit shows one fully open channel with transmission probability 1 and a partially open one with transmission 0.19. We tentatively calculated the excess noise for a channel combination of $\tau_1 = 0.97$ and $\tau_2 = 0.22$ (see blue line in figure 6.1 (a)), corresponding to a non-perfect saturation of the dominating channel as studied for Au contacts before [114]. This line is clearly above the experimental data. No other combination of transmissions of two channels describes the experimental data more accurately than $\tau_1 = 1$, $\tau_2 = 0.19$. The Fano factor with the accuracy of 1 percent for a collection of atomic gold contacts in the conductance range between 0.5 and 2 G_0 is given in figure 6.1 (b).

The noise is suppressed at integer values of G_0 , which demonstrates the quantummechanical suppression of noise due to the presence of fully transmitted channels. All data points lie on or above the expected curve for *n* channels (for $(n-1) < G/G_0 \le n$), where *n*-1 channels become fully saturated before an additional channel partially opens (black line, labeled 0%). The colored lines are calculated assuming that *n*-1 channels are fully open, while a further channel opens before the already opened nth channel is fully saturated [114]. As it is visible from the plot, the contribution of this additional channel varies between 0 and 6%. These findings are consistent with those reported in Ref. [114], where atomic Au contacts were studied, formed with the MCBJ technique and made from macroscopic gold wires. There, a typical admixture of the additional channel of 3% was observed. Since the elastic mean free path is shorter in lithographic break junctions, that we investigate here, due to disorder, we expect a higher admixture than for wire MCBJs [223]. Figure 6.2 (a) shows the *I-V* for a contact with a conductance of 0.23 G_0 . The single-level

fit to the *I-V* yields an energy level of $E_0 = 0.25$ eV and the coupling constants of $\Gamma_R = 0.076$ eV and $\Gamma_L = 0.067$ eV (corresponding to a slight asymmetry $\alpha = \Gamma_L/\Gamma_R = 0.88$) in agreement with the earlier findings and demonstrating that the molecule is bound to the electrodes almost symmetrically. Further support that charges flow through the molecule was obtained by studying the IET spectra. The vibrational modes of the molecule are detected by their effect on the current through the molecular junction. In the off-resonant situation $\tau_n \ll 1$ and for a rather symmetrical coupling to both electrodes $\alpha \approx 1$, the excitation of a molecular vibration by the charge carriers gives rise to a peak in the d²*I*/d*V*² [82,212].



Figure 6.2. (a) Experimental *I-V* of an Au-BDT-Au junction with a conductance of 0.23 G_0 (black symbols) fitted with the single level model (solid red line). (b) Experimental (black) IET spectrum for the same junction and theoretical (red) one for a configuration with stretching length d = 6.4 Å and G = 0.26 G_0 for in TT configuration, calculated for T = 4.2 K and an AC modulation of 5 mV as used in the experiment. Pronounced peaks at the voltages corresponding to the known vibrational modes of Au-BDT-Au junctions confirm the presence of the BDT molecule between two Au leads.

For the theoretical description of the IET spectra, the optimization of the geometry as well as accurate evaluations of the vibrational modes and of the electron-vibration (EV) coupling constants are necessary. These quantities can be calculated using a combination of DFT and NEGF [215,224]. For the quantum transport calculations in this work, we apply the quantum chemistry package TURBOMOLE 6.5 [160]. The DFT calculations to obtain self-consistent electronic structures and optimized geometries are performed with the exchange-correlation functional PBE [225]. We utilize the def-SV(P) basis set [226], which is of split-valence quality with polarization functions on all non-hydrogen atoms. Elastic charge transport is determined as described in Ref. [140], while the inelastic interactions due to the EV coupling are treated at the level of the so-called lowest-order expansion (LOE) [215]. In figure 6.2 (b) we show an experimental (black line) IET spectrum and a theoretical one (red line). The character of those modes, which are responsible for the peaks in the spectra, is indicated. The assignment of the vibrational modes according to previous experimental results and our theoretical calculations is summarized in Table 6.1. Next the excess noise was measured for the same contact as studied in figure 6.2.

| Modes | Description | Peak position | Theory (mV) | Literature values (mV) |
|----------------|--------------------|---------------|---------------|-------------------------|
| LOP | Au-Au longitudinal | 10-12 | 10-17 | 10-20 [86,87,215] |
| v(Au-S) | Au-S stretching | 37-44 | 22-38 | 35-45 |
| | | | | [81,88,179,220,227,228] |
| v(C-S) | C-S stretching | 50-68 | 32-45 | 60-70 [88,227,228] |
| δ (C-C- | C-C-C bending, in | 81-100 | 80-100 | 85-95 |
| C) | plane | 01 100 | 00 100 | [81,88,179,220,227,228] |
| S(C II) | C II in plana | 120-135, 150- | 120-130, 140- | 117-124,146-154 |
| 0(С-П) | C-ri ili pialle | 160 | 160 | [81,88,179,220,227,228] |
| v(C=C) | C=C stretching | 170-197 | 180-195 | 185-195 |
| | | | | [81,88,179,220,227,228] |

Table 6.1. Summary of the vibrational mode assignment in the experimental IET spectra for BDT molecular junctions, as shown in figures 6.2 (b), 6.4, and C.3 in the appendix C. In the experiments v(Au-S) and v(C-S) appear blue shifted compared to theory in agreement with literature. The data has been collected over four contacts.

The Total noise spectra including the thermal noise and shot noise between 1 and 100 kHz is shown in figure 6.3 (a) for an Au-1,4-benzenedithiol (BDT)-Au contact. Above a frequency of $f \approx 10$ kHz the noise increases weakly, caused by contributions due to the wire capacitances. The excess noise is then calculated by subtracting the thermal noise $S_{l}(V=0)$. The subtraction also removes the capacitive noise that is independent of current. After subtraction the spectra are constant in a frequency range from $f \sim 20$ to 80 kHz as expected for thermal noise and shot noise. They are then averaged over a range from 60 to 80 kHz to avoid the 1/f noise and also artifacts due to the roll off of the wiring, the cut-off frequency of which is estimated to be > 180 kHz, see figure 6.3 (b). In figure 6.3 (c) and (d) we plot the noise in two different ways according to Eq. (3.33) and (3.41). The red lines are calculated according to these equations, assuming a single channel with transmission $\tau_1 =$ 0.23. As visible, this assumption yields an excellent agreement with the experimental findings. We tentatively calculated the noise for several channels with the same total transmission. All combinations of transmissions with more than one channel lead to a noise higher than compatible with the experimental observation. To exemplify, the green and blue lines in figure 6.3 (d) are calculated shot noise curves for contributions of two and three channels with equal transmission. The results support our claims that also the highly transmissive Au-BDT-Au contacts exhibit a single transport channel. We repeated the experiment for several contacts with conductance $G > 0.01 G_0$.



Figure 6.3. (a) Total noise spectra including the thermal noise and shot noise ranging from 1 to 100 kHz for an Au-BDT-Au contact with zero-bias conductance of $G = 0.23 G_0$. (b) Excess noise spectra after subtraction of the thermal noise of the system. (c) Shot noise as a function of the bias voltage applied across the Au-BDT-Au junction. The zero bias conductance for this junction is 0.23 G_0 . The red line is the fit to Eq. (3.33), yielding $\tau_1 = 0.23$. (d) The excess noise, plotted for the reduced parameters X and Y. The red line is the fit to the data and gives a Fano factor of F = 0.77 for a transmission probability of $\tau_1 = 0.23$. The green line is the calculated excess noise for two channels with the same transmission probabilities of $\tau_1 = \tau_2 = 0.115$ and the blue line is those for three channels with $\tau_1 = \tau_2 = \tau_3 = 0.0766$.


Figure 6.4. (a), (b), (c) and (d) are the IET spectra for four Au-BDT-Au single-molecule junctions with conductance values of 0.244, 0.15, 0.10 and 0.037 G_0 . (e), (f), (g) and (h) are the corresponding excess noise, plotted for reduced parameters X and Y, respectively.

Figure 6.4 displays the IET spectra (left) and the shot noise (right) of 4 stable Au-BDT-Au contacts in a conductance range of 0.05 to 0.24 G_0 . The contacts have been broken fully to obtain a tunnel contact and closed again to reach a conductance of more than 10 G_0 between each measurement. In all cases the observed noise is best described by a single channel, but contributions of additional channels with transmissions in the order of 10% of the dominating one cannot be fully excluded because of the finite measurement resolution. For decreasing conductance the Fano factor increases to 1, corresponding to the full shot noise, and a disentanglement of several channels is not possible, although the measurement

scheme itself works well for conductance values in the range of $0.01 < G/G_0 < 0.1$. Table 6.2 shows the transmission probabilities and the Fano factor for five BDT single-molecule junctions at different conductance values.

| <i>Conductance (G/G₀)</i> | Transmission probability τ_1 | Fano factor |
|--------------------------------------|-----------------------------------|-------------|
| 0.24 | $0.24{\pm}0.02$ | 0.76±0.02 |
| 0.23 | 0.23±0.02 | 0.77±0.02 |
| 0.15 | 0.15±0.01 | 0.85±0.01 |
| 0.10 | 0.10±0.01 | 0.90±0.01 |
| 0.037 | 0.037±0.002 | 0.96±0.002 |

Table 6.2. Transmission probabilities and the Fano factor for five BDT single-molecule junctions at different conductance values.

We calculated the IET spectra for different configurations and binding positions and find slight variations of both the positions and the amplitudes of the peaks. While this is in qualitative agreement with the experimentally observed variations of the IET spectra, they are much less than found in the experiment (see figure C3). As discussed further in the appendix C, this may be due to an insufficient sampling of the configurational space or effects not accounted for theoretically, such as a strong energy dependence of the transmission function due to conductance fluctuations.

In order to inspect the experimental results, we compare with transport calculations performed for Au-BDT-Au contacts upon stretching. There are comprehensive experimental and theoretical studies on Pt-benzene-Pt contacts [140,229,230]. Moreover, the transport through BDT junctions has also been widely examined theoretically [231-236]. Prior computational work studying the evolution of the stretching process was done either based on DFT methods [94,218,237] or by means of combined molecular dynamics-Monte Carlo (MD-MC) simulations [238]. However, in these works on Au-BDT-Au junctions, the number of open conduction channels was not determined.

Theoretically, it is well established that the conductance of single-molecule Au-BDT-Au junctions depends sensitively on the Au-S binding geometry at the molecule-electrode contacts [231,233]. The fact that the sulfur can bind to almost any position on the Au electrodes [231] is believed to be the reason for the large spread of conductance values in single-molecule junction experiments [239]. In order to sample part of the space of possible geometries that are realized in our MCBJ experiments, we have set up two kinds of molecular junctions. Using Au pyramids oriented along the (111) direction, we consider either atomically sharp tips with a single metal atom at their tip or where the tip atom is removed. Putting a BDT molecule close to the point where the tips touch, a molecular junction is formed. An adiabatic trajectory for a stretching process is simulated by separating the metal electrodes symmetrically in each step by 0.4 Å, followed by a subsequent geometry optimization. Our Au pyramids consist of 20 or 19 atoms at each side, of which the outermost two gold layers are kept fixed in the optimization step, while the rest of the junction is fully relaxed. The steps are repeated until the junction breaks, and conductance values resolved into contributions from individual conduction channels are determined.

The evolution of the Au-BDT-Au structure and its total energy in the junction breaking process as a function of lead-lead separation *d* is presented in figure 6.5 (a) and (b) for the case of atomically sharp tips. A selected number of simulation snapshots are shown, and the complete process can be found in the appendix C. Starting from an Au-Au contact with the molecule wired in parallel, the BDT moves into the contact as the tips are being retracted. While the orientation of the BDT molecule typically changes abruptly whenever bonds break, as the S atoms slide along the electrodes, see e.g. the distances of d = 2.4 and 5.2 Å, it varies continuously in elastic stages, when forces build up and energies increase. The contact breaks at d = 8.8 Å between an S and Au atom and not at an Au-Au bond, as might have been expected [180,240]. This is presumably due to the high symmetry of the chosen Au electrodes and the limited number of flexible metal atoms. The variation of the conductance, resolved in terms of conduction channels, is shown in figure 6.5 (c). It decreases rather monotonically upon stretching in the elastic stages, while it jumps to higher values after plastic deformations, see d = 3.2 and 5.6 Å.



Figure 6.5. (a) Junction geometries at selected stages of the stretching process. The displacement *d* of the left and right electrodes is counted from our initial configuration. (b) Total energy and (c) total conductance as well as those of the first three conduction channels for Au-BDT-Au junctions as a function of *d*. The insets of (c) show the first two left-incoming transmission eigenchannel wavefunctions, evaluated at the Fermi energy, for the contacts at d = 0.8 and 6.4 Å.

This confirms that the conductance depends sensitively on the contact configuration, i.e. the binding sites of the sulfur anchors on the gold, the molecule's orientation, and the separation between the electrodes. The most remarkable feature is that a single conduction channel dominates the transport for most of the electrode separations. As soon as electrode separations are larger than d > 1.6 Å, corresponding to a conductance of G < 0.3 G_0 , the ratio G_2/G_1 is below 10%, i.e. below the measurement resolution. For smaller distances, a gold-dominated transmission channel arises, bypassing the molecule. Left-incoming transmission eigenchannel wavefunctions for selected stretching stages in Fig. 6.5 (c), evaluated at E_F , corroborate these statements.

At distances of d = 3.6 and 6.4 Å, we find local energy minima with conductance values of $G = 0.307 G_0$ (with, omitting the energy argument E_F , $\tau_1 = 0.302$, $\tau_2 = 4.1 \cdot 10^{-3}$, $\tau_3 = 5.8 \cdot 10^{-4}$) and $G = 0.267 G_0$ ($\tau_1 = 0.267$, $\tau_2 = 2.7 \cdot 10^{-4}$, $\tau_3 = 1.6 \cdot 10^{-4}$), respectively. In the latter case, the molecule is contacted to the two tip atoms only, i.e., it is bonded in a top-top (TT) configuration. According to our DFT calculations this configuration is a possible candidate for the most stable junctions, found in the high-conductance range of around $G \approx 0.2$ to 0.24 G_0 . The fact that electronic transport in Au-BDT-Au junctions is due to a single channel is further supported by the simulations for blunt tips, discussed in the appendix C. For all conductance values computed, which lie in the range from 0 to 0.6 G_0 , only a single channel contributes.

6.3 Conclusions

In conclusion, we studied the transport properties of Au-BDT-Au junctions including conductance, IET spectra and shot noise measurements. Shot noise measurements have been obtained by a simplified and versatile measurement scheme and are used for revealing the number of transport channels in this particular system, i.e. for a hydrocarbon-based molecule with only partially transmitted channels. The agreement between the experimental results and the DFT calculations supports the formation of a stable high-conductance Au-BDT-Au junction with one channel, as suggested before by studies of the nonlinear conductance. This underlines the important role of BDT as a fruit-fly molecule for studying novel concepts of quantum transport through molecules as well as a broad range, single channel conductor.

7. Large Magnetoresistance in Single Radical Molecular Junctions

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Organic radicals are promising building blocks for molecular spintronics. Little is known about the role of unpaired electrons for electron transport at the single molecule level. Here, we examined the impact of magnetic fields on electron transport in single oligo(pphenylene ethynylene) (OPE)-based radical molecular junctions which are formed with a mechanically controllable break junction technique at a low temperature of 4.2 K. Surprisingly huge positive magnetoresistances (MRs) of 16 to 287% are visible for a magnetic field of 4 T, and the values are at least 1 order of magnitude larger than those of the analogous pristine OPE (2-4%). Rigorous analysis of the MR and of current–voltage and inelastic electron-tunneling spectroscopy measurements reveal an effective reduction of the electronic coupling between the current-carrying molecular orbital and the electrodes with increasing magnetic field. We suggest that the large MR for the singleradical molecular junctions might be ascribed to a loss of phase coherence of the charge carriers induced by the magnetic field. Although further investigations are required to reveal the mechanism underlying the strong MR, our findings provide a potential approach for tuning charge transport in metal-molecule junctions with organic radicals.

7.1 Introduction

Molecule-based spintronics, which combines the molecular spin degree of freedom with molecular electronics, has attracted considerable attention for exploiting functional logic and memory devices through a bottom-up process [156,158,159,241,242]. Purely organic radicals, which consist of light elements such as H, C, N, O and S, are promising materials for device applications [243-245]. The reason is that these molecules possess low spin-orbit coupling due to the light component elements as opposed to, e.g., many transition metal complexes [246,247]. This property is expected to realize long spin relaxation times in the radical molecules, which is beneficial for molecular spintronics devices. Furthermore, the magnetism induced by localized magnetic moments, which originates from unpaired electrons, leads to versatile magnetic properties such as paramagnetic, ferromagnetic and antiferromagnetic behaviors [248-251]. Such spin systems reveal physical aspects that differ fundamentally from bulk materials built up from spin-polarized molecules. Little is known about the impact of magnetic moments on the charge transports in radical molecules

at the single molecule level, in contrast to the many reported results on 3d spins in magnetic molecules containing transition metal atoms [174,252-254].

Some examples have recently been reported on the interaction between localized electronic moments and conduction electrons, the so-called Kondo resonance, in single radical molecules by means of scanning tunneling spectroscopy (STS) and the mechanically controllable break junction technique (MCBJ) [176,178,255,256]. Several stable radical molecules, including nitronyl-nitroxide radicals [174], verdazyl radicals [254], and phenylmethyl radicals [178], were employed in these studies. In all cases, obvious Kondo resonance peaks were observed, thus demonstrating that unpaired electrons act as superior spin impurities. However, so far the detection of a Kondo resonance remains their only manifestation in single radical molecular junctions. Much less attention has been paid to other charge transport phenomena such as magnetoresistance (MR) effects and magnetic-field-induced inelastic electron tunneling (IET), whereas abundant results have been reported for transition metal complexes [166,257-259]. Further understanding of the role of unpaired electrons in radical molecules and the manipulation of charge transport are challenging requirements.

7.2 Results and discussions

In this chapter, we evaluate the charge transport properties in single radical molecules by a MCBJ technique at a low temperature of 4.2 K under magnetic fields perpendicular to the transport direction (figure 7.1 (a)). In this study, stable and neutral radical molecules based on an oligo(*p*-phenylene ethynylene) (OPE) backbone, (methyl)amino]-2,2,6,6-tetramethylpiperidin-1-yl}oxidanyl (TEMPO-OPE), are placed on a freestanding gold (Au) bridge made with a standard lithography technique (figure 7.1(b)) [88,180]. The process used to synthesize the radical molecules and the details of the experimental procedures are described in the appendix D. A feature of the radical molecules is that they are composed of an OPE backbone molecule which is archetypical in the field of molecular electronics and offers coherent charge transport between two electrodes through Au-S bonds [40,202,260].



Figure 7.1. Experimental setup. (a) A scanning electron microscopy image of a MCBJ sample with Au freestanding bridges. A schematic illustration of single-molecule junctions for (b) TEMPO-OPE and (c) pristine OPE. Magnetic fields are applied perpendicular to the sample plane for the charge transport measurements.

In addition, the orbital of the unpaired electron on the TEMPO radical is not conjugated with the π -orbitals of the OPE backbone molecule, that is, the radical part is electrically isolated from the main transport channel. This property makes it possible to preserve the localization of the unpaired electron on the molecules. Moreover, Kohn–Sham density functional theory (KS-DFT) calculations (carried out in the absence of a magnetic field) suggest that the radical molecules bridging between Au electrodes have two possible configurations (see Figure D1-D5 in the appendix D). In one structure, the TEMPO radical is oriented towards one of the thiols and thus can potentially interact directly with an Au electrode. Calculations with Grimme's dispersion correction also imply that the sterical interaction between the TEMPO radical and the OPE backbone may be strong enough to induce a tilt of one of the phenyl rings (Figure D1-D4 in the appendix D).



Figure 7.2. Transport properties of Au/TEMPO-OPE/Au molecular junctions. (a) Conductance traces in breaking process of TEMPO-OPE molecular junctions. (b) Conductance histograms of TEMPO-OPE molecular junctions. (c) A typical *I-V* characteristic of TEMPO-OPE single- molecule junctions. The solid red line indicates a fitting curve calculated with the single-level model eq. (1). (d) Experimental and symmetrized IET spectra $(d^2I/dV^2)/(dI/dV)$ at a molecular junction. The red line is given by the point-symmetric function, (f(x) - f(-x))/2. The respective vibration peaks are assigned with reference to IETS, infrared and Raman spectroscopy measurements of OPE and TEMPO radical molecules.

In this study, we observed considerably large positive MRs from TEMPO-OPE molecules when a magnetic field was applied perpendicular to the samples. The change in resistance was one order of magnitude larger than that of the analogous non-radical OPE molecule (Figure 7.1 (c)), obtained via deprotection of S,S'–[1,4–phenylenebis(ethyne–2,1–diyl–4,1–

phenylene)]diethanethioate, and investigated under the same conditions. Our detailed analysis of current-voltage (*I-V*) measurements and inelastic electron tunneling spectroscopy (IETS) measurements suggested that the large MR from radical molecules is induced by a loss of coherence of the electron transport with increasing magnetic field amplitudes. These results imply that the unpaired electron may contribute to the localization of π -orbitals in TEMPO-OPE molecules, which would provide a new physical approach for tuning the charge transport via radical molecules.

First, we evaluated the fundamental charge transport properties through Au-TEMPO-OPE-Au junctions without magnetic fields, complemented by conductance histograms, I-V and IETS measurements. All measurements were made at a low temperature of 4.2 K. The single molecular junctions were formed by repeatedly breaking and reforming Au contacts. Figure 7.2 (a) shows some representative opening curves of the junctions in the range of 3 to $10^{-6} G_0$, where $G_0 = 2e^2/h$ is the conductance quantum, e is the elementary charge and h is Planck's constant. Clear plateaus appeared in the range of 10^{-4} to 10^{-3} G₀ after breaking the Au single atom contacts. The lengths of the pronounced plateaus were estimated to be 1.5-2.0 nm, which is in good agreement with that of the OPE backbone (2.07 nm) [40,202]. Subsequently we obtained the conductance histogram shown in figure 7.2 (b). Here, the histogram was constructed from only the opening traces of the junctions. The most probable conductance was estimated to be $6.0\pm3.8\times10^{-4}$ G₀. The conductance value is also close to those for OPE molecules with Au-S bonds $(3.7\pm2.0\times10^{-4} G_0$ for our measurement (Figure D12 in the appendix D) and $1.2-2.8 \times 10^{-4}$ G₀ for the reported values [40,202,261,262]. I-V measurements were carried out to obtain an insight into the charge transport mechanism of TEMPO-OPE junctions. The I-V curves were analyzed with the Breit-Wigner single level model (see section 3.4.2), which is widely used to describe the charge transport via π -conjugated molecules [179,263,264].

The closer proximity of the highest occupied molecular orbital (HOMO, around -6.3 eV; see figure D6) to the assumed Fermi level of -5 eV compared with the lowest occupied MO (LUMO; around -2.5 eV) suggests that it is reasonable to use such a single-level model, but it should be kept in mind that the location of EF cannot be determined with certainty from our calculations, as the description of metal-molecule interfaces is a challenge for DFT, and adsorbate layer effects are not taken into account by the theoretical description of a single molecule on which our analysis is based. The assumption of the singlelevel model is further justified by the fact that transmission function is well-described by a Lorentzian line shape close to the Fermi energy (see Figure D7). We evaluated 130 I-V curves form TEMPO-OPE junctions, of which 113 curves were well-fitted by the single-level model.

Figure 7.2 (c) shows a typical *I-V* curve for a contact with $7.4 \times 10^{-4} G_0$. The curve was well fitted by a model whose parameters were an energy level of $|E_0| = 0.49$ eV and coupling constants of $\Gamma_L = 6.6$ meV and $\Gamma_R = 6.8$ meV. The coupling symmetricity factor, $\alpha = \Gamma_L/\Gamma_R$, was calculated to be 0.97, revealing that the molecule is symmetrically connected to both electrodes. These estimated parameters coincide with those reported for OPE molecules ($|E_0| = 0.50\pm0.15$ eV, $\Gamma = 8.4\pm4.2$ meV) [202]. The DFT calculations on the electronic structure of the TEMPO-OPE and the local transmission contributions of the junctions suggest that the current flows through the OPE backbone in the TEMPO-OPE molecule; the HOMO -1 level (for majority spins) and the HOMO level (for minority spins) work as

conductive channels (figure D6-D9 in the appendix D). For further information on the charge transport, a statistical analysis of the *I-V* curves is given in the appendix D (figure D13). IETS measurements were performed to identify excited vibrational modes for TEMPO-OPE junctions. Here, we measured the spectra of 50 different junctions recorded on 2018 opening traces after complete reclosure of the junctions and on five samples. Figure 7.2 (d) shows a representative IET spectrum with a positive bias voltage for a molecular junction and one that has been symmetrized by the following point-symmetric function, y = (f(x)-f(-x))/2. Here, the IET spectrum was symmetrized to correct the asymmetricity in positive and negative voltages [179]. In addition, the amplitude of the IETS signals $(d^2 I/dV^2)$ was normalized by that of dI/dV to compensate for the change in conductance. The spectrum over the entire voltage range is described in the appendix D (figure D14). All the vibrational peaks were observed at the same bias voltages in both the raw and symmetrized spectra, which also demonstrated symmetric coupling between the molecule and the electrodes. We assigned the pronounced peaks to specific vibrational modes in the TEMPO-OPE molecules by comparison with those of OPE and the derivatives (fFigure D15 in appendix D). We also referred to infrared and Raman spectroscopy measurements of TEMPO radical molecules for the assignment of N-C vibrations [212,265,266], and compared with vibrational spectra calculated by DFT (figure D10 and D11 in the appendix D). The detected vibration peaks are summarized in Table D1 in the appendix D. The detection of characteristic vibration peaks in the TEMPO-OPE molecules, e.g. N-C, C=O stretching modes and benzene-ring vibrations, provides further verification that the current passes through a single TEMPO-OPE molecule.

We now turn to a discussion of the charge transport under a magnetic field, namely MR measurements and the Kondo resonance effects on single molecule junctions of the radical. Figure 7.3 shows typical MR curves for TEMPO-OPE junctions in different conductance ranges, where magnetic fields were applied perpendicular to the sample plane. The magnetic field sweep rate was fixed at 400 mT/min. The resistance was measured at a dc voltage of 30 mV to be close to the linear regime and to avoid current-driven rearrangements during measurements. For comparison, MR curves obtained from OPE junctions are also displayed in the same figure. We observed remarkably large positive MRs and the value is one order of magnitude larger than that of non-radical OPE molecules, despite the fact that both molecules have a similar molecular structure.



Figure 7.3. Magnetoresistance curves from TEMPO-OPE molecular junctions. For comparison, the curves from pristine OPE are shown in the same figure and with the same scale. The magnetic fields were applied up to ± 4 T, starting at 0 T, increasing to + 4 T (black), returning to 0 T (red), decreasing to - 4T (blue) and finally returning to 0 T (magenta). The resistances are shown as $[R(B) - R(0)] \times 100/R(0)$ (%), where R(B) and R(0) are respective resistances at maximum magnetic fields and at 0 T. Please note that individual curves are shifted vertically for better visibility.

The magnetoresistance histogram from TEMPO-OPE and OPE junctions is given in figure D16. Here, the MRs were measured at 23 junctions for TEMPO-OPE, out of which 17 junctions (74%) indicated large MR values of more than 16% at 4 T. The maximum value was 287%. The other junctions revealed the same shape of MR curves; however, the amplitudes were 2-6%. The average value of all observed MRs was estimated to be 43.7% at 4 T, in contrast to 2.2% for OPE junctions. In addition, it is notable that the MR curves from TEMPO-OPE junctions revealed a saturation and subsequent decrease at a high magnetic field of 4 T to 6 T (figures D17a and D18). Similar behavior is also observed for OPE and Au atom junctions (figure D17b,c), which shows that the shape of the MR traces is not a unique feature of TEMPO-OPE junctions. In some of the dI/dV curves, we observe zero-bias anomalies that resemble Kondo resonances, as recently reported by Frisenda et al. for single-molecule junctions of polychlorotriphenylmethyl (PTM), a molecule bearing a radical in its conduction path at very low temperature [176]. In our case, the width of the zero-bias anomaly is much larger than that reported in ref [176] and would correspond to a Kondo temperature of ~360 K. Furthermore, the peaks did not split, even by the application of magnetic fields up to 5 T (see figure D19). This result is in agreement with results from the DFT calculations, which suggest that the TEMPO radical part is electrically only very weakly coupled to the main transport channel (figures D8 and D9). Therefore, we do not expect to observe the Kondo effect in the TEMPO-OPE junctions.

Measurements in a wider temperature range and at much higher magnetic fields would be required to verify the presence or absence of the Kondo effect.

Furthermore, we discuss the origin of the large MR of the TEMPO-OPE junctions. Such huge MRs have not been reported in single-molecule junctions to date. For example, in the study by Frisenda et al. on PTM junctions [176], no MR measurements were reported. Recently, some examples have been reported on charge transport through organic materials under magnetic fields. Sugawara et al. demonstrated negative MRs for Au nanoparticles linked by a nitronyl-nitroxide radical molecule, where the current was assumed to flow through radical molecules bridging between Au particles. The negative MRs are explained by reduction of spin-flip scattering [267,268]. This is because magnetic fields define a preferable orientation for localized spins and thereby the spin-flip scattering of conductive electrons is restricted by an increasing magnetic field. Meanwhile, in our case only positive MRs were visible, and therefore the spin-flip scattering model is ruled out. In addition, Au surfaces have been reported to be magnetized through Au-S bonds, which may affect the charge transport through a bridged molecule [269]. However, the spin-polarization effect is unlikely to dominantly contribute to the variation in MRs because only small change in the MRs was observed for OPE junctions, despite the fact that the molecule has the same Au-S bonds (even though a facilitation of Au-S spin polarization through the presence of the radical cannot be fully excluded). Furthermore, the overall transmission calculations clarify that the TEMPO-OPE molecules do not work effectively as spin filters because the radical parts are located far from the backbone molecules, resulting in virtually equal transmission probabilities for majority and minority spins (figure D7 in the appendix D).

The same conclusion has been pointed out in the theoretical study of the spin filtering effects of stable radical groups including nitronyl-nitroxide and *tert*-butylphenylnitroxide radicals, which are similar to that of our molecule [270,271]. On the other hand, markedly large positive MRs (10 % at 10 mT) have been demonstrated in pure organic thin films and molecular wires with nonmagnetic electrodes such as Au and tin-doped indium oxide electrodes [272-274]. In these studies, the positive MRs are interpreted by the hyperfine interaction between conductive electrons and nuclear spins of molecules during the electron hopping conduction. Whereas, the MRs appeared at the magnetic field of a few Tesla in our case and the amplitude is much larger than that of hyperfine fields of typical organic molecules (2-6 mT) [272,273].

The Zeeman splitting of molecular orbitals also cannot explain the MRs obtained from TEMPO-OPEs because of the marginal change in MRs for OPEs. Hence, a different mechanism from those already proposed for organic molecules is required to explain the origin of the positive MR in our study. To understand why such a huge MR appeared for TEMPO-OPE molecules, we performed *I-V* measurements under different magnetic fields (figure D20 (a)). The *I-V* curves were analyzed with the single level model (see section 3.4.2). Figure 7.4 (a) and 7.4 (b) show the changes in the conductance and fitting parameters, $|E_0|$, Γ_L and Γ_R , as a function of the magnetic field. The conductance was reduced by 62 % when the magnetic field was increased to 5 T, corresponding to a 162% positive MR. This conductance change is caused by a strong decrease in the coupling constants, which dropped markedly to almost 50 % as the magnetic field increased to 5 T. In contrast, the slight decrease in the energy level from 0.5 to 0.4 eV with increasing magnetic field reveals a marginal improvement in the level alignment between the

molecular orbital and the Fermi level of the electrodes, and this would result in an increase of conductance if the coupling constants were independent of the magnetic field. A similar tendency was observed in the other junctions. Another example is shown in figure D21. In the junction, the change in $|E_0|$ was estimated to be 3%. In contrast, the variations in Γ_L and Γ_R amounted to 20%. These results clarify that the huge MR for TEMPO-OPE molecules is dominantly induced by a reduction in the coupling strength between the current-carrying molecular orbital and the electrodes. For comparison, equivalent experiments were made with OPE molecules. No variation was observed in *I-V* curves with magnetic fields (figure D20 (b)). These results indicate that the unpaired electron plays an essential role in the change in the orbital coupling between molecules and electrodes.



Figure 7.4. Magnetic field dependence of the charge transport through a Au/TEMPO-OPE/Au single-molecule junction. Change in (a) conductance and (b) energy level position, $|E_0|$, and coupling constants, Γ_L and Γ_{R} , as a function of magnetic field.

Here, we consider possible origins for the observed reduction in the coupling strength under magnetic fields. Prior to the discussion, it should be noted that the junction region would be surrounded by many molecules because of their deposition from a solution. We cannot ignore the contribution of the magnetic moments of unpaired electrons in the surrounding molecules to the charge transport via the bridged molecule, although only one molecule is electrically contacted to both sides of the electrodes [251,275]. A possible reason is the change in conformation of a molecule under a magnetic field. Structural changes caused by magnetic fields are well known in transition metal complexes, and the effect is employed to control molecular orientation in grown films [276,277]. Here, the magnetic moments of surrounding molecules might induce a magnetic distortion of the electrodes. The second reason could be a variation in the electronic structure, e.g. by

narrowing the Breit-Wigner resonance, which might be caused by a confinement of the π -orbital system induced by the attached radical group.

Another possible electronic effect would be the loss of the phase coherence of the conduction electrons in the metal electrodes. Because constructive quantum interference contributes to the transport, the reduction of phase coherence might cause an increase of the resistance [278]. Since similar changes of $|E_0|$, Γ_{L_1} and Γ_R under a magnetic field were visible when the molecules were subjected to tensile stress by gradually displacing the electrodes (figure D22 in the appendix D), an additional experiment is required to dispel this effect. To this end we evaluated the development of the IETS with magnetic fields and compared the result with the development with stretching, since the IET signals are sensitive to molecular vibrations caused by both the geometrical and electronic structures.



Figure 7.5. Magnetic field dependence of the inelastic transport properties of a Au/TEMPO-OPE/Au junction. (a) Symmetrized IET spectra in different magnetic fields up to 5T. (b) The change in peak intensities for representative vibration modes as a function of magnetic field. Here the intensities are normalized to those without a magnetic field.

Figure 7.5 (a) shows symmetrized IET spectra in different magnetic fields varying from 0 to 5 T. The IETS peak positions remained almost unchanged, but a clear attenuation of the peak intensities was visible. This result manifests that the change of the electronic structure in the molecule is more dominant than that of the molecular conformation. Figure 7.5 (b) shows the variation in the intensities of representative vibration peaks. Here, the peak

intensities are normalized by those without a magnetic field. All the molecular vibration peaks were suppressed by increasing the magnetic field. In particular, the peak intensities for benzene-ring vibrations and the side group (v(N-C) and v(C=O)) were definitely reduced. The Au phonon mode peak also decreased, although the variation is quite small (less than 10 %). Such suppression of the vibration peaks was not seen in the IET spectra for OPE junctions (figure D24 in the appendix D). The corresponding peak intensities fluctuated with a deviation of only 20 %, regardless of magnetic fields.

In addition, a very distinct behavior was observed when stretching a molecular junction (figure D22 in the appendix D). We observed a pronounced increase of the peak intensity of the longitudinal optical phonon of Au-Au bonds which is a typical behavior of atomic chains and molecular junctions. A similar tendency was demonstrated in our previous results on Au-1,6-hexanedithiol molecule-Au junctions [179]. No such large change in Au-Au optical phonons was visible with magnetic fields. In addition, the peak intensities attributed to the stretching vibration of C=C bonds and benzene ring vibrations were enhanced by increasing the electrode displacement, while the peak positions remain unchanged.

These differences provide clear evidence that the conductance reduction in magnetic field is not caused by a change in geometry but by a variation in the electronic structure. To be more specific we suggest the following model. The magnetic field confines electronic wave functions, as known in mesoscopic physics [279]. In the present system this localization has a twofold effect; first it confines the π -orbitals of the molecule, thereby reducing their coupling with the conduction electrons of the electrodes. Second, the magnetic field acts on the conduction electrons of the metal electrodes themselves, leading to dephasing, as known from e.g. weak localization studies [280]. While no clear weak localization feature is visible in the magnetoconductance due to its small amplitude, this loss of decoherence would be reflected in the reduction of the IET amplitudes. However, both effects should also be active in pristine OPEs. Therefore, we consider that the presence of the localized magnetic moments of the unpaired radical electron enhances the dephasing and/or localization effect. In these regards, our DFT calculations suggest that the unpaired electrons may be located at spatially quite close to the Au surface and/or may induce the tilt of the phenyl-ring in OPE backbone in the initial state, while the radical's π system is electronically decoupled from the π system of the OPE backbone (figures D1-D6 in the appendix D). Such specific configurations may facilitate the dephasing of conduction electrons in Au electrodes by the local magnetic moments and the confinement of the π orbitals in the radical molecules under magnetic fields. Further investigation is necessary to clarify the mechanism.

7.3 Conclusion

In summary, we investigated electron transport through single TEMPO-OPE molecular junctions under magnetic fields by a MCBJ technique at 4.2 K. Substantially large positive MRs of 16 to 278 % were observed at 4 T, in contrast to those of non-radical OPE molecules which exhibited MRs in the range of 2-4 %. A detailed analysis based on *I-V* and IETS measurements with magnetic fields provided clear evidence that the large MRs for TEMPO-OPE were caused by reducing the coupling of the current-carrying molecular orbital with the metal electrodes. These results suggest that the confinement of π -orbitals in magnetic fields may be caused or enhanced by the magnetic moment of an unpaired electron on the TEMPO-OPE molecules. Therefore, our finding offers a possible new approach to manipulate the charge transport in organic radical molecules.

8. Inelastic noise of gold atomic junctions

In this chapter, we report the inelastic noise measurements on single-atom gold contacts due to the influence of electron-phonon scattering. We confirm the previous experiments on shot noise reported by Kumar et al. [86] with a new, simple and versatile noise measurement setup, obtaining a similar conductance threshold of ~ 0.96 G_0 for the sign change of the inelastic noise contribution.

8.1 Introduction

The study of electron-phonon scattering on nanoscale systems can provide useful information and can be addressed and revealed by point-contact spectroscopy (PCS) [87] inelastic electron tunneling spectroscopy (IETS) [180] or Raman spectroscopy [281,282]. Similar to PCS, IETS or Raman spectroscopy, inelastic current noise of atomic scale junctions provides useful information about the system such as unique information on the local phonon population and lattice temperature of the nanoscale system.

There are several theoretical works on inelastic noise or noise induced by electron-phonon interaction [142-151], but up to know only few experiments have been reported [86,152,154]. In the first experimental effort, Tsutsui et al. investigated the current fluctuations flowing through a single molecule. They found increased current oscillations synchronous to electric field excitations of characteristic molecular vibrational modes that contribute to the inelastic electron tunneling [152]. In the other experimental work by Kumar et al., the shot noise from Au atomic contacts was measured at 4.2 K and it is found that the inelastic noise correction is positive for the zero-bias conductance close to G_0 and this correction is negative for zero-bias conductance below 0.95 G_0 [86]. As mentioned in sections 3.4.3 and 3.4.4, when the transmission (τ) exceeds the so called crossover transmission ($\tau_{crossover}$), the conductance variation by inelastic processes, undergoes a crossover from an increase to a decrease [89,92]. Several theoretical efforts also suggest similar crossovers in the inelastic noise correction at $\tau = 2 \pm \sqrt{2}/4$ (~0.86 and ~0.15) [86,145,147,149,151] (see section 3.5.3). In this work, with the help of the (MCBJ) technique and shot noise measurement at 4.2 K [211], we also observed the higher threshold of $\tau \sim 0.96$ for single-atom Au contacts compared to the higher theoretical value of $\tau = 0.86$. Our results confirm the previous experimental results [86] obtained with a different setup. These results can motivate more theoretical and experimental works in this field.

8.2 Results and Discussion

The shot noise of Au atomic junctions was acquired at 4.2 K using a simple setup [211]. With the help of the MCBJ technique, the Au atomic-scale contacts have been formed. Since we are interested in the of shot niose of single gold atom contacts, all of the measurements were performed at contacts around $G \simeq 1 G_0$. For single-atom contacts the

last conductance plateau (see figure 3.7) can be stretched to values slightly below 1 G_0 (0.6 $G_0 < G < 1 G_0$).

After identifying a stable contact, the current-voltage characteristics (*I-Vs*), the differential conductance (dI/dV) and the shot noise S_I from the contact are measured. As described in section 4.4, the current of the junction is amplified using a transimpedance amplifier. Then by help of a spectrum analyzer, the noise spectrum between 1 and 100 kHz is measured. We averaged over the white frequency spectrum (between 1/f noise at low frequencies and roll-off of the spectra at high frequencies) to determine the shot noise. Finally the shot noise ($S_I(V) - S_I(V=0)$) is calculated by subtracting the thermal noise of the junction and the system $S_I(V=0)$ from the total noise at applied bias voltage V, $S_I(V)$.

In order to investigate the influence of the electron-phonon interaction on the excess noise, we follow a procedure presented by Kumar et al. [86], for or Au atomic contacts. The difference between our measurement set up and Ref. [86] is that here we use a simple setup which relies on careful calibration of all unavoidable noise contributions [211,222] and without the necessity of double wiring and performing cross-correlation [86,114-118].



Figure 8.1. (a) Point contact spectroscopy (black line) and its symmetrized curve (red line) for an Au atomic contact. The dashed lines indicate the position of the vibration mode (b) Excess noise for the same contact. The red line is the fit corresponding to Eq. 3.33. (c) The Y and X representation of the current noise. The solid blue line is the fit for the elastic noise and the dashed blue line is the fit for the noise after the inelastic influence. (d) The Y and X representation for six contacts with different conductance values.

As described in section 3.5.3, the Fano factor can be extracted with two dimensionless, voltage-dependent parameters X(V) and Y(V) according to Eq. 3.41. Figure 8.1 (a) shows

the point contact spectroscopy (black line) and its symmetrized curve (red line) for a gold atom contact with zero-voltage conductance of 0.987 G₀. The dip at 15 ± 1 mV indicates the scattering process with a vibrational mode. Stretching the Au atomic chain results in bond softening which can decrease the phonon frequency (energy range of 10 meV to 20 meV) [87]. Figure 8.1 (b) represents the shot noise as a function of the bias voltage applied across the same junction. The red line in figure 8.1 (b) is a fit according to Eq. 3.33 and shows one channel with transmission probability of $\tau = 0.987\pm0.002$. Figure 8.1 (c) shows the linear fit according to Eq. 3.41 for elastic noise (solid blue line), without the influence of the vibration mode on the noise gives the Fano factor $F_1 = 0.013\pm0.002$ and for inelastic noise the linear fit (dashed blue line) give the modified Fano factor of $F_2 = 0.053\pm0.002$. The kink in the noise signal matches the energy of the vibration mode around 15 mV (see figure 8.1 (a)). The relative change in Fano factor for this contact is equal to $\delta F/F_1 = (F_2-F_1)/F_1 \approx 3.07$.

Figure 8.1 (d) shows the *Y* and *X* representation for six contacts with conductance of 0.825 G_0 to 0.987 G_0 . Determination of vibration mode energy for most of the contacts was difficult due to conductance fluctuations. We took the first minimain the PCS as a sign of a vibration mode. Figure 8.2 shows the inelastic correction for 28 contacts. We observe negative correction for several contacts above the theoretical prediction of 0.86 G_0 . For conductance above ~ 0.96 G_0 we find positive values for $\delta F/F1$. Below $G \sim 0.96 G_0$ the relative Fano factors did not change or have negative values. The green dashed line in the figure 8.2 shows the observed threshold (~ 0.95 G_0) in Ref. [86] and the pink dashed line shows the predicted theory value of ~ 0.86 G_0 .



Figure 8.2. Inelastic correction for 28 contacts. The relative Fano factor sign change occurs around 0.96 G_0 . For conductance (i.e., transmission) close to 1 we observe positive values for $\delta F/F1$. Below ~ 0.96 G_0 several contacts with negative values for relative Fano factor is observed. The green dashed line is the observed threshold (~ 0.95 G_0) in Ref. [86] and the pink dashed line indicates the theory threshold of 0.86 for inelastic noise correction.

As suggested by Ref. [86], the discrepancy between the observed threshold and theoretical calculation can be due to the fluctuations in the background of the differential conductance. Recently, motivated by the results of Kumar et al., Chen et al. also reported shot noise measurements on single-atom Au contacts up to 200 mV and at multiple temperatures from 4.2 to 100 K [154]. They found that the temperature dependence of the shot noise is minimal and Fano factors are observed to be enhanced near 0.5 G_0 which can be due to either contamination or the intrinsic atomic configurations favored by the Au junction formation. They also observed that for contacts with conductance close to 1 G_0 , the bias dependence of the shot noise shows geometry-dependent small nonlinearities [154]. Despite these experimental efforts (including our observations) the origin of the discrepancy from theory regarding the crossover is still not understood.

8.3 Conclusions

In summary, in this chapter we report shot noise measurements by mechanically controlable break junction technique with the help of a versatile simple setup. We observe nonlinearities in the shot noise power for bias voltages above the vibration mode energy for Au single-atom contacts. The observed crossover from positive to negative for relative Fano factr $\delta F/F_1$ is around ~ 0.96 G_0 . Our results confirm the previous experimental results by Kumar et al. [86] who observed the crossover at 0.95 G_0 , and motivate more theoretical efforts to investigate the discrepancy for the noise sign crossover threshold.

9. Summary

In this thesis, we report on the charge transport properties of Au atomic contacts and single-molecule junctions. The goal of the work was to address particular questions such as: what is the preferred current path through a tripodal single molecule, how many conduction channels are contribute to the current through single-molecule junctions, what are the influences of an unpaired electron on the charge transport through a single-radical-molecule junction and what is the influence of vibration modes on the shot noise of gold single-atom contacts.

To address these questions atomic and molecular junctions have been fabricated using a sophisticated nano-fabrication process. Three molecules including the well-known 1,4-benzenedithiol, a new tripodal platform based on a rigid 9,9'-spirobifluorene equipped with a phenylene-ethynylene wire and an oligo(p-phenylene ethynylene) (OPE)-based radical molecule have been investigated at liquid helium temperature. Several types of measurements including current-voltage characteristics, inelastic electron tunneling spectroscopy (IETS) and magnetic field-dependent conductance measurements have been carried out. In addition, to study the shot noise in Au-1,4-benzenedithiol-Au and Au single-atom junctions we developed a versatile setup, which enables us to determine noise in a broad range of conductance values without the necessity of double wiring and performing cross-correlation, and without going to high frequency measurements.

In chapter 5, the transport properties of single-molecule junctions of 9,9'- spirobifluorene, contacted to Au electrodes have been studied. Our findings demonstrated that this tripodal molecular platform with a rigid molecular wire (arm) that points almost perpendicular to the surface, is a promising candidate to establish a conducting path with a high degree of conjugation between two electrodes while the π -system is separated from the substrate and can be exploited, e.g. for incorporating functional units like switches or photosensitive moieties.

In chapter 6, the shot noise measurements on single-molecule Au-1,4-benzenedithiol (BDT)-Au junctions in a wide range of conductance values have been studied. The agreement between the experimental observations and theoretical calculations demonstrated that the current is carried by a single conduction channel throughout the whole conductance range for BDT single-molecule contacts. The results further support the important role of BDT as a fruit-fly molecule and broad range, single channel conductor.

In chapter 7, we addressed the role of unpaired electrons for electron transport for a singleradical-molecule. We observed substantial positive magnetoresistance (MR) of TEMPO-OPE molecules when the magnetic field was applied perpendicular to the sample plane. The MR was one order of magnitude larger than that of the analogous non-radical OPE molecule. Our detailed analysis of the current-voltage characteristics and the inelastic electron tunneling spectroscopy measurements suggested that the large MR from radical molecules is correlate with decoherence of the electron transport with increasing magnetic field amplitudes. These results imply that the unpaired electron may contribute to the localization of π -orbitals in TEMPO-OPE molecules, which would provide a new physical approach for tuning the charge transport via radical molecules. In chapter 8, we studied the electron-phonon scattering in single-atom gold contacts with point-contact spectroscopy (PCS) and shot noise measurements. We confirmed the previous experiments and obtained almost the same conductance threshold for the sign change of inelastic noise contribution as observed before. Discrepency with theory has to be solved.

To conclude, the charge transport of single-molecule and single-atom junctions have been studied extensively using several measurement techniques including IETS, PCS and shot noise. These findings can play important roles in the field of molecular electronics and spintronics and for understanding the fundamental questions of quantum transport.

(Amin Karimi, September 2016)

9. Zusammenfassung

In dieser Arbeit werden die Eigenschaften des Ladungstransports von Gold-Einatom- und Einzelmolekülkontakten untersucht. Es wurden vier spezifische Fragen adressiert: Die Ziele der Arbeit waren es, herauszufinden, welches der bevorzugte Strompfad durch ein Dreibein-Einzelmolekülkontakt ist, wie viele Leitungskanäle zum Stromfluss durch einen Einzelmolekülkontakt beitragen, welcher Einfluss ungepaarte Elektronen auf den Ladungstransport durch Einzelmolekülkontakte mit Radikalen haben und welcher Einfluss von Vibrationsmoden auf das Schrotrauschen eines Gold-Einatomkontakts ausgeht.

Um diese Fragestellungen zu beantworten wurden atomare und molekulare Kontakte in einem fortgeschrittenen Nano-Fabrikationsverfahren hergestellt. Drei Moleküle, das wohl bekannte 1,4-Benzoldithiol, ein neues auf einer Dreibein-Plattform aufbauendes steifes 9,9'-Spirobifluoren, ausgestattet mit Phenyl-Ethynylen Draht und ein Oligo(p-Phenyl Ethynyl) (OPE)-basiertes Radikal-Molekül wurden bei tiefen Temperaturen (4,2 K) untersucht.

Verschiedene Messmethoden, darunter Strom-Spannungs-Kennlinien, Inelastische Elektronentunnelspektroskopie (IETS) und Magneto-Leitwertmessungen wurden durchgeführt. Zusätzlich wurde ein verbesserter Aufbau entwickelt, um das Schrotrauschen in Au-1,4-Benzoldithiol-Au- und Gold-Einatomkontakten zu untersuchen. Dieser Aufbau ermöglicht es, das Schrotrauschen in einem großen Bereich von Leitwerten aufzunehmen, ohne die Notwendigkeit von doppelter Verkabelung, von Kreuzkorrelation oder bei hohen Frequenzen zu messen.

In Kapitel 5 wurden die Transporteigenschaften von Einzelmolekülkontakten von 9,9'-Spirobifluoren in Kontakt mit Goldelektroden untersucht. Unsere Ergebnisse zeigen, dass diese Dreibein-Molekülplattform mit einem steifen molekularen Draht (Arm), der fast senkrecht zur Oberfläche steht, ein erfolgversprechender Kandidat ist, um einen leitenden Pfad mit hoher Konjugation zwischen zwei Elektroden herzustellen. Hierbei bleibt das π -System getrennt vom Substrat und kann z.B. für die Einbindung funktionaler Gruppen, wie Schalter oder fotosensitiver Baugruppen, genutzt werden.

In Kapitel 6 untersuchten wir das Schrotrauschen von Au-1,4-Benzoldithiol (BDT)-Au Einzelmolekülkontakten in einem weiten Leitwertbereich. Die Übereinstimmung zwischen den experimentellen Befunden und den theoretischen Berechnung zeigt, dass über den gesamten Leitwertbereich von BDT der Strom von einem einzigen Transportkanal getragen wird. Diese Ergebnisse unterstreichen die Wichtigkeit von BDT in der molekularen Elektronik als ein Leiter mit einem Kanal und großem Leitwertbereich.

In Kapitel 7 wendeten wir uns dem Einfluss ungepaarter Elektronen in Einzelmolekülkontakten mit Radikalen auf den Stromfluss zu. Wir fanden einen großen positiven Magnetowiderstand (MR) vom TEMPO-OPE Molekül bei einem Magnetfeld senkrecht zur Probenebene. Der MR war eine Größenordnung stärker ausgeprägt als bei dem gleichen Molekül ohne Radikalgruppe. Unsere umfangreiche Analyse der Strom-Spannungs-Charakteristik und IETS deuten darauf hin, dass der große MR der Radikalmoleküle mit einer Abnahme der Kohärenz des Elektronentransports bei steigender magnetischer Feldstärke einhergeht. Diese Ergebnisse implizieren, dass das ungepaarte Elektron zur Lokalisierung des π -Orbitals im TEMPO-OPE Molekül beiträgt, wodurch eine neue physikalische Möglichkeit zur Kontrolle des Ladungstransports durch Radikalmoleküle gefunden wurde.

In Kapitel 8 untersuchen wir die Elektron-Phonon Streuung in Einzelatomkontakten aus Gold mittels Punktkontaktspektroskopie (PCS) und Messungen von Schrotrauschen. Wir konnten vorangegangene Messungen bestätigen und erhielten den gleichen Grenzwert für den Vorzeichenwechsel des inelastischen Rauschens, der jedoch von der theoretischen Vorhersage abweicht, was von weiterführenden Experimenten geklärt werden muss.

Zusammenfassend wurde der Ladungstransport in Einzelmolekül- und Einatomkontakten mittels verschiedener Messtechniken, darunter IETS, PCS und Schrotrauschen, ausführlich untersucht. Diese Ergebnisse spielen eine wichtige Rolle in der molekularen Elektronik und Spintronik für ein vertieftes Verständnis der grundlegenden Fragen des Quantentransports.

(Amin Karimi, September 2016)

Appendix A

A1. Polyimide coating

- 1. Bake the polished substrate on a hotplate for 5 min at 115 °C to remove wet layer
- 2. Spincoat Polyimide (Durimide 115A, thickness ~ 2 μ m)
- Ramp for 3 sec to 400 rpm and stay 4.5 sec
- Ramp for 3 sec to 5000 rpm and stay 90 sec
- Ramp down for 2 sec to 0 rpm and stay 0 sec
- 3. Bake the spincoated wafer in an oven for 30 min at 130 $^{\circ}\mathrm{C}$
- 4. Anneal the wafer in vacuum
- Ramping up for 100 min to 430 °C and keep the temperature for 90 min

A2. E-beam resist coating

- 1. Bake the wafer on a hotplate for 5 min at 115 °C to remove wet layer
- 2. Spincoat copolymer (MMA-MAA EL 11, thickness ~ 540 nm)
- Ramp for 3 sec to 400 rpm and stay 4.5 sec
- Ramp for 0 sec to 2500 rpm and stay 90 sec
- Ramp down for 2 sec to 0 rpm and stay 0 sec
- 3. Bake the wafer on hotplate for 90 sec at 115 $^{\circ}\mathrm{C}$
- 4. Spincoat PMMA (950 A4, thickness ~ 160 nm)
- Ramp for 3 sec to 400 rpm and stay 4.5 sec
- Ramp for 0 sec to 5000 rpm and stay 90 sec
- Ramp down for 2 sec to 0 rpm and stay 0 sec
- 5. Bake the wafer in an oven for 30 min at 170 $^{\circ}\mathrm{C}$

A3. E-beam lithography

- 1. Cut the wafer into proper dimensions $(4x19 \text{ mm}^2)$.
- 2. Vent the chamber, Put the sample on the stage and Evacuate chamber to less than 10^{-5} mbar (Note: The working distance between the samples and the end of electron-beam column was kept ~ 5.5 mm).
- 3. Start electron beam gun (30 keV) and wait 20 minutes until the gun warm up and current rise up.
- 4. Bring Faraday cup into focus and maximize the current by gun-tilt and save the position of Faraday cup.
- 5. Calculate the center of the sample and reset the coordinates.
- 6. Set the area dose to 200 μ As/cm² and write the nanoscale pattern (junction) with the working field of 100 μ m with 20 pA current.
- 7. Set the area dose to 250 μ As/cm² and write the large pattern (contact pads and leads) with the working field of 1000 μ m with 5 nA current.
- 8. Turn off the gun, vent vacuum, put out the sample and evacuate chamber.

Appendix B

B1. Electronic structure calculations (theoretical calculations are done by Safa Golrokh, Marius Bürkle and Fabian Pauly)

To model the geometric and electronic properties of the SBF-based molecular junctions, we use DFT as implemented in the TURBOMOLE software package [283] with the PBE generalized gradient exchange-correlation functional [225,284-286]. As the basis set we employ def-SV(P) [226,287,288], which is of split valence quality. Total energies are converged to a precision of better than 10^{-6} atomic units, and structure optimizations are carried out until the maximum norm of the Cartesian gradients has fallen below values of 10^{-5} atomic units. To determine the junction geometries we proceed as described in Ref. 28 by first connecting the molecule to one electrode, optimizing the structure and then connecting the molecule to the other electrode in a symmetric manner. Then the junction except for the outermost gold layers is relaxed. In this way we obtain approximate equilibrium geometries for the molecular junctions.

Vibrational modes and EVIB couplings are determined after the geometry optimization by using the "aoforce" and "evib" modules of TURBOMOLE [215,289] based on accurate analytical derivative techniques. We assume that the "dynamical region" of the molecular junction, i.e. the region where the atoms are allowed to vibrate, is identical to its relaxed part, while we assign an infinite mass to the fixed atoms. We characterize the modes by considering the displacement vectors. Due to the larger number of atoms, which are free to vibrate, and since symmetries are generally absent, the classification of vectors remains approximate only. The theoretical investigation of the quantum transport properties of complex molecules like SBF remains challenging because of the large number of atoms and the infinite, nonperiodic geometry of the system. DFT is one of the few operative ab-initio electronic structure methods which can handle the hybrid metal-molecule-metal contacts. On the other hand, due to self-interaction errors in the standard exchange-correlation functional and missing image charge effects, DFT-based methods have difficulties to accurately describe the energy gap and level alignment of molecules on metal surfaces. This can be improved by adding a self-energy correction, resulting in the DFT+ Σ method [290].

The main difference between DFT and DFT+ Σ results for a given contact geometry is typically a pronounced increase of the HOMO-LUMO gap by several eV in DFT+ Σ as compared to DFT that arises from a decrease of the HOMO and increase of the LUMO energies. DFT+ Σ results often show a good agreement with the experimental results for the conductance [236,290]. Details regarding our method can be found in Ref. [291]. In Fig. B1 we present the DFT calculations for the transmission of the SBF molecule, the SBF' configuration where the tip couples to the top of the spirobifluorene foot, and the backbone in HH, TT, and TT' configurations.

They exhibit a HOMO-related resonance close to the Fermi energy and we compute conductance values of $G_{\text{DFT}_\text{SBF}} = 0.0076G_0$, $G_{\text{DFT}_\text{SBF'}} = 0.005 \text{ G}_0$, $G_{\text{DFT}_\text{HH}} = 0.018 G_0$, $G_{\text{DFT}_\text{TT}} = 0.52 G_0$ and $G_{\text{DFT}_\text{TT'}} = 0.67 G_0$. We assume that the unrealistically high

conductance values of the DFT calculations are an artefact of the level-alignment problem and underestimation of the HOMO-LUMO gap common to DFT.



Figure B1. (a) SBF (tripod) molecule on an Au(111) surface. (b) SBF molecule when one electrode couples to the middle of the molecule, called SBF'. Backbone molecule in (c) hollow-hollow (HH) and (d) top-top (TT) configurations. (e) The stretched molecule in TT (TT') position. (e) Computed transmission curves for the SBF, SBF', HH, TT, and TT' configurations in the DFT framework.



Figure B2. (a) SBF molecule on an Au(111) surface. (b) SBF' configuration of SBF, when one electrode couples to the middle of the molecule. DFT+ Σ results for SBF and SBF': (c) Transmissions as a function of energy, (d) IET spectra. The data for SBF are the same as discussed in the chapter 5 (see figures 5.4 and 5.7).

Also the spread of the conductance values is much higher than in the DFT+ Σ calculations, presented in the chapter 5. For the TT configuration also in the DFT framework a pronounced shoulder develops around $E_{\rm F}$ +1.3 eV, in agreement with the findings for DFT+ Σ . In figure B2, we compare the DFT+ Σ results for the transmissions of SBF and SBF' as well as their IET spectra. The conductance of SBF' is G_{SBF'} = 0.0039 G₀, which is

a factor of 4 larger than what we calculate for SFB in the configuration displayed in B2 (a). The IET spectrum reveals that the C-C triple bond stretching mode is shifted to 252 mV. Its peak shows a factor of three smaller amplitude than those found for SBF.

B2. AC broadening

Several vibrational modes can be hidden in one peak of an IET spectrum due to the AC broadening, as shown in figure B3 for the Au-S and C-S stretching modes.



Figure B3. Theoretical IET spectra for several AC voltages (3, 5, 7 and 9 mV) show how the related broadening leads to the overlapping of mode-related peaks, in particular of the Au-S and C-S vibrational modes. The spectra for 5, 7 and 9 mV are offset for clarity.

B3. Lorentzian fit

Our energy-dependent transmission curves in figure 5.4 of the chapter 5 show that the conductance of the SBF-based junctions is largely dominated by a single level, the HOMO. For this reason the single-level model is applicable, and to compare to the experiments we extract the level alignment E_0 and the coupling strengths Γ_L and Γ_R by fitting Lorentzians to the HOMO-peaks of the transmission curves calculated in the DFT+ Σ framework. Since left and right coupling strengths cannot be distinguished, we choose $\Gamma_L \leq \Gamma_R$.

| DFT+Σ | $\Gamma_{\rm L}({\rm eV})$ | $\Gamma_{\rm R}({\rm eV})$ | $E_0 (\mathrm{eV})$ |
|-------|----------------------------|----------------------------|---------------------|
| SBF | 0.010 | 0.048 | 1.20 |
| HH | 0.023 | 0.027 | 1.57 |
| TT | 0.014 | 0.017 | 0.76 |
| TT' | 0.009 | 0.010 | 0.95 |

Table B1. Single-level model parameters extracted from a Lorentzian fit to the transmission curves shown in figure 5.2 of the chapter 5 for SBF, HH, TT and TT'

configurations. The HOMO resonance is fitted with the single-level model of Eq. (3.18), see figure B4.

Figure B4 shows the quality of the fit by comparing the original and fitted theoretical transmission curves. The values presented in figure 5.5 of the chapter 5 range between 0.5 $eV \le E_0 \le 1 eV$ and 0.004 $eV \le \Gamma_L$, $\Gamma_R \le 0.024 eV$.

The theoretical values that we list in Table B1 are in reasonable agreement. In detail, our theoretically estimated level alignment of 0.76 eV $\leq E_0 \leq 1.57$ eV is slightly shifted towards stronger off-resonance conditions, while the electronic couplings with 0.008 eV $\leq \Gamma_{\rm L}$, $\Gamma_{\rm R} \leq 0.048$ eV appear to be more accurately represented.



Figure B4. Computed transmission curves for (a) SBF, (b) HH, (c) TT, and (d) TT' configurations in the DFT+ Σ framework and related fits within a single-level model that describes the HOMO resonance by a Lorentzian function.

B4. Additional examples of IET spectra

Figure B5 shows three experimental IET spectra recorded on an opening trace when stretching an Au-SBF-Au contact. The black curve shows the theoretical result for the TT configuration, calculated in the DFT + Σ framework. The arrows indicate the most prominent vibrational modes.



Figure B5. Same as Fig. 5.4 (b) of the chapter 5 but for three other junctions recorded on the same opening trace. Comparison of experimental (coloured lines) and theoretical (black line, TT position) IET spectra. The arrows show the peak positions in the experimentally and theoretically obtained spectra.

Appendix C

Theoretical analysis for Au-BDT-Au junction (theoretical calculations are done by Safa Golrokh and Fabian Pauly)

The evolution of the Au-BDT-Au structure with the blunt electrode tips in the junction breaking process is presented in figure C1. The relaxed atomic configurations as a function of the electrode separation d are shown in figure C1 (a), while figure C1 (b) displays the total energy and figure C1 (c) the total conductance G as well as those of the two largest transmission eigenchannels G_1 and G_2 .

Different binding configurations of the BDT molecule to the electrodes are realized in the pulling process. At d = 2.0 Å, a hollow-hollow (HH) geometry is reached, where the sulfur atoms at each end bind to three Au atoms. The junction breaks after 2.8 Å of displacement.

As for the junction with the atomically sharp tips discussed in the paper, the data in figure C1 confirms that the charge transport in Au-BDT-Au contacts is carried by a single channel, even for high conductance. Thus, throughout the whole pulling process, sampling conductances between 0 and 0.6 G_0 , a single transmission channel is present within the measurement resolution of 10%.

In figure C1 (c) we show furthermore the shape of the transmission eigenchannel wavefunctions of the two most transparent channels at d = 2.0 Å, when the HH configuration is first realized. Our based calculation based on density functional theory (DFT) for this junction yields conductance values of $G = 2.5 \cdot 10^{-2} G_0 (\tau_1 = 2.3 \cdot 10^{-2}, \tau_2 = 8.9 \cdot 10^{-4})$, which is one order of magnitude smaller than the conductance of the top-top (TT) structure, realized at d = 6.4 Å in figure 6.5 in the chapter 6.

We attribute this to a reduced hybridization between the conducting highest occupied molecular orbital (HOMO) level and the gold electrodes due to the parallel orientation of the molecular π -orbitals and the metal surface as well as the different binding sites of the sulfur atoms in HH and TT positions. The consequently modified interfacial charge rearrangement leads to a HOMO level that is both more distant from the Fermi energy as well as less broadened in HH than in TT, explaining the reduced conductance in the HH configuration.

We want to mention that due to the strong orbital hybridization between substrate and molecule for Au-BDT-Au junctions, the frontier molecular orbitals are strongly modified as compared to the isolated BDT. In such a case, the validity of the DFT+ Σ method [290] is questionable. As a result, our current approach stays within the framework of DFT+NEGF. For reasons of completeness, we show in figure C2 all the evolution steps of the Au-BDT-Au single-molecule junction, discussed in figure 6.5 of chapter 6, as well as its total energy and conductance as a function of *d*. For the junctions shown in figure C1 and C2, we also calculated the IET spectra for selected configurations during the stretching process.



Figure C1. (a) Evolution stages of BDT in a gold contact with blunt metal tips at both sides. *d* is the displacement of the leads, measured from the starting configuration. (b) Total energy and (c) total conductance, *G*, as well as those of the first two conduction channels as a function of the displacement *d*. The inset of (c) shows the first two left-incoming transmission eigenchannel wavefunctions, evaluated at the Fermi energy, for the HH structure at d = 2.0 Å.

As in the chapter 6, a temperature of T = 4.2 K is assumed and the modulation voltage V_{ω} is set to the experimental value of 5 mV [215]. A relatively large vibrational broadening $\eta = 1$ eV is chosen in all of our plots to avoid effects from the current-induced heating of vibrational modes [215]. It is visible from figure C3 that the amplitude and the position of the IET peaks vary during the stretching process. When comparing the junctions with blunt and sharp electrode tips, the IET amplitudes are much higher for those with blunt tips due to different electron-vibration couplings. Despite these changes, the vibrational modes that couple to charge transport remain at very similar energies in all of our calculations, irrespective or the precise geometry realized.



Figure C2. (a) All the evolution steps of the Au-BDT–Au single-molecule junction, shown in Figure 6.5 of the chapter 6. (b) Total energies and (c) logarithmic representation of the total conductance, G, and those of the highest three conduction channels, $G_i = G_0 \tau_i (E_F)$ with i = 1,2,3 of the configurations displayed in (a). (d) Ratio G_2/G_1 as a function of the displacement d. The horizontal dashed line indicates the measurement resolution for that ratio of around 10%.

Our theoretical observations are in qualitative agreement with the experimental ones shown in figure 6.4 with regard to changes in IET peak heights and positions in dependence of the precise junction geometry. However, experimental peak widths are larger and variations in

the computed spectra are less pronounced than in the experimental ones. In this regard, one has to keep in mind that the theory studies only a few selected geometries. Additional effects, such as conductance fluctuations, which are not accounted for in the calculations based on the wide-band approximation [215], may furthermore influence the experimental spectra. This prevents us from deducing the exact binding position of BDT between the Au electrodes based on a comparison of experiment and theory.



Figure C3. Evolution of IET spectra upon stretching for two different Au-BDT-Au junctions. (a) Selected IET spectra for the junction with sharp tips, shown in figure 6.5 of the chapter 6 and figure C2, for electrode separations d = 5.2 Å (black), d = 6.4 Å (red), d = 8.4 Å (blue). (b) The same for the junction with blunt tips, shown in Fig. C1, for d = 0.8 Å (black), d = 1.6 Å (red), d = 2.4 Å (blue). In both panels, the spectra at different electrode separations are displaced vertically for clarity.

Appendix D

D1. Theoretical calculation of molecular structures, molecular orbitals, total and local transmission and vibrational spectra of TEMPO-OPE molecules (theoretical calculations are done by Martin Sebastian Zöllner and Carmen Herrmann).

Kohn-Sham molecular orbital energies were obtained for TEMPO-OPE molecules employing the program package TURBOMOLE 7.0 [292], using the BP86 exchange-correlation functional [293-295] in combination with the resolution of the identity (RI) approximation and a def2-TZVP [296,297] basis set. The structures of the isolated TEMPO-OPE molecule were relaxed using the same basis set and several exchangecorrelation functionals (BP86-D3, BP86, TPSS-D3 [298], TPSSh-D3 [299,300], M06-2X [301], where D3 refers to the third generation of Grimme's empirical dispersion correction with Becke–Johnson damping [302]), until the gradient was below 10^{-4} hartree bohr⁻¹ and the change in energy in the self-consistent field (SCF) algorithm was less than 10^{-6} hartree. The SCF convergence criterion for the single-point calculations was set to 10^{-7} hartree. The structure optimization using the M06-2X functional could not be fully converged, but was stopped at a gradient of 1.7×10^{-3} hartree bohr⁻¹. The BP86-D3 optimized structures were used to calculate infrared (IR) spectra and transmission functions after attaching gold clusters modeling the electrodes. For this purpose, the hydrogens of the thiolate groups were removed and the molecule was placed between two gold clusters in hollow-site adsorption position, setting the gold-sulfur bond lengths to 2.48 Å [303] and the gold-gold distance to 2.88 Å as in crystalline gold. Cartesian coordinates of the resulting structures are given at the end of this document.

The IR spectra were calculated with SNF 5.0.1, a module of the MoViPac package [304], in combination with TURBOMOLE 7.0, using the same computational settings as used for the structure optimization. The convergence threshold for the SCF calculation was set to 10^{-8} hartree and the m5 grid was used.

The transmission functions (-8.0 to -2.0 eV, step size: 0.01 eV) were calculated based on the Landauer–Imry–Büttiker approximation [51,263] using the program ARTAIOS [270]. The overlap and the Fock matrices were calculated by postprocessing single-point calculations with GAUSSIAN 09 [305] employing the hybrid functional B3LYP [306,307] and the LANL2DZ [308] basis set. Local transmissions were evaluated as described in Ref. [309].

Two structures close in energy were obtained after structural optimizations (see figures D1-D5): structure A, in which the TEMPO radical is pointing towards one of the thiols and thus potentially close to an electrode, and structure B in which the TEMPO substituent is oriented more or less perpendicular to the OPE backbone. When Grimme's dispersion correction is used, the interaction between the radical and the OPE backbone in structure A is so strong that it leads to tilting of one of the phenyl rings, which would reduce conductance. However, the nearly optimized structures obtained with the functional M06-2X (which is geared towards noncovalent interactions) do not point towards such a tilting. The energy differences between structures A and B depend on the functional, but they are never larger than roughly 6 kJ/mol, which is below the DFT error bar. Also, interactions between neighboring molecules and between molecules and electrodes can influence these

relative energies. What can be concluded from these calculations is that the TEMPO-OPE molecule can adopt two configurations which are quite close in energy and thus likely to be both important for understanding the measured properties. One of these configurations has the radical unit potentially close to an electrode, which could allow for interactions.

Figure D6 shows the energy diagrams of molecular orbitals and isosurface plots for both TEMPO-OPE molecule structures for α (majority) and β (minority) spins. In our case electron transport can be considered to be dominated by the HOMO-1 for α and by the HOMO for β , since they are (a) energetically closest to the Fermi energy (roughly -5 eV for gold electrodes) and (b) have coefficients on both anchoring groups. The effectively singly occupied orbital, the HOMO for α , is also close to reasonable values for the Fermi energy, but its shape suggests that it does not take part in transport across the molecule. This is confirmed by the transmission functions, which are very similar for majority and minority spins close to the Fermi energy (figure D7), and by the local transmission contributions (figures D8 and D9). The fact that the transmission peak close to the HOMO energy is smaller for structure A than for B may be related to the tilting of one of the phenyl rings in structure A (see above).

To evaluate whether a single-level model is reasonable for the structures under study here, we fitted the α transmission in the energy range from -6.6 eV to -5.0 eV to a Breit-Wigner function of the shape. (see Eq. 3.15 and figure D7, bottom). For structure A, we obtained values of $\Gamma_L = 22.0$ meV, $\Gamma_R = 79.1$ meV, $E_0 = 6.46$ eV, with a fit quality characterized by $r^2 = 0.995$, RMSE = 0.0129, RSS = 0.0265. For structure B, the analogous values were $\Gamma_L =$ 65.4 meV, $\Gamma_R = 65.4$ meV, $E_0 = -6.41$ eV, $r^2 = 0.994$, RMSE = 0.0232, RSS = 0.0847. Note that the peak positions are given on an absolute scale, as the exact location of the Fermi energy is unknown. It is estimated to be around -5 eV. The larger electronic coupling Γ found in the calculations compared with the experiment may be attributed to the fact that in the calculations, the thiolate anchoring group is bound to an fcc hollow site, which corresponds to the largest possible electronic coupling. In the experiment, different binding configurations with smaller coupling are likely to play a role. Also note that the strongly asymmetric coupling in structure A may be attributed to the twisted benzene ring due to interaction with the radical. As discussed above, this twist may be caused by an overestimation of dispersion interaction and should thus not be taken too literally. In addition, the peak location E_0 is known to depend strongly on the exchange correlation functional employed. For all these reasons, the fits shown in figure D7 are meant to illustrate the compatibility of the calculated transmission functions with a single-level model rather than to provide a basis for a quantitative comparison with the experimental fit.
Optimized structures

BP86-D3





Structure B (favored by 6.3 kJ/mol)



BP86





Structure A (favored by 1.6 kJ/mol)



Structure B









Structure B (favored by 5.4 kJ/mol)

Figure D3. Two different optimized structures of TEMPO-OPE with TPSS-D3 /def2-TZVP.

TPSSh-D3





Structure A



Structure B (favored by 5.4 kJ/mol)

Figure D4. Two different optimized structures of TEMPO-OPE with TPSSh-D3 /def2-TZVP.



Structure B

Figure D5. Two different optimized structures of TEMPO-OPE with M06-2X /def2-TZVP. The structures did not fully converge (0.0017 hartree bohr⁻¹ structure A, 0.0015 hartree bohr⁻¹ structure A).

Molecular orbitals



Figure D6. Energies and isosurface plots of the spin-up α (majority spins) and spin-down β (minority spins) molecular subsystem orbitals in TEMPO-OPE molecules (B3LYP/LANL2DZ). Top: structure A. Bottom: structure B (both optimized with BP86-D3/def2-TZVP as dithiols and then attached to gold clusters). The Fermi energy of the electrodes is expected to be around -5 eV (or slightly higher). Molecular subsystem orbitals were obtained by solving the secular equations for the blocks of the Fock and overlap matrix blocks corresponding to atom-centered basis functions localized on the molecule (including the sulfur atoms). HOMO: Highest occupied molecular orbital (MO). LUMO: Lowest unoccupied MO. SOMO: Singly occupied MO (note that the energies for the spin-up and spin-down version of this orbital are very different due to their different occupation).

Calculated total and local transmissions



Figure D7. Top: Transmission functions calculated with B3LYP/LANL2DZ for both spin channels (α : spin-up, majority; β : spin-down, minority). Left: structure A. Right: structure B (both optimized with BP86-D3/def2-TZVP as dithiols and then attached to gold clusters). The Fermi level is indicated at -5 eV. This is a reasonable choice for gold with its bulk work function at -5.4 eV. Modeling the effect of parameters such as electrode shape and the number and configuration of the adsorbed molecules on the Fermi energy is not straightforward, which is why this value of the Fermi energy should not be taken too literally. Bottom: Breit-Wigner fit to α transmission (see text for details).



Figure D8. Calculated local transmission for both spin channels (α : spin-up, majority; β : spin-down, minority) for structure A. Three energies around the Fermi energy were chosen to illustrate the constant character of the local transmission over that energy range.



Figure D9. Calculated local transmission for both spin channels (α : spin-up, majority; β : spin-down, minority) for structure B. Three energies around the Fermi energy were chosen to illustrate the constant character of the local transmission over that energy range.

Calculated normal modes



Figure D10. Displacement vectors and excitation energies (meV) of selected normal modes calculated for structure A placed between two electrodes (BP86-D3/def2-TZVP).



Figure D11. Displacement vectors and excitation energies (meV) of selected normal modes calculated for structure B placed between two electrodes (BP86-D3/def2-TZVP).

D2. Experimental section

D2.1 Molecule deportation and deposition

TEMPO-OPE, ketone-OPE or pristine OPE molecules were deposited on samples with Au freestanding bridges by immersing them in a diluted solution for 24 hours at room temperature. Here, the concentration of the molecular solutions was 4 mM in tetrahydrofuran (THF). Two molar equivalent tetra-n-butylammonium fluoride (TBAF) was added to the solution to deprotect the trimethylsilane end groups of TEMPO-OPE and ketone-OPE and then to promote the formation of Au-S bonds [310,311]. Meanwhile, an ammonium hydroxide (NH₄OH) was used for the deprotection of the acetyl end groups of OPE. The concentration of NH₄OH is the same as that of TBAF. After that, the samples were rinsed in pure THF solution and then dried in nitrogen flow.

D2.2 Charge transport measurements for TEMPO-OPE/OPE molecular junctions

(a) Fundamental charge transport measurements

A sample with TEMPO-OPE/OPE molecules was mounted in a MCBJ setup. The sample was evacuated at a pressure of 10^{-5} mbar for 1 hour. A small amount of He gas was introduced into the sample space and then the sample was cooled to 4.2 K. After that, a freestanding Au bridge was broken gently by displacing a pushing rod (see figure 7.1 in the chapter 7). Single molecule junctions of TEMPO-OPE/OPE were formed by repeatedly breaking and reforming the Au junctions.

The charge transport from the TEMPO-OPE/OPE molecules was examined by dc linear conductance, current (*I*)-voltage (*V*), differential conductance (d*I*/d*V*) and inelastic electron tunneling spectroscopy (IETS) (d^2I/dV^2) measurements. To obtain a conductance histogram, the dc conductance was measured at a fixed voltage of 60 mV with a sub-femtoamp source meter (Keithley 6430). The *I-V* measurements were performed by detecting the current signal through a low-noise current amplifier (Femto DLPCA-200) [111]. Here, the voltage was supplied by a dc source meter (Yokogawa 7651). For d*I*/d*V* and IETS (d^2I/dV^2) measurements, a standard ac modulation technique with a lock-in amplifier (Stanford Research Systems SR830) was used to detect the first and second harmonic [82,212]. The ac modulation amplitude and the detection frequency in the lock-in amplifier were 4 mV and 165.5 Hz, respectively. The dc voltage was varied in the range of ± 0.5 V.

(b) Charge transport measurements under magnetic field

We examined the charge transport from TEMPO-OPE molecules under magnetic fields at 4.2 K, including magnetoresistance (MR), *I-V* and IETS measurements. Here, magnetic fields at a maximum of 5 T were applied perpendicularly to the sample plane by a

superconducting magnet. For the MR measurements, the fields were varied in the range of ± 4 T, starting at 0 T, increasing to +4 T, decreasing to 4 T and finally returning to 0 T. The color codes in figure 7.3 in the chapter 7 correspond to the following notations: black (0 \rightarrow +4 T), red (+4 T \rightarrow 0 T), blue (0 \rightarrow -4 T) and magenta (-4 T \rightarrow 0 T). The applied dc voltage and the sweeping rate of the magnetic fields were fixed at 30 mV and 400 mT/min, respectively, to minimize reconfigurations of the junctions due to their limited lifetime. We verified that the temperature increased by less than 20 mK during the field sweeps. For comparison the MR from pristine OPE molecules was measured under the same conditions as those used for the TEMPO-OPE molecules.

D2.3 Conductance histogram and statistical analysis of *I-V* curves with single level model

(a) Conductance histograms of TEMPO-OPE and OPE molecule junctions

Figure D12 shows conductance histograms of TEMPO-OPE and OPE molecule junctions. The most favorable conductance for TEMPO-OPE junctions was estimated to be $6.0\pm3.8\times10^{-4}$ G₀. The conductance value is close to that of OPE molecules $(3.7\pm2.0\times10^{-4}$ G₀).



Figure D12. Conductance histograms of (a) TEMPO-OPE and (b) OPE molecule junctions.

(b) Statistical analysis of *I-V* curves for TEMPO-OPE molecule junctions

I-V curves, which were obtained from 130 different TEMPO-OPE junctions, were analyzed with the Breit-Wigner single level model to understand the charge transport. The estimated energy level, $|E_0|$, and coupling constants, Γ_L and Γ_R , are plotted as a function of the linear conductance of individual TEMPO-OPE junctions with relatively symmetric coupling constants of more than $\alpha = 0.8$ (figure D13).



Figure D13. Conductance dependence of fitting parameters, (a) $|E_0|$, (b) Γ_L and Γ_R , for TEMPO-OPE junctions.

The estimated energy level position, $|E_0|$, does not show a clear dependence of the conductance. The average value was 0.49 ± 0.2 eV, which agrees well with that reported for pristine OPE molecules from measurements at room temperature [202]. In contrast, Γ_L and Γ_R increase strongly with conductance. These results reveal that the charge transport is determined by the coupling strength between the molecule and the electrodes rather than by a shift in the energy level position.

In addition, we note that the variation of $|E_0|$ in our experiment is somewhat higher than that shown in Ref. [202]. We argue that this larger value originates from the smaller statistical ensemble and the fact that in our study contacts were examined that had been

deliberately stretched, whereas unstrained junctions were investigated in Ref. [202]. When following the development of $|E_0|$ of an individual junction upon stretching we usually observe a slight increase in $|E_0|$ (see below, section D2.3-8 and figure. D22). However, the coupling constants, Γ_L and Γ_R , strongly depend on conductance; the values increase with increasing conductance while the symmetry factor remains constant. The analysis also clarifies that the charge transport in TEMPO-OPE junctions can be well described by the Breit-Wigner single level model and that the conductance changes are governed by changes in the coupling strength between the molecules and both electrodes.

D2.4 Symmetrization of IET spectrum and assignment of molecular vibration peaks

Figure D14 shows an experimental IET spectrum for a TEMPO-OPE junction and a symmetrized spectrum obtained with the following point-symmetric function [179], y=[f(x)-f(-x)]/2, for positive and negative bias voltages. The spectra with only a positive voltage are shown in figure 7.2(d) in the chapter 7. The symmetrization of the IET spectrum was undertaken to correct the asymmetricity with the positive and negative voltages. All the peaks were visible at the same bias voltages in both the experimental and symmetrized spectra, indicating symmetric coupling between the molecule and the electrodes.



Figure D14. Experimental (black line) and symmetrized (red line) IET spectra $(d^2I/dV^2)/(dI/dV)$ at a TEMPO-OPE junction for positive and negative bias voltages.

The visible peaks in the IET spectra were assigned by comparison with those for pristine OPE and ketone-OPE molecules as shown in figure D15. In addition, we referred to infrared and Raman spectroscopy measurements for polymers with TEMPO radicals to assign a vibration peak for the N-C stretching and in comparison with vibrational spectra calculated by DFT (figure D10 and D11). The detailed assignments of vibration peaks for 50 different molecular junctions are summarized in Table D1.



Figure D15. Comparison of IET spectra taken from single molecule junctions of (a) TEMPO-OPE, (b) Ketone-OPE and (c) OPE. The molecular structures are indicated in (d)-(f).

| Peak position (mV) | Modes | Description | Literature values (mV) |
|-----------------------|-------------|-------------------------|---------------------------|
| 1. 10-20 | v (Au-Au) | Au-Au optical phonon | 10-20 |
| 2. 28-48 | v (Au-S) | Au-S stretching | 35-80 |
| 3. 55-72 | Ring vib. 1 | Ring vibrations | 57 |
| 4. 83-106 | Ring vib. 2 | Ring vibrations | 80-104 |
| 5. 105-131 | v (C-S) | C-S stretching | 130-133 |
| 6. 130-156 | Ring vib. 3 | Ring vibrations | 133-146 |
| 7. 150-171 | v (N-C) | N-C stretching | 145-158 |
| 8. 191-219 | Ring vib. 4 | Ring vibrations | 195-199 |
| 9. 225-252 | v (C=O) | C=O stretching | 211-215 |
| 10. 252-279 | ν (C≡C) | C-C triple bond stretch | ing 274-276 |

Table D1. Vibrational mode assignment in IETS measurements for TEMPO-OPE junctions. The table was made with IET spectra from 50 distinct contacts.

The following references were used for the above assignments: v(Au-Au) [Ref. [86,265], v(Au-S) [Ref. [85,88,228,265,312]], benzene-ring vibrations 1 and 2 [Ref. [85]], v(C-S) [Ref. [85,265,312]], benzene-ring vibrations 3 and 4 and v(C=C) [Ref. [85,212,265,312-314]], v(N-C) and v(C=O) [Ref. [266,313,315-317]].

D2.5 Magnetoresistance measurmennts

(a) Histogram of magnetoresistance for TEMPO-OPE and OPE junctions

Figure D16 shows the magnetoresistance histogram of TEMPO-OPE junctions with different conductance. For comparison, the MRs from OPE junctions are shown in the same figure. We measured MR curves for total 23 TEMPO-OPE junctions obtained from 5 samples, out of which 17 junctions (74 %) indicated large MR of more than 16 % at 4T and the maximum value was 287 %. The other junctions exhibited the same shape of the MR curves. However, the amplitudes remained in the variation of 2-6 %. The average in all MR values was 43.7 % at 4T for TEMPO-OPE junctions. We examined in total 9 OPE junctions formed from a sample and the average was 2.2 % in contrast to the large MRs of TEMPO-OPE molecules.



Figure D16. Magnetoresistance histogram of TEMPO-OPE and OPE junctions.

(b) Magnetoresistance curves from TEMPO-OPE, OPE and Au junctions

Figures D17 (a) and (b) show the same magnetoresistance (MR) curves from TEMPO-OPE and OPE junctions as those indicated in Figure 3 in the manuscript but with different resistance scales for better visibility. For comparison, the curves from Au atomic contacts are shown in figure D17 (c).

The MRs of TEMPO-OPE junctions increased with elevating the magnetic fields up to 4 T. The values were at least one order of magnitude higher than those of OPE junctions. The MR saturated in the range of 4 T to 6 T and then started decreasing at higher magnetic field (figure D18). The same behavior was also observed in the OPE and Au atom junctions (figures D17 (b) and (c)). We found that the saturation and/or decrease of MRs at high magnetic fields are not unique features in TEMPO-OPE junctions. Besides, after applying very high magnetic field the resistance did not return to its initial value at 0 T, what we interpret as reconfigurations of the junctions. To suppress the effect, we measured the curves up to 4 T in most cases.



Figure D17. Magnetoresistance curves from (a) TEMPO-OPE, (b) OPE and (c) Au atom junctions. The magnetic fields were swept from 0 T to 6 T (black) at the maximum and returned to 0 T (red), decreasing to -4T (blue) and finally returning to 0 T (magenta) again. The traces are offset vertically for better visibility. The values in the panels on the left hand side indicate the maximum MR values of the individual traces, the numbers at the right hand side indicate the zero field conductance.



Figure D18. (a) Saturation and subsequent decrease of MR at high magnetic field in TEMPO-OPE junctions. (b) Irreversible MR curves after application of very high fields indicating a reconfiguration of the junctions under high magnetic field over 4T.

D2.6 Magnetic field dependence of a zero bias peak in differential conductance (dI/dV) curves

We show a typical example of the magnetic field dependence of a dI/dV curve for a TEMPO-OPE junction (figure D19). Magnetic fields of up to 5 T were applied out of plane. A peak is visible at zero bias voltage. However, the peak was not split with increasing magnetic fields, revealing that it was not ascribed to the Kondo effect but simply to an interference effect.



Figure D19. Magnetic field dependence of differential conductance (dI/dV) curves. Here the spectra are normalized to the amplitudes at zero bias voltages.

D2.7 Magnetic field dependence of *I-V* curves for TEMPO-OPE and OPE junctions



Figure D20. *I-V* curves with different magnetic fields for (a) TEMPO-OPE and (b) OPE junctions. The fitting curves with the single level model are indicated by red lines in both figures. The following fitting parameters were obtained for Γ_L and Γ_R at the TEMPO-OPE junction: 6.9 mV for Γ_L and 7.9 mV for Γ_R (0T), 6.0 mV for Γ_L and 6.5 mV for Γ_R (2T), 5.1 mV for Γ_L and 5.4 mV for Γ_R (3T), 3.4 mV for Γ_L and 3.5 mV for Γ_R (5T).

Figure D20 (a) and D20 (b) show *I-V* curves with different magnetic fields for TEMPO-OPE and pristine OPE molecules. Magnetic fields of up to 5 T were applied out of plane. We can see a clear difference in the magnetic field dependence of the *I-V* curves.

With the TEMPO-OPE molecules, the current was obviously reduced by elevating the magnetic field and the current reduction was estimated to be 62 %. On the other hand, negligible change was observed in the current through the OPE molecules. The abovementioned variations of the estimated conductance and the fitting parameters with the single-level model for TEMPO-OPE molecules are seen in Figure 4 in the manuscript. We found that the conductance change induced by magnetic field is closely corrrelated to the variation of $\Gamma_{\rm L}$ and $\Gamma_{\rm R}$ and uncorrelated or even weakly anti-correlated to that of E_0 . The same behavior was confirmed in all junctions with MRs of more than 10 %. We show one more example in figure D21 to support our claim.



Figure D21. Magnetic field dependence of the charge transport through an Au/TEMPO-OPE/Au molecule junction. Here, the initial conductance was $8.5 \times 10^{-4} G_0$. Change in (a) conductance and (b) energy level position, $|E_0|$, and coupling constants, Γ_L and Γ_{R} , as a function of magnetic field.

D2.8 Impact of stretching TEMPO-OPE junctions on I-V and IETS measurements

The variation in conductance and parameters, $|E_0|$, Γ_L and Γ_R , estimated from fitting with the single-level model are shown in figure D22 (a) and D22 (b). We observed similar changes in the conductance and the fitting parameters to those with magnetic fields. The conductance decreased as the displacement between two electrodes increased (figure D22 (a)). The reduction in conductance coincided with that of the coupling constants, $\Gamma_{\rm L}$ and $\Gamma_{\rm R}$ (figure D22 (b)). In contrast, the energy level, $|E_0|$, was almost independent of the conductance while the contact was stretched. Meanwhile, we can see distinct changes in the IET spectra for the samples with stretched contacts and with magnetic fields. Figure D23 (a) and (b) show the variation in the IET spectra when stretching a contact and the displacement dependence of peak intensities for typical molecular vibration modes.



Figure D22. Change in (a) conductance and (b) energy level position, $|E_0|$, and coupling constants, Γ_L and Γ_{R} , as a function of electrode displacement.

An obvious feature of stretching is the increase in peak intensity for the optical phonon of Au-Au bonds. In addition, the peaks attributed to the stretching vibration of C=C bonds and benzene ring vibrations 3 were enhanced by increasing the electrode displacement. These features of stretched contacts agree well with those obtained from calculations for pristine OPE molecules reported by Kula et al. [265]. On the other hand, such variations were not seen in samples with magnetic fields. These differences in IETS measurements also support the view that the conductance reduction under magnetic fields cannot be ascribed to a change in geometry but to a variation in the electronic structure in TEMPO-OPE molecules.



Figure D23. (a) IET spectra with different electrode displacement. Here, the spectra were symmetrized. (b)The change in peak intensities for representative vibration modes while stretching the molecular contacts.

D2.9 Magnetic field dependence of IET spectra for a OPE junctionWe examined the magnetic field dependence of the inelastic transport properties of a OPE junction. Figure D24 (a) and D24 (b) show IET spectra with different magnetic fields of up to 5 T and the change in the intensities of representative vibration peaks as a function of the magnetic field. The peak intensities are independent of the magnetic fields and fluctuate with a deviation of 20 % in contrast to the suppression of peak intensities for TEMPO-OPE junctions.



Figure D24. (a) Symmetrized IET spectra in different magnetic fields of up to 5 T for a OPE junction. (b) The change in peak intensities for typical vibration modes as a function of magnetic field. Here the intensities are normalized to those without a magnetic field.

List of Publications

Shot noise of 1,4-benzenedithiol single-molecule junctions.
M. A. Karimi, S. G. Bahoosh, M. Herz, R. Hayakawa, F. Pauly and E. Scheer. Nano Lett., 2016, 16, 1803–1807.

Identification of the current path for a conductive molecular wire on a tripodal platform.
M. A. Karimi, S. G. Bahoosh, M. Valášek, M. Bürkle, M. Mayor, F. Pauly and E. Scheer.
Nanoscale, 2016, 8, 10582-10590.

• Large Magnetoresistance in Single Radical Molecular Junctions.

R. Hayakawa, M. A. Karimi, J. Wolf, T. Huhn, M. S. Zöllner, C. Herrmann, and E. Scheer. Nano Letters, 2016, 16 (8), 4960–4967.

• *Inelastic noise of gold atomic junctions*. M. A. Karimi and E. Scheer. In preparation.

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