# **Molecular Electronics** An Experimental and Theoretical Approach

<sup>edited by</sup> Ioan Bâldea



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# **Contents**

Preface

Pre	face			xiii		
1.	Sing	le-Mol	ecule Devices	1		
	Kai S	Kai Sotthewes and Harold J. W. Zandvliet				
	1.1	Introd	luction to Molecular Electronics	1		
	1.2	The A	rt of Catching and Probing a Single Molecul	le 2		
	1.3	Trans	port Properties of a Single Molecule	4		
		1.3.1	Quantization of Conductance	4		
		1.3.2	Coherent and Incoherent Transport	7		
		1.3.3	Coulomb Blockade	9		
		1.3.4	Transport Mechanisms in Molecules	14		
			1.3.4.1 Coherent tunneling	15		
			1.3.4.2 Incoherent tunneling	17		
			1.3.4.3 Hopping	18		
			1.3.4.4 Thermionic emission	18		
			1.3.4.5 Fowler–Nordheim tunneling or field emission	18		
	14	Molec	ular Devices	20		
	1.1	141	Contacting of a Single Octanethiol Molecu	le 20		
		142	Single Molecule Switch	22		
		143	Transport through a Single Octanethiol			
		1.1.5	Molecule Junction	26		
		1.4.4	Single-Molecule Transistor	27		
	1.5	Outlo	ok	29		
2.	Mał Ense	king Co embles	ntact to Molecular Layers: Linking Large of Molecules to the Outside World	37		
	Chris and (	stina A. H Curt A. R	łacker, Sujitra Pookpanratana, Mariona Coll, lichter			
	2.1	Introc	luction	37		

vi Contents

	2.2	2 Challenges Facing Ensemble Molecular Junctions			
	2.3	Investigating Metal-Molecule Interactions			
	2.4 Novel Fabrication Approaches			46	
		2.4.1	Conducting Polymer Top Contacts	46	
		2.4.2	Liquid Metal Top Contacts	48	
		2.4.3	Crossed Wire Top Contacts	50	
		2.4.4	Conducting Probe AFM Top Contacts	52	
		2.4.5	Deposition of Preformed Metal Contacts	53	
	2.5	Juncti	on Characterization Approaches	55	
		2.5.1	Electrical Characterization	55	
		2.5.2	Spectroscopic Characterization	57	
	2.6	Conclu	usion and Outlook	58	
3.	Char	ge Tra	nsport in Dynamic Molecular Junctions	65	
	Stéph	ane Ler	nfant		
	3.1	Introd	luction	65	
		3.1.1	Light Stimulus	67	
		3.1.2	Electric Field Stimulus	69	
		3.1.3	Other Stimuli: pH, Biomolecule, Ion	70	
	3.2	Fixati	on of pi-Conjugated Molecules on		
		Gold S	Surfaces via Thiol Bond	72	
		3.2.1	Systems Studied: With One or Two		
			Anchor Groups	72	
		3.2.2	Structural Characterization: Orientation		
			of the Molecule on the Surface	74	
	3.3	A Cati	on-Binding Switchable Molecular Junction	77	
		3.3.1	Preparation and Characterization of the SAM	78	
		3.3.2	Electronic Transport Properties	80	
	3.4	An Op	tical Switch Molecular Junction	82	
		3.4.1	Preparation and Characterization of the SAM	83	
		3.4.2	Characterization under Irradiation	84	
		3.4.3	Electronic Transport Properties	86	
		3.4.4	Origin of This High Conductance	00	
	2 5		Switching Katio	89	
	3.5	Concli	usion	91	

4. M T	Mod Tran	lulate a sport o	nd Control of Detailed Electron of Single Molecule	10	
В	Bingqian Xu, Kun Wang, Joseph Hamill, and Ryan Colvard				
4	ł.1	Introd	uction	10	
		4.1.1	Evolution of Experimental Determination		
			of Single-Molecule Conductance	10	
		4.1.2	Statistical Analysis	10	
		4.1.3	Measured Molecule	11	
4	1.2	Contro	oversy in SMBJ Measurements	11	
4	ł.3	Exper	imental Modulations and Controls		
		of SMI	3J System	11	
		4.3.1	Modulations of SPMBJ Measurement Process	11	
		4.3.2	Tuning Molecular Structures	12	
		4.3.3	Environmental Controls of SMBJ System	12	
		4.3.4	Characteristic Current–Voltage Behavior	13	
4	ł.4	The D	evelopment of Data Analysis Approaches	13	
4	ł.5	Summ	ary and Outlook	13	
5. \	/ibr	onic Ef	fects in Electron Transport through		
S	ing	le-Mol	ecule Junctions	15	
R	laine	er Härtle	e and Michael Thoss		
5	5.1	Introd	uction	15	
5	5.2	Theor	etical Description of Vibrationally		
		Coupl	ed Electron Transport	15	
		5.2.1	Model Hamiltonian	15	
		5.2.2	Survey of Theories for Vibrationally Coupled		
			Charge Transport	16	
		5.2.3	A Non-Equilibrium Green's Function		
			Approach	16	
			5.2.3.1 Electronic Green's functions	16	
			5.2.3.2 Vibrational Green's functions	17	
			5.2.3.3 Self-consistent solution scheme	17	
			5.2.3.4 Observables of interest	17	
5	5.3	Proces	sses and Mechanisms in Vibrationally	4 -	
		Couple	ed Electron Transport	17	

viii Contents	/iii
---------------	------

		5.3.1	Non-Resonant Transport		
			Process	ses/Co-Tunneling	180
		5.3.2	Resona	nt Transport	
			Process	ses/Sequential Tunneling	186
			5.3.2.1	With respect to a single	
				electronic state	186
			5.3.2.2	With respect to multiple	
				electronic states	190
		5.3.3	Local h	eating and cooling in a	400
			molecu	larjunction	193
			5.3.3.1	Role of resonant electron–hole pair	105
			<b>F</b> 2 2 2	Creation processes	195
			5.3.3.2	cooling in the presence of multiple	200
	51	Tho D	olo of El	electronic States	200
	5.4	for Po	ole of Electronic-vibrational coupling		202
	55	Conclu	uding Re	marks	204
	0.0	Gomer	uuiing ite		201
6.	Vibr	ation S	pectroso	copy of Single Molecular Junctions	223
	Mana	abu Kigi	ichi and R	lyuji Matsushita	
	6.1	Introd	luction		224
	6.2	IETS a	and PCS		225
		6.2.1	Princip	les of IETS and PCS	225
		6.2.2	Applica	tion of IETS and PCS to Single	
			Molecu	lar Junctions	226
		6.2.3	Atomic	Motion Induced by Excitation	
			of Vibra	ation Mode	230
	6.3	SERS			233
		6.3.1	Princip	les of SERS	233
		6.3.2	SERS of	f Molecular Junctions	234
		6.3.3	SERS of	f Single Molecular Junctions	237
		6.3.4	Single N	Molecule Dynamics	239
		6.3.4 6.3.5	Single M SERS A	Molecule Dynamics ctive Mode in Single Molecular	239
		6.3.4 6.3.5	Single M SERS A Junctio	Molecule Dynamics ctive Mode in Single Molecular ns	239 242

viii

Contents	ix
----------	----

7. Cur Jun	rents fr	om Pulse-Driven Leads in Molecular A Time-Independent Scattering Formulation	249	
Мас	iyan Kup	erman and Uri Peskin		
7.1	7.1 Introduction			
7.2	Dress the Le	ing Long-Range Field Interactions with eads	253	
7.3	Time-	Independent Scattering Theory for Transient	255	
	731	The Hamiltonian	255	
	7.3.2	The Scattering Amplitude	256	
	7.3.3	The Current Formula	258	
7.4	The T	ransmission Functions and Generalized		
	Tien–	Gordon Formulas	259	
	7.4.1	The Trace Formula	259	
	7.4.2	The Molecular Green Operator	260	
	7.4.3	The Wide Band Limit	261	
	7.4.4	Generalized Tien–Gordon Formulas	263	
7.5	Analy	tic Model Applications	265	
	7.5.1	A Single Level Conductor	265	
	7.5.2	A Narrow Transmission Resonance	266	
	7.5.3	A Perfect Conductor	270	
7.6	Concl	usions	271	
8. Bio	molecu	lar Electronics	281	
Juan	Manuel	Artés Vivancos, Joshua Hihath, and Ismael Díez-Pérez		
8.1	Introd	luction	282	
	8.1.1	The Birth of Molecular Electronics	283	
	8.1.2	Introduction to CT Mechanisms: From		
		Tunneling to Hopping	287	
		8.1.2.1 Coherent Tunneling	288	
		8.1.1.2 Hopping Transport	289	
	8.1.3	Two-Terminal versus Three-Terminal		
		Devices: Towards the Molecular Transistor	290	
8.2 Peptides and Proteins 29				

**x** Contents

		8.2.1	Peptide	s in Molecular Electronics	294
		8.2.2	Protein	S	296
			8.2.2.1	Azurin: Photochemical and	
				electrochemical approaches to CT	296
			8.2.2.2	Full azurin electronic	
				characterization using ECSTM	298
			8.2.2.3	Other proteins	304
	8.3	Condu	ctance o	f DNA Duplexes	306
		8.3.1	Early D	NA Conductance Experiments	308
		8.3.2	Conduc	tance of Short DNA Duplexes	310
			8.3.2.1	Statistical DNA conductance	
				measurements	310
		8.3.3	Outlook	x for DNA Charge Transport	313
	8.4	Conclu	ision and	d Future Perspectives	313
9.	EC-S	TM/ST	S of Red	ox Metalloproteins and Co-Factors	325
	Andre	ea Alessa	andrini ar	nd Paolo Facci	
	9.1	Introd	uction		326
	9.2	The El	ectroche	emical Scanning Tunneling	
		Micros	scope		328
	9.3	Redox	Metallo	proteins	330
		9.3.1	The Azı	ırin	332
	9.4	Redox	Co-Fact	ors	334
	9.5	ECSTM	1 of Azur	'n	335
		9.5.1	ECSTS of	of Azurin	339
	9.6	ECSTM	1/STS of	the Benzoquinone/Hydroquinone	
		Couple	<u>e</u>		345
10.	Elect	ron Tra	ansport i	in Atomistic Nanojunctions from	
	Dens	sity Fur	nctional	Theory in Scattering Approaches	353
	Yu-Ch	ang Che	en		
	10.1	Introd	uction		353
	10.2	Theory	y of Elec	tron Transport	354
		10.2.1	The Bir	netal Junction	355
		10.2.2	Inclusi	on of an Atomistic Nanostructure	
			in the H	Bimetal Junction	361

	10.2.3	Solving the Problem in the Plane				
		Wave Bas	sis	364		
10.3	3 Quantum Transport Properties Calculated by					
	Curren	t-Carrying	g Wavefunctions	365		
	10.3.1	Moments	s of Current	365		
		10.3.1.1	First moment-current	367		
		10.3.1.2	Second moment-shot noise	368		
		10.3.1.3	Third moment-counting statistics	369		
	10.3.2	Current-	Induced Forces	371		
	10.3.3	Thermoe	lectric Properties	373		
		10.3.3.1	Seebeck coefficient	374		
		10.3.3.2	Thermal current carried by			
			electrons	376		
		10.3.3.3	Thermal current carried by			
			phonons	378		
		10.3.3.4	Thermoelectric figure of merit	379		
10.4	Vibron	ic Effects		380		
	10.4.1	Hamilton	ian of Electron–Vibration			
		Interaction	ons	381		
	10.4.2	Local Hea	ating	385		
	10.4.3	Inelastic	Current and Thermal			
		Current (	Carried by Electrons	387		
	10.4.4	Inelastic	Seebeck Effects and ZT	390		
10.5	Summa	ary		394		
11. Tran	sition V	/oltage Sp	ectroscopy: An Appealing Tool of			
Inve	stigatio	n in Mole	cular Electronics	397		
Ioan	Bâldea					
11.1	Introd	uction		398		
11.2	The Relative Molecular Orbital Alignment Relative					
	to Electrodes' Fermi Energy: A Key Parameter					
	for Cha	arge Trans	fer	400		
11.3	The Ba	rrier Mod	el Artefacts of the			
	Simmo	ons-Based	Approach	404		
11.4	TVS for	r Vacuum	Nanojunctions	410		

11.5	Describing TVS within the Newns-Anderson Model	411
11.6	Effect of Stochastic Fluctuations	419
11.7	Analytical Results for I–V Spectroscopy	421
11.8	A Remarkably Simple Universality Class	423
11.9	Summary and Outlook	423

Index

439

# Preface

The field of molecular electronics, to which the present book is devoted, has rapidly evolved into a very active interdisciplinary field of research at the interface between nanotechnology, chemistry, and physics. It aims at fabricating devices with sizes of nanometers under atomic control, by developing novel bottom-up approaches, as opposed to the classical top-bottom approaches.

It is of course impossible, within a reasonable volume, to discuss or even list all of the topics in a field of science whose size is quickly approaching the "thermodynamic limit." One of the most difficult decisions one is faced with in editing a book on molecular electronics is the selection of the material. I proceeded by sampling a few definite topics, which are discussed in rather great detail in separate chapters by experts in their fields. Adopting a pedagogical style, with own introduction and written in a self-contained manner, the chapters mainly aim to provide guidelines for young scientists (physicists, chemists, engineers) planning to actively contribute, as experimentalists or theorists, to molecular electronics. Still, a series of results as well as the manner of presentation are new and can be inspiring and of interest to specialists in the field.

There are, of course, important problems that are practically not touched upon. This inherently reflects the state-of-the-art of a vivid field, which is very far from being in a "steady state."

I thank Pan Stanford Publishing for having invited me to edit such a book and all the authors for having accepted to contribute to it. I hope that the readers will find its content both useful and enjoyable.

> **Ioan Bâldea** Heidelberg, September 2015

# **Chapter 1**

# **Single-Molecule Devices**

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# 1.1 Introduction to Molecular Electronics

Molecular electronics is the research field that deals with the design and implementation of electronic devices that rely on a single or a few molecules. The idea to use single molecules as elementary electronic building blocks has been put forward in 1974 by Aviram and Ratner in a seminal paper [1]. It is evident that a proper understanding of the properties of an individual molecule is of utmost importance for molecular electronics. The transport properties of a single molecule are evidently the most relevant properties for basically all molecular electronics applications [2–9]. Measuring the resistance or conductance of a single molecule seems trivial: One connects both ends of the molecule to macroscopic electrical contacts and records a current-voltage (I-V)trace. However, there are several challenging hurdles that have to be overcome before a successful measurement can be executed. One cannot simply take two alligator clips and connect them to both ends of the molecule. The size of a molecule is of the order

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2 Single-Molecule Devices

of a nanometer, and therefore one has to apply clever tricks to capture a molecule between two macroscopic electrical contacts. In the next section, we will briefly discuss several methods that have been applied to "catch" a single molecule between two macroscopic electrical contacts. Once the molecule is properly contacted, the transport experiment is rather straightforward; however, the interpretation of the current-voltage traces is far from trivial. The molecular orbitals of the molecule can hybridize with the electronic states of the contacts leading in general to shifts and broadening of the molecular orbitals. Rather than measuring the conductance of a single molecule, one measures the conductance of the complete contact-molecule-contact junction. As pointed out by K. W. Hipps in 2001 in a Science article entitled "It's all about the contacts" molecular electronics is mainly a "contact" problem [10]. Regarding the properties of single molecules, we will restrict ourselves in this contribution to transport properties only. It should be pointed out here that recently many studies in the field of molecular electronics have been performed that go beyond the electronic transport characterization of single molecules. These studies involve thermoelectric. optoelectronic, mechanical. and spintronic phenomena. We would like to emphasize that these studies fall outside the scope of this chapter.

In the next section, we will provide the reader with a brief update of the various methods that are applied to capture a single molecule between two macroscopic electrodes. Subsequently, in Section 1.3 we will, in a rather scholarly manner, address the physical ingredients that are useful to understand electronic transport through a single molecule. In Section 1.4, we will discuss two elementary molecular electronic devices: a single-molecule switch and a single-molecule transistor. This chapter concludes with a short outlook.

# **1.2** The Art of Catching and Probing a Single Molecule

The available methods to capture an individual molecule between two electrical contacts can roughly be divided into two approaches. In the first approach, one uses a quantum mechanical break junction to capture a single molecule [11–18]. In a quantum mechanical break junction experiment, a thin metallic wire with an incision is carefully stretched by using piezo actuators. During stretching, the wire gets thinner and thinner until it eventually has a cross section of only one atom and breaks. After breaking one usually attempts to capture a single molecule from either the gas or the liquid phase. Unfortunately, it is rather difficult to figure out whether only a single molecule or a bundle of molecules is captured between the electrical contacts. Since the electrical contacts are mounted on piezo actuators one can easily "repair" the break junction by moving both electrodes towards each other. By repeating this process many times, a conductance histogram can be obtained that provides valuable information on the preference for certain conductance values.

The second method makes use of a scanning tunneling microscope or an atomic force microscope and a substrate [6, 9, 19-31]. A small number of molecules are deposited on a welldefined single crystal surface and subsequently imaged with the scanning probe microscope. One can attempt to pick up a single and pre-selected molecule by parking the scanning probe microscope tip on top of the molecule, open the feedback loop, and move the tip towards the surface. In close vicinity of the molecule one usually applies a short voltage pulse to the tip in the hope that the molecule is picked up by the apex of the tip. After this picking up attempt, one has to scan the same area again in order to check if the molecule has really been picked up by the tip of the scanning probe microscope. If this is not the case, one has to repeat the same procedure again. Molecules that have well-chosen end groups that can anchor to the substrate and tip respectively are the molecules that can be captured most easily. The end groups are often chemisorbed to the electrical contacts usually resulting into stable contacts with low contact resistances. There are, however, also a few examples where one of the end groups is only physisorbed to either the substrate or the tip [20, 24, 25, 32]. Figure 1.1 shows an artist's impression of the capturing process of a single molecule between the tip of a scanning tunneling microscope and a substrate.



**Figure 1.1** Artist's impression of a single molecule that is captured between the tip of a scanning tunneling microscope and a substrate. Image courtesy René Heimbuch.

Another method that has been applied by various research groups involves the preparation of inserted monolayers. A surface is covered with a self-assembled monolayer of insulating organic molecules (for instance alkanemonothiols) and subsequently another organic molecule (for instance a conjugated mono- or dithiol) is "inserted" into the insulating self-assembled monolayer. The insertion technique relies on an exchange process, where a molecule of the self-assembled monolayer is replaced by another molecules. These exchange processes mainly occur at positions where the molecules are not so firmly bound to the substrate, i.e., defects, impurities, vacancies, and anti-phase boundaries [33–41].

# 1.3 Transport Properties of a Single Molecule

# 1.3.1 Quantization of Conductance

Ohm's law states that the resistance, R, of an object is given by V/I, where V is the voltage applied across the object and I the current that flows through the object. The resistance of a

macroscopic metallic wire of length *L*, cross section *A* and specific resistance  $\rho$  is given by  $\rho L/A$ . The resistance of such a macroscopic wire scales linearly with the length of the wire. One would probably naively assume that this relation holds down to the nanoscale. However, as we will show below, this is not necessarily true. In case that the mean free path between successive collisions of the charge carriers,  $\lambda$ , is larger than the length of the wire, the resistance turns out to be quantized in units of  $h/2e^2$  and independent of the actual length of the wire, at least, as long as the condition  $\lambda > L$  is satisfied.



**Figure 1.2** Energy diagram of two reservoirs with chemical potentials  $\mu_1$  and  $\mu_2$ , respectively. The two reservoirs are adiabatically connected via a one-dimensional wire.

It is not so difficult to derive this result. Consider a onedimensional wire that connects adiabatically two reservoirs with chemical potentials  $\mu_1$  and  $\mu_2$ , respectively (see Fig. 1.2). The connections are assumed to be non-reflecting. The current, *I*, that flows through the wire is given by

$$I = -nev_{\rm F} = -ev_{\rm F}(\mu_1 - \mu_2)D(E_{\rm F}), \qquad (1.1)$$

where  $v_{\rm F}$  is the Fermi velocity of the electrons, *n* the electron density, *e* the charge of the electrons and  $D(E_{\rm F})$  the density of states at the Fermi level. The difference in chemical potential, i.e.,  $(\mu_1 - \mu_2)$ , is -eV. Equation (1.1) represents the current per mode. The voltage difference *V* between the two reservoirs could involve more modes. The current is equally distributed among the *N* modes. This equipartition is due to the fact that electrons at the Fermi level in each mode have different group velocities *v*. However, this difference in group velocities is canceled by the

# 6 Single-Molecule Devices

density of states, which is inversely proportional to the group velocity. The density of states, D(E), is given by

$$D(E) = \frac{2\left(\frac{1}{2\pi}\right)}{\left(\frac{dE}{dk}\right)} = \frac{2}{hv}.$$
(1.2)

In expression (1.2), a factor of 2 for the spin degeneracy has been taken into account. The current I carried per mode is then

$$I = e^2 v_{\rm F} V \frac{2}{h v_{\rm F}} = \frac{2e^2}{h} V.$$
(1.3a)

The total current is found by summing over all modes,

$$I = N \frac{2e^2}{h} V \tag{1.3b}$$

The resistance quantum is  $\frac{h}{2e^{2}}$ , where the spin degree of freedom is included. The conductance quantum is  $\frac{e^{2}}{h}$  per channel and per spin. Interestingly, the conductance quantum is independent of the material properties.

A conductor is referred as ballistic if the mean free path of the charge carriers is larger than the length of the conductor. The conductance of a ballistic wire in quantized in units of  $\frac{e^2}{h}$ . Since no scattering takes place in a ballistic conductor it is a natural question to ask what the actual cause of the resistance is. It turns out that the quantum resistance is in fact a contact resistance because the incoming electron waves have to "find" the entrance of the wire. Only a small integer number  $N \approx \frac{2w}{\lambda_F}$  of transverse modes can propagate at the Fermi level ( $\lambda_F$  is the Fermi wavelength and *w* is the width of the wire). In experiments, small deviations from the exact quantization are found. These deviations, typically of the order of 1% or so, are caused by the series resistance of the wire. It should be pointed out here that the deviations in the quantization of the Hall conductance are much smaller, i.e., deviations as small as 0.00001% can be achieved.

The first experimental evidence of the quantization of conductance came from papers in 1988 by a paper from a Delft-

Philips collaboration [42] and a paper from a Cambridge team [43]. These authors realized a quantum point contact in a twodimensional electron gas. By tuning the width of the construction using a split gate they could show that the conductance is indeed quantized in units of  $\frac{2e^2}{h}$ . In molecular transport, one typically deals with only one, or at most a few conduction channels.

### 1.3.2 Coherent and Incoherent Transport

The transport through a one-dimensional wire can be described within the framework of the Landauer theory. In 1957, Landauer proposed that electrical transport in a one-dimensional system could be considered as a transmission problem [44]. An incoming electron wave has a probability *T* to be transmitted through the one-dimensional channel. The probability that the electron wave is reflected is represented by R (T + R = 1). Since a molecule that is contacted by electrical contacts can be considered as quasi one-dimensional object, its conductance is given by

$$G = \frac{2e^2}{h}T,$$
(1.4)

where *T* represents the average probability that an electron injected at one end of the molecule will make it to the other end of the molecule (for the sake of simplicity we assume that we are dealing with a single conduction channel) and  $2e^2/h = 77.5 \ \mu$ S. In the case of perfect transmission, i.e., *T* = 1, we are dealing with a ballistic conductor. Thus a ballistic conductor has a non-zero resistance even though there are no impurities! This key result is at variance with the classical picture where one expects infinite conductance in the absence of impurity scattering.

Here we proceed by considering a wire that has several scattering centers. The latter is a good starting point for an electrode-molecule-electrode junction. In practice both ends of the molecule need to be connected to macroscopic electrical contacts and therefore the total conductance of a metal-molecule-metal junction depends on at least three transmission probabilities, the transmission probabilities of the left ( $T_L$ ) contact, right contact ( $T_R$ ) and molecule ( $T_M$ ). We first consider the case of incoherent transport, i.e., we assume that the phase information is lost during the transport through the molecule. For the sake of clarity,

# 8 Single-Molecule Devices

we assume we only have two incoherent scattering centers with transmission probabilities  $T_1$  and  $T_2$ . One might naively assume that the total conductance is given by  $\frac{2e^2}{h}T_1T_2$ . However, this is wrong since the multiple scattering events where the incoming electron wave bounces back and forth between the two scattering centers also contribute to the total transmission (see Fig. 1.3). The total transmission is given by

$$G = \frac{2e^2}{h} [T_1 T_2 + T_1 T_2 R_1 R_2 + T_1 T_2 (R_1 R_2)^2 + T_1 T_2 (R_1 R_2)^3 + \cdots] = \frac{2e^2}{h} \left[ \frac{T_1 T_2}{1 - R_1 R_2} \right],$$
(1.5a)

where  $R_1 = 1 - T_1$  and  $R_2 = 1 - T_2$  are the reflection probabilities. Equation (1.5a) can be written as



**Figure 1.3** Two incoherent scattering centers in series. The total transmission is given by  $T_{\text{total}} = T_1T_2 + T_1T_2R_1R_2 + T_1T_2(R_1R_2)^2 + T_1T_2(R_1R_2)^3 + \dots$ .

For three incoherent scattering centers in series one finds

$$G = \frac{2e^2}{h} \left[ \frac{T_{\rm L} T_{\rm M} T_{\rm R}}{T_{\rm L} T_{\rm M} + T_{\rm L} T_{\rm R} + T_{\rm M} T_{\rm R} - 2T_{\rm L} T_{\rm M} T_{\rm R}} \right]$$
(1.6)

In the case of coherent scattering, the total transmission also depends on the phase difference between both scattering centers. We introduce the complex transmission and reflection coefficients,  $t_{1,2} = |t_{1,2}|e^{i\phi_{1,2}}$  and  $r_{1,2} = |r_{1,2}|e^{i\theta_{1,2}}$ . The transmission probability of the first and second scattering centers is  $T_{1,2} = |t_{1,2}|^2$ . The total transmission is then,

$$G = \frac{2e^2}{h} \left[ \frac{|t_1|^2 |t_2|^2}{1 + |r_1|^2 |r_2|^2 - 2|r_1| |r_2| \cos(\theta)} \right],$$
(1.7)

where  $\theta = 2kL + \theta_1 + \theta_2$ , k the wave vector and L the separation between the scattering centers (see Fig. 1.4). Interestingly, the total transmission probability can become unity despite the fact that both scattering centers have a transmission probability smaller than 1. A total transmission of unity (i.e., resonant coherent transport) is achieved for a phase difference that is an integer multiple of  $2\pi$ , i.e.,  $\theta = 2\pi n$ , irrespective of the actual values  $T_1$  and  $T_2$ . For three scattering centers in series, one can derive a similar, albeit a bit more difficult. relation.



Figure 1.4 Two coherent scattering centers in series.

### 1.3.3 **Coulomb Blockade**

In this section, we will briefly touch upon another transport mechanism that is applicable to a subset of molecules. There are molecules, such as metal phthalocyanines, that have a metallic core surrounded by an organic shell [45-50]. Electrons that are transported through these molecules can reside on the metallic core leading to charging of the molecule. The charging energy of such a small entity is usually large since the capacitance with respect to its environment can be very small. These charging effects will only show up in the *I–V* curves if the charging energy exceeds the thermal energy. In case the latter condition is satisfied, the transport through the molecule will be fully blocked if the energy of the electrons is insufficient to overcome the charging energy.

In order to explain the essence of this transport mechanism we consider a simple system that consists of two tunnel junctions in series (see Fig. 1.5). The tunneling resistances of these junctions,  $R_1$  and  $R_2$ , are assumed to be substantial, i.e., much larger than

the quantum resistance. Furthermore, we assume that the total capacitance of the region in between the two tunnel junctions,  $C = C_1 + C_2$ , is small enough so that the charging energy,  $\frac{e^2}{C}$ , is larger than the thermal energy  $k_BT$ . We apply a voltage  $V = V_1 + V_2$  across both junctions and assume that at V = 0 the region in between the two tunnel junction does not contain any charge. Upon increasing the voltage V, electrons will tunnel across junctions 1 and 2. The total number of electrons that have passed junction 1 is denoted by  $n_1$ , whereas the total number of electrons that have passed junction 2 is denoted by  $n_2$ . The total charge on the region between the two tunnel junctions (from now on referred as the quantum dot)  $Q_{dot} = -n_1e + n_2e = -ne$ , where  $n = (n_1 - n_2)$  is the number of electrons on the quantum dot. The voltage drops across junction 1 and 2 are given by

$$V_1 = \frac{(C_2 V + ne)}{(C_1 + C_2)}$$
(1.8a)

$$V_2 = \frac{(C_1 V - ne)}{(C_1 + C_2)}.$$
 (1.8b)



**Figure 1.5** Two tunnel junctions in series with tunneling resistances and capacitances  $R_{1,2}$  and  $C_{1,2}$ , respectively.

The total static energy stored in the quantum dot,  $E_{\rm s},$  can be written as

$$E_{s} = \frac{1}{2}C_{1}V_{1}^{2} + \frac{1}{2}C_{2}V_{2}^{2} = \frac{C_{1}C_{2}V^{2} + n^{2}e^{2}}{2(C_{1} + C_{2})}.$$
(1.9)

In addition to this static energy, we also have to consider the energy transferred by the voltage source. The voltage source provides not only the energy to transfer an integer number of electrons across the tunnel junctions, but it also provides the energy that is required to compensate for the polarization charge when an electron tunnels across one of the junctions. In order to derive the total energy of the system we consider an electron on its journey from electrode 1 to electrode 2. When the electron tunnels across junction 1 the total charge on the quantum dot increases from  $-ne = -(n_1 - n_2)e$  to  $-(n + 1)e = -((n_1 + 1)-n_2)e$ . Due to the transfer of an electron across junction 1 also the voltage drop across junction 2 will change with an amount  $\Delta V_2 = -\frac{e}{(C_1 + C_2)}$ . This potential change leads to polarization charge flow given by  $\Delta Q_2 = -\frac{eC_2}{(C_1 + C_2)}$  In order to transfer  $n_1$  electrons across junction 1 and  $n_2$  electrons across junction 2, an energy of  $E_V$  is required.

$$E_{v} = -\frac{eV(n_{1}C_{2} + n_{2}C_{1})}{(C_{1} + C_{2})}$$
(1.10)

The total energy of the system  $E_{tot}(n_1, n_2)$  is then,

$$E_{\text{tot}}(n_1, n_2) = E_s - E_v = \frac{C_1 C_2 V^2 + n^2 e^2}{2(C_1 + C_2)} + \frac{eV(n_1 C_2 + n_2 C_1)}{(C_1 + C_2)}$$
(1.11)

To transfer an electron across junction 1, the following requirement should be met:

$$\Delta E_1^{\pm} = E_{\text{tot}}(n_1 \pm 1, n_2) - E_{\text{tot}}(n_1, n_2) \le 0$$
(1.12)

After some simple math this leads to

$$V = \mp \frac{e}{C_2} \left( \frac{1}{2} \pm n \right)$$
 (1.13)

Similarly one finds for the second junction,

$$V = \mp \frac{e}{C_1} \left(\frac{1}{2} \mp n\right). \tag{1.14}$$

In case  $C_2 > C_1$  the first electron will tunnel through junction 1, whereas the first electron will tunnel through junction 2 if  $C_1 > C_2$ . It is clear that the largest capacitance will determine the size of the Coulomb gap. Let us assume, for the sake of simplicity, that  $C_1 = C_2 = C$  and T = 0 K. For  $|V| < \frac{e}{2C}$ , the transport through the

# 12 Single-Molecule Devices

quantum dot is fully blocked. This regime is referred as Coulomb blockade. For  $|V| > \frac{e}{2C}$  there is a net current flowing through the quantum dot. Under certain conditions, a Coulomb staircase can be observed. In order to observe Coulomb blockade the charging energy should be larger than the thermal energy, i.e.,

$$\frac{e^2}{2C} > k_{\rm B}T. \tag{1.15}$$

However, there is another important requirement that should be fulfilled; the tunneling resistances should be larger than a certain threshold value. This threshold value can be determined using Heisenberg's uncertainty relation.

$$\Delta E \Delta t \ge \frac{\hbar}{2} \tag{1.16}$$

The energy spacing between subsequent energy is  $\Delta E = \frac{e^2}{2C}$  and the tunneling time  $\Delta t = RC$ . Inserting  $\Delta E$  and  $\Delta t$  gives

$$R \ge \frac{\hbar}{e^2} \tag{1.17}$$

In order to resolve the energy levels, the tunneling resistances must be larger than  $\frac{\hbar}{e^2}$ . If requirements (1.15) and (1.17) are met, the Coulomb gap will be observed. The Coulomb staircase can only be observed for asymmetric tunnel junctions, i.e.,  $R_1C_1 \neq R_2C_2$  (see Fig. 1.6). So, one of the tunnel junctions should be the rate-limiting step in the transfer of electrons.



**Figure 1.6** Schematic *I*–*V* curves of a double tunnel junction at T = 0 K. Left: asymmetric junction,  $R_1C_1 \neq R_2C_2$  (Coulomb staircase). Right: symmetric junction,  $R_1C_1 = R_2C_2$  (only a Coulomb gap).

The last aspect of the Coulomb blockade that we want to address deals with the fractional charge. Due to polarization effects the net charge on the quantum dot is not necessarily an integer value of *e*. The presence of a fractional charge,  $\delta e$ , will shift the Coulomb gap and Coulomb staircase.

We now consider the case of a quantum dot that has a fractional charge,  $\delta e$ , with  $-1 < \delta < 1$ . The energy of the quantum dot that contains *n* electrons and a fractional charge is given by

$$E_n = \frac{(n+\delta)^2 e^2}{2C}.$$
 (1.18)

When an additional electron is added to the quantum dot, the energy increases with an amount,

$$\Delta E = E_{n+1} - E_n = \frac{2(n+\delta)e^2 + e^2}{2C}$$
(1.19)

An additional electron will be added to the quantum dot for  $\Delta E = eV$ . The threshold voltages for transferring an additional electron to the quantum dot are

$$V = \frac{e}{2C}(2n+2\delta+1).$$
 (1.20)

A fractional charge will shift the Coulomb gap from  $\left[-\frac{e}{2C}, \frac{e}{2C}\right]$  to  $\left[-\frac{(2\delta-1)e}{2C}, \frac{(2\delta+1)e}{2C}\right]$ , but the size of the Coulomb gap remains unaltered (see Fig. 1.7).



**Figure 1.7** Coulomb staircase of a quantum dot that has a fractional charge at V = 0 (T = 0 K).

In Fig. 1.8a, Coulomb staircase recorded on a small Pd cluster deposited on a decanethiol self-assembled monolayer is shown [50]. The experimental results are compared with the orthodox theory of single electron tunneling [51].



Figure 1.8 (a) Experimental (dotted line) and theoretical (solid line) *I–V* curve recorded at 77 K on a small Pd cluster deposited on a decanethiol self-assembled monolayer. (b) *dI/dV* versus *V*. Each oscillation corresponds to the addition or subtraction of one electron. Copyright AIP reprinted with permission from Oncel, N., *J. Chem. Phys.*, 123, 044703 (2005).

# 1.3.4 Transport Mechanisms in Molecules

There are several conduction mechanisms for molecules, such as resonant and non-resonant coherent tunneling, incoherent diffusive tunneling, thermally induced hopping, Fowler–Nordheim tunneling, and thermionic emission [3, 5, 11–13, 52–56]. The properties of the electrical contacts can affect the transport through the molecule significantly. Electrical contacts can be chemically

attached to the molecule or physically bound. Chemical binding leads to hybridization of the molecular orbitals with the electronic states of the contacts. This affects the position of the molecular orbitals, which, in turn, can influence the transport through the molecule. Physisorbed contacts lead to less interaction and only to minor changes in the positions of the molecular orbitals.

Below we briefly summarize the possible transport mechanisms in molecules.

### 1.3.4.1 Coherent tunneling

Coherent or classical tunneling dictated by quantum mechanics relies on the probability of an electron to tunnel through a barrier. The rate of coherent tunneling decays exponentially with the width of the barrier. The current, *I*, is given by

$$I = \frac{CV\sqrt{\phi - \frac{eV}{2}}}{d}e^{-2\frac{\sqrt{2m}}{\hbar}d\sqrt{\phi - \frac{eV}{2}}}$$
(1.21)

where *V* is the voltage, *d* the width of the barrier,  $\phi$  the effective barrier height,  $\beta = 2 \frac{\sqrt{2m}}{\hbar} \sqrt{\phi - \frac{eV}{2}}$  the inverse decay length, and *C* a constant.

Quantum mechanical tunneling is temperature independent and the phase of the electron is preserved during the tunneling process [57]. The inverse decay length is  $\sim 2$  Å<sup>-1</sup> for tunneling between two metal electrodes in vacuum. The inverse decay length of molecules is usually, however, much smaller, i.e., for alkanethiols the inverse decay length is  $\sim 0.5-1$  Å<sup>-1</sup> resulting in an effective barrier height that is substantially smaller than the work function [4, 20, 28]. This value is much smaller than the typical highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of alkanethiols, which amounts ~8 eV (see Fig. 1.9). A commonly accepted explanation for this, much smaller than expected, inverse decay length is "superexchange." Interaction of the electron with the orbitals and electronic structure of the molecule enhance the tunneling rate, making "through bond" tunneling more efficient than "through space" tunneling. Another important effect that can lower the tunnel barrier and reduces its width is the presence of an image charge (see Fig. 1.10). About half a century ago, Simmons showed that for two planar electrodes the barrier height reduces to [58, 59],

$$\phi(x,d) = \phi_0 - \frac{eV}{2} \frac{\Delta x}{d} - \frac{1.15e^2 \ln 2}{16\pi\varepsilon} \frac{d}{x(d-x)}$$
(1.22)

$$\Delta x = d \sqrt{\left(1 - \frac{1.15e^2 \ln(2)}{16\pi\varepsilon\phi_0 d}\right)},$$
(1.23)

resulting in a mean barrier height,

$$\phi_{\rm eff} = \varphi_0 - \frac{eV}{2} \frac{\Delta x}{d} - \frac{1.15e^2 \ln 2}{8\pi\varepsilon\Delta x} \ln\left(\frac{d+\Delta x}{d-\Delta x}\right), \tag{1.24}$$

where  $\varepsilon$  is the dielectric constant of the material in the junction,  $x_{1,2}$  are the zero's of the potential  $\phi(x_1) = \phi(x_2) = 0$  and  $\Delta x = x_2 - x_1$  is the effective barrier width. It should be pointed out here that the formulas that we used for image charge effect assumes that we are dealing with two planar electrodes, which is of course for a scanning tunneling microscopy junction not correct. The results obtained here should therefore be considered as an upper bound for the image charge potential.



**Figure 1.9** Schematic energy diagram of a molecular junction. The metallic electrodes constitute a continuum of electronic states filled with electrons up to the Fermi level. The highest occupied Molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bands of the molecule are shown.

Another aspect of molecular transport that we want to highlight here is *quantum interference*. Quantum interference can

occur if the length scale of the molecule becomes comparable to the electronic phase coherence length. In case that the electron wave arrives at a joint, where it can propagate via two (or more) different routes that eventually cross each other again, constructive or destructive interference effects can severely affect the conductance [30, 60, 61]. The length of these paths should of course be smaller than the electronic phase coherence length. For example, quantum interference can substantially lower the conductance of a cross-conjugated molecule when compared to its linearly conjugated configuration. The reduction of the conductance of the cross-conjugated molecule is due to an anti-resonance in the transmission function [30].



**Figure 1.10** The effective barrier decreases with increasing bias voltage,  $\phi = \phi_0 - \frac{eV}{2}$ . The reduction of the effective barrier height and the reduction of the effective width of the tunneling barrier due to the image charge are not shown.

### 1.3.4.2 Incoherent tunneling

In the case of incoherent tunneling, the electron tunnels via a series of sites, which are characterized by potentials wells. The residence time in these wells is often long enough to disturb the phase of the electron. Also this tunneling process is in principle temperature independent. In case the "tunneling resistances" from site to site are larger than the quantum resistance, Coulomb charging and blockade effects can occur. In addition, during its journey the electron can also excite one of the vibronic modes of the molecule. The latter will only occur if the energy of the electron exceeds the threshold for excitation, i.e.,  $V > \hbar \omega / e$ .

# 1.3.4.3 Hopping

Hopping is an Arrhenius activated process and thus strongly temperature dependent [62]. Hopping involves electron motion over the barrier, while tunneling involves electron transport through the barrier. Since hopping involves a series of transfers between relatively stable sites, it does not exhibit an exponential distance dependence characteristic for coherent tunneling, but instead varies as  $\sim 1/d$ istance, i.e.,

$$I = \frac{GV}{d} e^{-E/kT},$$
(1.25)

where E is the diffusion barrier for hopping, T the temperature, k Boltzmann's constant, and G a constant [52]. Because of the temperature dependence, hopping conduction is likely to happen at elevated temperatures.

# 1.3.4.4 Thermionic emission

A barrier (usually referred as Schottky barrier) can arise due to partial charge transfer from one phase to another phase at the interface, resulting in a depletion layer and an electrostatic barrier (as in semiconductor/metal contacts) [63]. This electrostatic barrier is affected by the local (applied) field resulting in a non-linear I-V characteristic. The Schottky–Richardson relation has been invoked to explain the I-V characteristic of a few molecular junctions [64, 65]. Thermoionic emission plays an important role for high temperatures and low barrier heights. The Schottky–Richardson relation is given by

$$I = AT^{2} e^{-\phi/kT} e^{(B\sqrt{V}/kT\sqrt{d})},$$
(1.26)

where *A* and *B* are constants.

# 1.3.4.5 Fowler–Nordheim tunneling or field emission

Fowler–Nordheim tunneling occurs when the applied voltage exceeds the barrier height. In field emission, electrons tunnel through a potential barrier, rather than escaping over the barrier as in thermionic emission. The effect is purely quantum-mechanical, with no classical analog. Due to the applied voltage the barrier, which is rectangular for V = 0, has a triangular shape facilitating

the tunneling of the electrons. The field emission process is temperature independent and decreases exponentially with distance [52],

$$I = DV^2 e^{-(F\varphi^{3/2}/V)d},$$
 (1.27)

where *D* and *F* are constants. An elegant approach to obtain more detailed information on the transport process in a molecular junction is transition voltage spectroscopy (TVS) [54, 55, 66–71]. To extract meaningful information from the high-bias regime, it is useful to linearize Eq. (1.27):

$$\ln\left(\frac{I}{V^2}\right) \propto D - F\phi^{3/2} d\frac{1}{V},\tag{1.28}$$

Plotting  $\ln(I/V^2)$  versus 1/V, a so-called Fowler–Nordheim plot, will show a linear decay in the high-bias regime. Equations (1.21) gives the relation for the low-bias regime and when it is rewritten and simplified in terms of  $\ln(I/V^2)$  and 1/V one finds

$$\ln\left(\frac{I}{V^2}\right) \propto \ln\left(\frac{1}{V}\right) - \beta d, \qquad (1.29)$$

where  $\beta$  is the inversed decay length. Equation (1.29) exhibits a logarithmic dependence in the low-bias regime and therefore a transition is observed which corresponds to the voltage where the barrier transforms from a trapezoidal (low-bias regime) to a triangular shape (high-bias regime). The transport mechanism changes from quantum mechanical tunneling (low-bias regime) to field emission (high-bias regime). The transition point is referred as the transition voltage  $(V_t)$  and gives an experimental estimate of the energy spacing between the Fermi level and the LUMO (or HOMO for hole tunneling) orbital, i.e., the barrier height  $\phi$ . The specific value for the transition voltage remains a crude estimate because the original tunneling equation does not explicitly accounts for voltage drops over the contacts, image potential, potential profile across the junction and symmetry/asymmetry in the molecular junction [72–74]. Although the exact interpretation is still under debate, it is clear that TVS is an interesting spectroscopic tool in the field of molecular electronics. In vacuum tunnel junctions field-emission typically occurs at voltages that exceed the work function, i.e., at voltage larger than 4-5 V. In distance-voltage (*z*-*V*) or *I*-*V* traces well defined oscillations or resonances can be observed, which are interpreted as electronic standing waves patterns that can occur in triangular shaped potential wells. These field emission resonances are sometimes referred as Gundlach oscillations, after Gundlach who first discussed these resonances in 1966 [75, 76].

# 1.4 Molecular Devices

In the final section of this chapter, we will present a few examples of single-molecule devices. These devices all rely on a single octanethiol molecule. We will show that by simultaneously varying the separation and voltage difference between the macroscopic electrodes an octanethiol molecule can be captured controllably between a substrate and the apex of a scanning tunneling microscope tip. The method is so robust that it allows to open and close the molecular junction with a high accuracy over a temperature range from cryogenic temperatures all the way up to room temperature. This robustness not only allows one to measure the temperature dependence of the electronic transport through a single octanethiol molecule, but it also provides a simple an elegant route towards a single-molecule switch. In addition, by varying the contact's interspace once the octanethiol molecule is captured the electronic transport through the octanethiol molecule can be manipulated. This approach allows one to realize a single-molecule transistor that requires only two, rather than the conventional three terminals. The role of the gate terminal is replaced by a mechanical gate that can be tuned by varying the contact's interspace.

# 1.4.1 Contacting of a Single Octanethiol Molecule

Figure 1.11 shows a scanning tunneling microscope image of a germanium (001) surface covered with metallic platinum (Pt) nanowires. The Pt nanowires have a cross section of only one atom and are kink- and defect-free. This substrate has been exposed to 60 Langmuir of octanethiol. The large white protrusions, which are almost exclusively adsorbed on the Pt nanowires, are octanehiol molecules. The head of the octanthiol molecule, i.e., the sulfur

(S) atom, binds to Pt whereas the carbon tail of the octanethiol molecule is lying flat down on the Pt nanowire. Upon the adsorption of the SH group the hydrogen atom is released and the octanethiol becomes an octanethiolate. In the remainder of this Chapter we refer to an adsorbed octanethiol, whereas we formally dealing with an octanethiolate.



Figure 1.11 Scanning tunneling microscopy image (25 nm × 25 nm; sample bias -0.90 V and tunneling current 0.5 nA) of a platinum-modified germanium (001) surface after exposure to 60 Langmuir of octanethiol, recorded at 77 K (a). The octanethiol molecules (circular white spots) almost exclusively adsorb on the platinum atomic chains. In panel (b), we show a model of the region enclosed by the square in panel A. Grey dumbbells are substrate dimers, dark dumbbells are platinum dimers, and the adsorbed molecule is shown in orange. Copyright ACS reprinted with permission from Kockmann, D., et al., *Nano Lett.*, 9, 1147 (2009).

In Fig. 1.12 a current-time trace with the feedback loop disabled recorded on top of a pre-selected octanethiol molecule is shown. The set point current is 1 nA, but after about 6 s the current jumps up to a value of around 12 nA and 15 s later the current jumps back to its original value of 1 nA. The only viable

### 22 Single-Molecule Devices

explanation for these abrupt and huge changes in the tunnel current is that the carbon tail of the octanethiol molecule flips up and attaches to the apex of the scanning tunneling microscope tip. The vacuum junction is thus replaced by a molecular junction and the electrons flow through the molecule rather than that they tunnel through the vacuum barrier. The length of the octanethiol molecule is  $\sim 1$  nm and therefore nicely fits in the vacuum junction. One could argue that this system behaves as a molecular switch; however, the jump in and out of contact occurs randomly and the lack of control makes that this system does not resemble a molecular switch.



Figure 1.12 (a) Current-time trace recorded on top of an octanethiolate molecule at 77 K. The sample bias was 1.5 V and the setpoint current 1 nA. The cartoons in (b) and (c) show the octanethiolate molecule absorbed at a Pt atom chain and an octanethiolate molecule captured between a Pt atom chain and the apex of an STM tip. Copyright AIP reprinted with permission from Sotthewes, K., *Appl. Phys. Lett. Mater.*, 2, 010701 (2014).

# 1.4.2 Single Molecule Switch

Unfortunately, we do not have any control over the Ge(001)/Pt-octanethiol-STM tip junction. This situation drastically alters if a

single octanethiol molecule is attached to the apex of the scanning tunneling microscope tip. The sulfur head of the octanethiol can be attached to the apex of the scanning tunneling microscope tip by parking the tip onto a pre-selected octanethiol molecule that is adsorbed on a Pt nanowire. Subsequently, the feedback loop is disabled and the tip is moved a few Ångstroms towards the surface where a short voltage pulse in applied to the tip. When the sulfur atom of the octanethiol makes contact with the tungsten STM tip. it can form a strong bond and therefore the tail of the octanethiol is usually fully released from the surface upon retraction of the tip. In order to check if the octanethiol molecule is picked up from the substrate we performed two tests. First, an regular scanning tunneling microscopy image is recorded in order to verify if the octanethiol molecule has indeed disappeared. Second, an *I–V* curve is recorded. *I–V* curves of the tunnel junctions recorded using a tip decorated with an octanethiol molecule are significantly different from *I–V* curves recorded with a clean, i.e., molecule-free, tip. In Fig. 1.13 *I–V* curves recorded with a clean tip and a tip decorated with an octanethiol molecule are shown. As a set points we have taken a bias of 1.5 V and a tunnel current of 0.5 nA and therefore the asymmetry of the *I–V* curves only shows up a negative sample biases.



**Figure 1.13** Tunneling current-voltage (*I*-*V*) curves of the tunnel junctions recorded at 77 K before and after the STM tip has picked up an octanethiol molecule. For both traces we have used a set point value of 0.5 nA at 1.5 V. Copyright IOP reprinted with permission from Kumar, A., et al., *J. Phys. Cond. Matter*, **24**, 082201 (2012).

24 Single-Molecule Devices

Once the octanethiol molecule is attached to the apex of the scanning tunneling microscope tip a series of current-distance measurements, on various locations at the sample surface, has been recorded. The sample bias was set to +1.5 V and the tunneling current to 0.2 nA, respectively (see Fig. 1.14). After bringing the scanning tunneling microscope tip closer to the substrate by a distance  $\Delta Z = 0.15 - 0.18$  nm ( $\Delta Z$  refers to the Z-displacement of the tip towards the surface with respect to the set point height), the tail of the octanethiol molecule flips into contact with the substrate and the current jumps to a much higher value of  $35 \pm 5$  nA. The slight variation in the conductance can be attributed to the various contact geometries that the molecule can have with the scanning tunneling microscope tip and the substrate. For a sample bias of -1.5 V the tail of the octanethiol molecule never flips into contact and the tunneling current shows an exponential dependence on distance. The position of the transition from "off" to "on" (inset in Fig. 1.14) depends on the actual value of the applied bias voltage. The current-voltage (I-V) and current-distance (I-Z) spectroscopy data provide strong evidence for a successful attachment of a single octanethiole molecule to the apex of the tip.



Figure 1.14 Current-distance traces recorded with an octanethiol molecule attached to the apex of the STM tip. Top: The sample bias is 1.5 V and the tunneling current is set to 0.2 nA. After the STM tip has approached, the substrate to ~0.15 nm the molecule makes contact and the current jumps to 35–40 nA. Bottom: The sample bias is –1.5 V and the tunneling current is set to 0.2 nA. The octanethiol molecule does not jump into contact. Copyright IOP reprinted with permission from Kumar, A., et al., *J. Phys. Cond. Matter*, **24**, 082201 (2012).

Figure 1.15 shows a series I-V and I-Z measurements for three different octanethiol molecules (red, blue, and green curves). A series of ten I-V curves recorded at different sample-tip distances has been recorded. The sample-tip distance is changed in increments of 0.5 Ångstroms. In the first two traces (labeled 1 and 2) the distance between the tip and substrate is too large for the tail of the octanethiol molecule to bridge the gap between tip and substrate. In trace 3 the sample-tip distance is 1 Ångstrom smaller as compared to trace 1. In two of the three cases, the tail of the octanethiol molecule flips into contact with the substrate at the starting voltage of 1.5 V. However, at a sample bias of about



A set of three I-V curves (middle section, red, blue, and Figure 1.15 green curves) recorded in series, with varying tip-substrate distance and the feedback loop disabled. The top section shows a cartoon of the molecule attached to the apex of the tip and its relative position with respect to the substrate. The bottom section shows a series of voltage ramps from +1.5 V to -1.5 V as the tip has moved, in steps of 0.05 nm. Traces 1 to 6 correspond to the tip's relative position from the set point height (i.e., 0.2 nA and 1.5 V) to 0.25 nm, while traces 7 to 10 correspond to the relative position from 0.20 nm to 0.05 nm. After approaching the substrate by 0.1–0.15 nm (traces 3–4), the octanethiol molecule jumps into contact and for IV curve no. 8 the molecule jumps out of contact. Copyright IOP reprinted with permission from Kumar, A. et al., J. Phys. Cond. Matter, 24, 082201 (2012).

0.5 V the octanethiol molecule flips out of contact again. A similar behavior is found for traces 4–8. It should be pointed out here that the reduction of sample-tip distance leads to (1) a higher current, i.e., a larger conductance and (2) lower threshold voltage at which the tail of the octanethiol molecule flips out of contact. The higher conductance at smaller sample-tip distances is due to the fact that the tail of the octanethiol molecule is bended during compression of the molecule [7] rather than that the tail molecule is sliding along the contact. If the octanethiol molecule would slide along the contact the conductance would increase in exponentially with decreasing sample-tip distance. From data presented in Fig. 1.15, it is clear that the molecular junction can be controllably closed and opened by varying the tip-sample distance and the bias voltage. Therefore, the substrate-octanethiol-molecule junction behaves as a molecular switch that can be operated with high precision.

# 1.4.3 Transport through a Single Octanethiol Molecule Junction

Since we can open and close the octanethiol junction controllably, it is very straightforward to measure the conductance of a single octanethiol molecule as a function of the temperature. The octanethiol switch works from cryogenic temperatures all the way up to room temperature. Figure 1.16 shows a plot of the conductance of a single octanethiol molecule measured in units of  $\frac{2e^2}{h}$ , i.e.,  $G_0$ , versus temperature. The conductance of the molecule has been measured at a sample bias of +1.5 V, i.e., well below the reported tunneling barrier of an octanethiol molecule [4]. The conductance of the sample-octanethiol-tip junction remains throughout the experiments at a constant value of  $\sim 30$  nS. Fowler-Nordheim tunneling and quantum-mechanical, or direct, tunneling are the only two transport mechanisms which are temperature independent. Fowler-Nordheim tunneling only occurs at voltages, V, that exceed the work function, i.e.,  $V > \phi/e$ . Since the voltages applied in our experiments are substantially smaller than the 4 eV barrier (assuming that the Fermi edge lies somewhere in the middle of the 8-9 eV gap between highest occupied and lowest unoccupied molecular orbitals of the octanethiol molecule), Fowler-Nordheim tunneling has to be excluded.



**Figure 1.16** Conductance of an electrode single octanethiol molecule electrode junction versus temperature.  $G_0 = \frac{2e^2}{h}$  is the conductance quantum. Copyright APS reprinted with permission from Heimbuch, R., et al., *Phys. Rev. B*, **86**, 075456 (2012).

These experiments reveal a single-molecule conductance, that is about a factor of 3 larger than obtained by Kockmann et al. [23] using a method where the sulfur atom of the octanethiol binds to the substrate rather than to the tip. We believe that this difference can be ascribed to the fact that in our experiment one carbon atom more is involved in the contact as compared to Kockmann's experiment. This interpretation is in agreement with the fact that the conductance of an alkanethiol molecule decreases with a factor of 3 per carbon atom.

# 1.4.4 Single-Molecule Transistor

In order to realize a single-molecule transistor one needs, in principle, three electrical contacts, a source, a drain and a gate. Capturing a single molecule between two contacts is already quite a challenging enterprise, but adding a third electrode is virtually impossible. A way out of this problem would be try to replace the third electrode, i.e., the gate, by another stimulus that could alter the transport through the molecular junction. In the previous section, we already saw that the conductance of the sampleoctanethiol-tip junction can be manipulated by compressing or stretching the octanethiol molecule. This mechanical gating approach has already been applied in several experimental studies [7, 8, 13, 32, 77–83].



**Figure 1.17** The current response of an electrode–octanethiolate– electrode junction (bottom graph, electrode–octanehiolate– electrode junction, black line, left axis) and a vacuum junction (bottom graph, vacuum junction, gray line, right axis) to a varying tip-substrate distance (top graph) at 77 K. The sample bias is +1.5 V and the starting current is 0.25 nA. The vacuum junction exhibits an exponential behavior, which is a hallmark for tunneling. The junction with a molecule initially shows the same exponential behavior, until the molecule jumps into contact (here ~0.17 nm). Upon further reducing the contact's interspace the conductance first marginally increases followed by a faster, but still nonexponential, increase. Copyright AIP reprinted with permission from Sotthewes, K., et al., J. Chem. Phys., **139**, 214709 (2013).

In Fig. 1.17, the effect of mechanical gating of a sampleoctanethiol-tip junction is shown. In the top graph the *z*-piezo displacement as a function of time is depicted. In the bottom graph, two curves are shown. The black curve refers to an experiment where an octanethiol molecule is attached the apex of the scanning tunneling microscope tip, whereas the grey curve refers to a clean, i.e., molecule-free, scanning tunneling microscope tip. The vacuum junction (gray curve) displays the expected exponential dependence of the current with sample-tip distance, whilst the molecular junction (black curve) exhibits a much weaker dependence on the sample-tip distance. After trapping the octanethiol molecule between tip and substrate the *z*-piezo is modulated with an amplitude of only 100 pm (from 0.25 nm to 0.35 nm). Each I(z) trace consists of five compression/stretching cycles. In total we have measured 1200 of these I(z) traces. The reproducibility of the experiments is extremely high, i.e., the variation from I(z) trace to I(z) trace is very small.

There is a small variation in the exact moment at which the tail of the octanethiol molecule flips into contact with the substrate. For more than 90% of the experiments the molecule jumps into contact between 0.16 nm and 0.19 nm. The variation of the conductance upon compressing or stretching of the octanethiol molecule is about 20%.

# 1.5 Outlook

Molecular electronics has a longstanding history that dates back to its invention in 1974 by Aviram and Ratner, but the progress in the first few decades after its birth has been rather modest due to the lack of experimental techniques that allowed a detailed study at the scale of an individual molecule. The advent of scanning probe microscopy in the 1980s has, however, spurred the field dramatically. Scanning probe microscopy has revolutionized our ability to explore and manipulate atoms and molecules on the size scale of atoms. Besides its unparalleled spatial power, scanning probe microscopy is also capable of a detailed spectroscopic study of the properties of single atoms and molecules. In this chapter, we have provided the reader only with a brief introduction to molecular electronics and a few very elementary examples of single-molecule devices. We believe the field is still its infancy and are convinced that the best has yet to come.

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