

A COMPUTATIONAL STUDY OF A SINGLE MOLECULE CHEMICAL SENSOR

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– LIST OF PUBLICATIONS –

Li M, Cucinotta C S, Horsfield A P. A computational model for a molecular chemical sensor[J]. *Nanoscale*, 2024, 16(10): 5334-5342.

Li M, Cucinotta C S, Horsfield A P. The influence of surface Fe on the corrosion of Mg[J]. *Journal of Physics and Chemistry of Solids*, 2022, 170: 110936.

– ABSTRACT –

An electronic nose is a portable device capable of detecting gases and recognizing odors. One of the problems limiting its widespread application is the insufficient selectivity of the device. In this study we propose a new type of electronic nose which can potentially be small, fast and cheap compared with traditional gas analysis tools like IR and Raman spectroscopies.

This device is composed of a molecular junction exhibiting a sharp Negative Differential Resistance (NDR) current peak which could potentially enhance the selectivity, thereby functioning as a molecular sensor for molecule recognition. Using DFT-NEGF simulations, we investigate the relationship between molecule-molecule coupling, molecule-electrode coupling, and the corresponding NDR peak shape. Based on this analysis, we put forward three design rules to control the sensitivity of a sensor and determine that one mechanism for NDR is when a localized molecular orbital involved in resonant tunneling enters and leaves the bias window.

After the inelastic interaction of electrons with phonons is included in the calculations, we modified the structure of the molecular junction so that the electrons are forced to travel through the odorant. With this modification, we successfully detected various molecules using the molecular sensor based on Inelastic Electron Tunneling Spectroscopy (IETS).

Our findings provide valuable insights that could aid in the development of single-molecule sensors for molecule recognition and also contribute to the understanding of inelastic tunneling behaviour of electrons.

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– LIST OF ACRONYMS –

4TPA	4-Thiophenylazide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
IETS	Inelastic Electron Tunneling Spectroscopy
DFT	Density Functional Theory
NEGF	Non-equilibrium Green's Function
IR	Infrared
1D	One Dimensional
GC-MS	Gas Chromatography Mass Spectrometry
RR	Rectification Ratio

CHAPTER 1



INTRODUCTION

It seems, gentlemen, that the human nose somehow houses some sort of spectroscope made of human flesh.

—Malcolm Dyson, *Chemistry and Industry*,

1938

1.1 Electronic nose

An electronic nose, a device that recognizes odours passing through it[1], holds great potential in areas such as disease diagnosis[2, 3], environmental monitoring[4, 5], and crime prevention[6, 7]. As illustrated in the Figure 1.1 , the recognition process of the electronics nose consists of several steps which are generally categorised to hardware components and software components. The hardware components consists of a set of sensors that mimic the receptors in the human olfactory systems[8]. Each sensor is designed to absorb a specific range of odours and produces a unique pattern of signals. The software components will go through the analysis, processing, and recognition of these signals, allowing the device to distinguish unknown odors. Compared to traditional gas detection

methods, such as gas chromatography mass spectrometry (GC-MS) and Fourier transform infrared (FT-IR) spectrometry, the electronic nose could be smaller, more inexpensive and even maybe faster, making its application in fields like crime prevention, environmental monitoring and security genuinely promising.

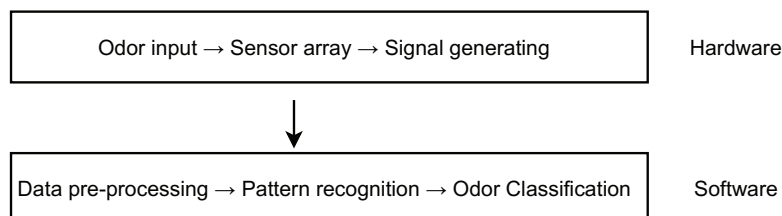


Figure 1.1: An illustration of Electronic Noses including both hardware and software components

Currently there are two types of electronic nose, semiconductor and polymer [9]. Metal-oxide-based chemiresistors are commercially dominant; however, the temperature at which these systems need to operate is larger than 300°C and non-negligible drift occurs when the resistors are heated. Also, it is difficult to accomplish selectivity through molecular recognition at such a high temperature. Conductive polymers with certain groups have been explored to achieve selectivity for gas detection. But the strict experimental conditions in the multiple-step fabrication process is not helpful for rapid and convenient industrial large-scale production and storage. What is more, the prices of most electronic noses range from \$20,000 - \$100,000. The high price limits their application and promotion. An ideal electronic nose should be user-friendly, widely applicable and inexpensive. Thus, it is necessary to find possible materials other than MOX and CP.

1.2 Inelastic Electron Tunneling Spectroscopy (IETS)

Inelastic Electron Tunneling Spectroscopy (IETS) is an experimental measurement of the vibrational modes of molecules, generating signals in the second derivative of the $I(V)$ figure. Discovering by Jaklevic and Lambe in 1966[10],

IETS has become a powerful all-electronic tool to study electron phonon interaction, as opposed to Raman Spectroscopy and Fourier Transform Infrared Spectroscopy which require optical setups.

The process of Inelastic electron tunneling is shown in Figure 1.2. If the energy carried by the travelling electrons is not enough to excite a vibrational mode, the tunneling process remains elastic. On the contrary, when the carried energy exceeds the required threshold, the vibrational mode is activated and an inelastic channel is open. This behaviour is manifested in the $I(V)$ figure by an increase in current and a corresponding peak in the second derivative.

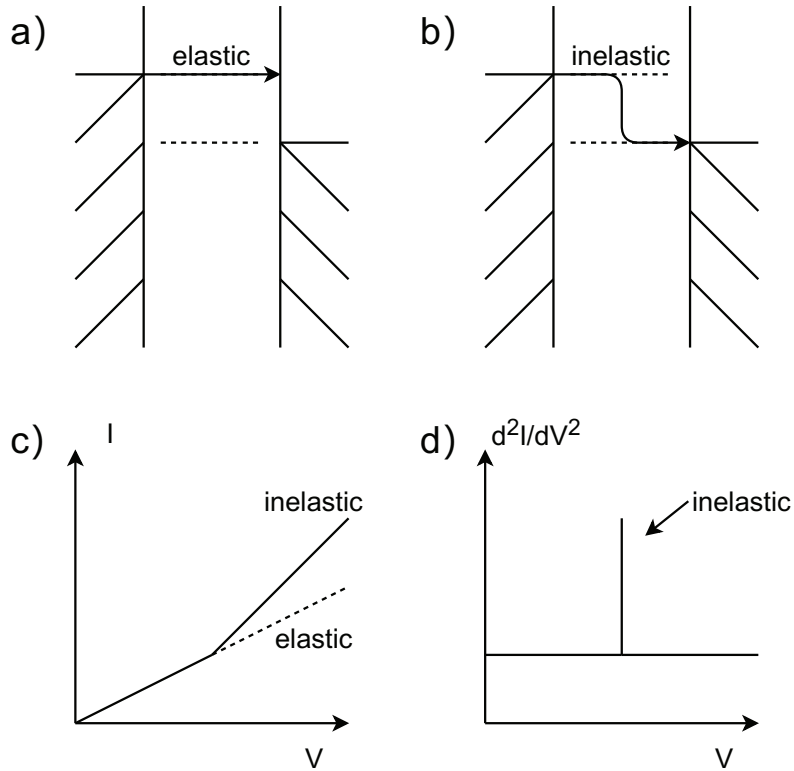


Figure 1.2: An illustration of Inelastic Electron Tunneling Spectrum. a) elastic process; b) inelastic process; c) the figure of dI/dV ; d) the figure of d^2I/dV^2

Traditional IETS is widely conducted through metal-insulator-metal junctions. One drawback with such system is that it needs to be operated at a cryogenic temperature. The peaks in IETS can be described by the full-width-half-maximum (FWHM) calculated by the following equation[11]

$$\frac{d^2I}{dV^2} = C \frac{e^2}{k_B T} \left[e^{\nu} \frac{(\nu - 2)e^{\nu} + (\nu + 2)}{(e^{\nu} - 1)^3} \right] \quad (1.1)$$

$$\nu = \frac{e(V - V_0)}{k_B T}$$

If the temperature is overly high, the FWHM would become quite broad. Therefore, the thermal broadening problem would highly affect the resolution and the selectivity of the spectroscopy, making the peak in the second derivative become quite broad.

If the junction is scaled down to the molecular level, the orbitals, instead of forming broad bands, will be well separated in energy due to quantum confinement, and would not suffer from the thermal broadening problem. In principle according to Fermi's Golden Rule, the inelastic signals generated in the molecule junction can be recognized even in the $I(V)$ figure rather than in the second derivative at a much higher temperature from the cryogenic temperature, which will be elaborated in Chapter 7.

1.3 4TPA-C60

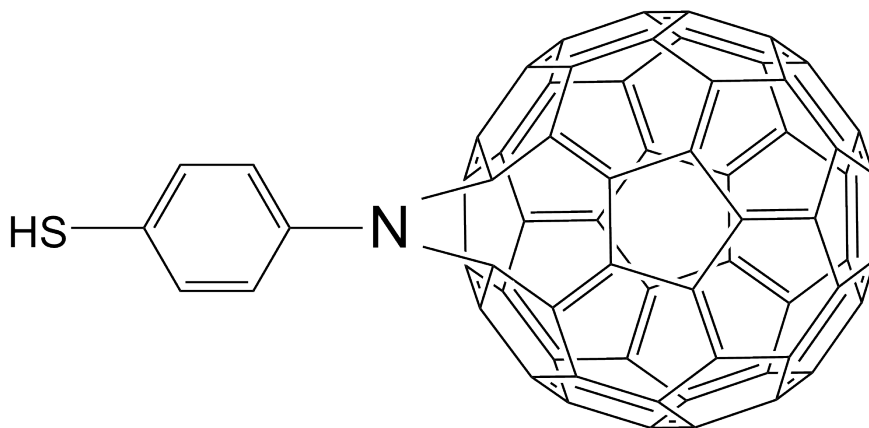


Figure 1.3: An illustration of 4TPA-C60

Aaron Thong explored one molecule, 4TPA-C60 as shown in Figure 1.3, as an alternative material for the molecular sensor. This molecule consists of a benzene ring acting as an electron donor, a fullerene acting as an electron acceptor and a

bridging nitrogen atom connecting them. The twisted nitrogen atom functions as the decoupling unit to separate the donor and the acceptor and the frontier orbitals are localized in the two fragments respectively. At near-zero bias, the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) prevents them aligning, resulting in minimal current flow. Upon application of a specific range of bias, the frontier orbitals of these two fragments move in opposite directions, tracking the shift in chemical potential within the electrodes and narrowing the gap between them. Upon reaching a specific bias threshold, the two orbitals go into resonance, creating a pathway for electron transport and maximizing the current flow. However, if the orbitals fall out of resonance, the pathway disappears, leading to a reduction in current. This phenomenon, termed Negative Differential Resistance (NDR), exhibits as a peak in the current-voltage (I-V) characteristic curve, as depicted in Figure 1.4.

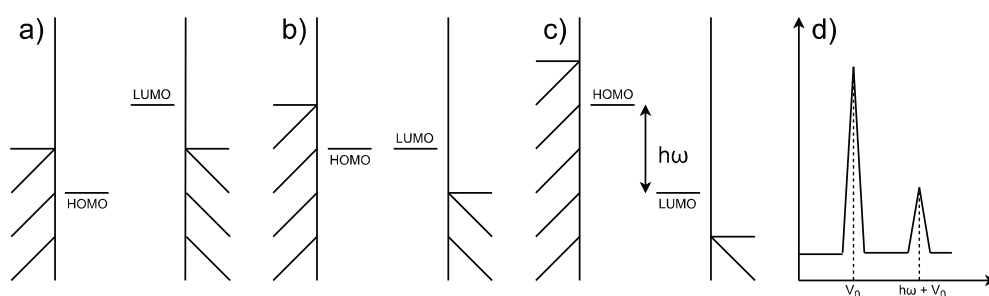


Figure 1.4: An illustration of the NDR mechanism. a) molecular junction at 0 V; b) the resonance state; c) the HOMO-LUMO gap corresponds to a vibrational energy of the odourant; d) the I(V) curve

The NDR peak, belonging to the sensor molecule, is labelled as the primary peak. With the existence of an external odour, if its vibrational energy corresponds to the gap between the frontier orbitals, a secondary peak would appear in the I(V) figure and the difference in the positions of the maxima between these two peaks is exactly the vibrational energy. As the vibrational energy is the unique information which belongs to the odour, the odour is recognized upon analysis of the peak positions. However, it was found that the NDR peak of 4TPA-C60 is

too broad for high resolution and that the additional peak introduced by odours will shrink into this broad peak. Thus, it is impossible to recognise the odours, which is the fundamental function of an electronic nose.

1.4 Objective and strategies

This thesis aims to investigate the use of IETS in molecular electronics as a mechanism of chemical sensing, and in particular to focus on the current/voltage ($I(V)$) characteristic of the sensor device within the electronic nose directly, rather than the second derivative of $I(V)$.

Primary attention would be paid to study the relationship between the features of the molecular sensor and the shape of Negative Differential Resistance (NDR) peaks in the $I(V)$ curve. The shape of the peak belonging to the sensor itself could have a significant effect on the selectivity of the sensor. After the correlation between the molecule composition and its NDR shape is determined and the conditions that generate a sharp NDR peak are developed, the odorant is added into the system to study the electron phonon interaction within the system and how it affects the sensitivity and performance of the sensor.

Our findings open new perspectives in the field of nanoscale engineering and provides a fundamental theoretical framework that could support the development of a new type of electronic nose, which recognizes odor merely relying on its $I(V)$ characteristics instead of the traditional IETS spectrum that is based on the second derivative of the current with respect to the bias. We believe our work could be of interest to the broader scientific audience interested in sensor development and molecular electronics.

CHAPTER 2

LITERATURE REVIEW

2.1 Smell Mechanism

Smell, one of the five senses of humans, impacts our daily life in all aspects. An unpleasant smell steers us away from spoiled food and prompting us to maintain cleanliness whereas fragrant smells, such as those found in perfumes, make people more attractive. Smell plays a crucial role in safety. With irritant chemicals added to coal gas, we will be alerted of a gas leak promptly, which is imperceptible due to its lack of colour and smell. Thus, smell is a perfect complementary sense to vision. However, unlike vision, the mechanism by which we smell remains unclear and is still a subject of heated debate within the scientific community. Two theories are occupying the smell mechanism, shape theory and vibration theory.

2.1.1 Shape theory

Shape theory, also called lock and key theory, states that the receptors of the olfactory system will be activated if the shape of an odorant matches a receptor like a key and lock pair [12, 13]. As illustrated in Figure 2.1 , the triangle-shaped odorant can only generate signals when it fits into the triangle receptors.

Complimentary to the original version, the factors that determine the smell have been developed to contain weak interaction between the the odor and the olfactory system, including hydrogen bonding, dipole moments and Van der Waals interactions. The shape and size of the molecule, which is the only factor in the original version of shape theory, turns out to be too simplified to explain the smell mechanism. Molecules with similar shapes and sizes may have different functional groups which affect its interaction with the olfactory receptors. If different receptors are activated, the molecules will have different smells, contradicting the original shape theory. Thus, the name of shape theory is corrected to Docking theory of olfaction to include more interaction.

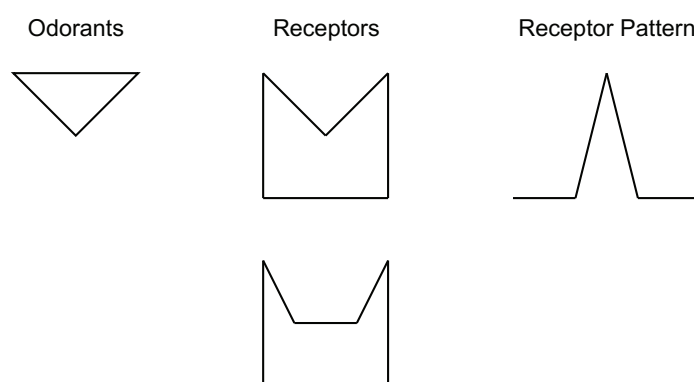


Figure 2.1: An illustration of shape theory

2.1.2 Vibration theory

In contrast, vibration theory, put forward by Dyson in 1938 [14, 15] and supported by Turin in 1996 [16, 17], states that the vibration energy, which represents the frequency the molecular bonds vibrate at, is the key factor that determines the smell of the odor [18]. Electrons travel across the odorants, picking up information about the vibrational energy, and arrive at the acceptor sites of the olfactory receptors. If the vibrational mode is compatible with a

receptor, the receptor is activated. Unlike infrared and Raman spectroscopies, which involve interaction with light and the absorption of photons at specific frequencies, the vibrational theory only requires electron interactions and detects the corresponding modes in IR and Raman spectra simultaneously. Molecules vibrating at the same frequencies may activate the same receptor and smell the same while the shape theory proposes that molecules will have a similar odour if they have a similar shape.

Evidence that supports the vibrational theory is a coincidence in olfactory perception that sulfur and boron hydride compounds have a similar “sulfurous” scent for the human nose, despite their lack of analogous chemical properties [19]. The unique commonality between these molecules is a shared stretch vibrational frequency of around 2600 cm^{-1} corresponding to their B – H and S – H bonds. In the same study, Klio Maniati also demonstrated that *Drosophila* do not exhibit a response to a cyanohydrin structure, which effectively enables nitrile groups to be negligible in IR spectroscopy. In the chemical structures, the (-CN) group is attached to the same carbon with a hydroxyl (-OH) group, so a distinct CN stretch vibration is suppressed giving reduced intensity. However, if the -OH group is relocated to another carbon atoms, even the nearest neighbour of the previous carbon atom, the intensity of both the -CN vibration and the associated odor are restored, which could be perceived by *Drosophila*.

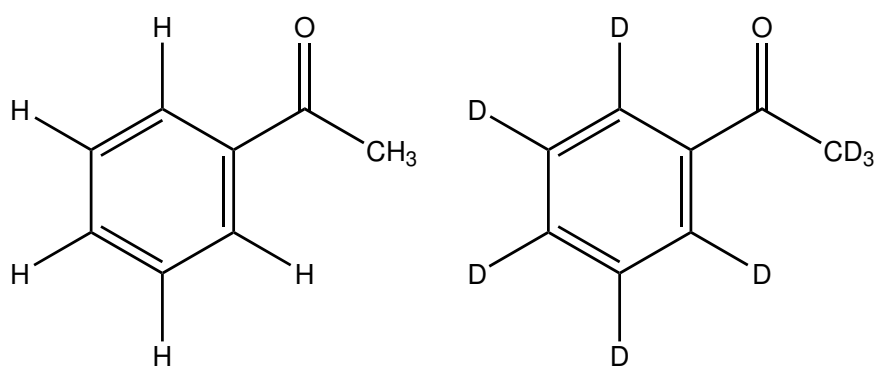


Figure 2.2: undeuterated and deuterated versions of acetophenone (AP)

Experimental research is being carried out to explore the theories. One study tested a honeybee’s ability to distinguish the undeuterated and deuterated

versions of acetophenone (AP)[20] as shown in Figure 2.2. The deuterated molecule is identical to the undeuterated one, but some of the hydrogen atoms have been substituted with isotopes containing a different number of neutrons. This substitution alters the mass of the nuclei significantly while leaving the electronic structure of the molecule unchanged. The successful distinction of these two molecules of similar shape and different vibration frequencies by honeybees could not be explained by the shape theory. This finding challenged Keller's work, which claimed that naive people could not distinguish the aforementioned molecules by smelling [21]. The reason why these two similar experiments generated totally different conclusions is that the olfactory system of persons and honeybees may be different. Later in 2013, Simon Gane [22] validated Keller's observation and extended their conclusion that even trained people cannot distinguish the undeuterated and deuterated versions of acetophenone which were purified to gas-chromatography(GC)-pure standards. However, they demonstrate that subjects can readily discriminate between GC purified deuterated and undeuterated musk odorants which contain 15–18 carbons and 28 or more hydrogens while acetophenone only contains 8 carbons and 8 hydrogens.

But from the reported research it is clear that neither theory is an end to this story. Although we cannot drive a conclusion which theory is more correct, molecular electronics used to produce an electronic nose can be designed based on Turin's vibration theory.

To elaborate the vibrational theory, Figure 2.3 shows a simplified model of the olfactory system. Electron (hole) sources diffuse in the cell fluid at a speed of v until they arrive at the receptors at a period of T_x . After T_I , the charges brought by X are delivered to the donor part of this receptor. It takes T_L time for the charge to pass through the D level where it has to hop into the acceptor part, A level. There are two ways of hopping, elastic tunnelling, which takes a time T_{T0} , and inelastic tunnelling, which takes a time T_{T1} . Resonant inelastic tunnelling requires an energy difference between the donor level and acceptor level which

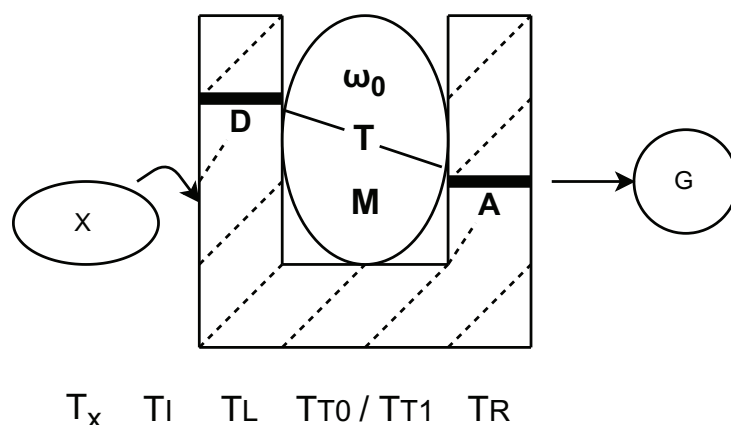


Figure 2.3: An illustration of vibrational theory, adapted from [23]

corresponds to the molecule M 's vibrational energy of frequency ω_0 . Once inelastic tunnelling dominates the hopping process, a protein G will be released to send a signal to the brain.

Therefore, molecules of the same frequencies enable inelastic tunnelling with the same donor and acceptor level differences. And a set of receptors will be activated identically, which triggers the release of the same protein G . Finally, identical activation of multiple receptors generate identical smell and these molecules will smell the same.

2.2 Molecule electronics

Molecular electronics[24] involves the fabrication of various components within electronic circuits, including molecular wires, switches, diodes, field-effect transistors, and memory devices, using organic molecules. Within the fields, the means to measure and analyze the electrical characteristics of these nanoscale components are also developed. In 1959, the American physicist and Nobel Prize winner Feynman delivered a lecture titled 'There is Plenty of Room at the Bottom' at the annual meeting of the American Physical Society[25]. His imaginative and forward-thinking ideas about electronic devices composed of molecules and 'bottom-up' nanotechnology anticipated the potential transformation that molecular electronics could bring to life in the future. In 1974, Aviram and Ratner demonstrated the feasibility of constructing molecular-scale diodes from single molecules [26] for the first time, which stimulated interest in molecular devices. Since then, numerous researchers have contributed to this field [27, 28]. Thanks to their efforts, progress in molecular electronics has become crucial for the applications in various fields such as integrated circuits, solar cells and sensors, including electronic noses.

2.2.1 Molecular diodes

Diodes are electronic components that exhibit an asymmetric voltage-current characteristic. Current flows through these devices predominantly in one direction, typically when a positive bias is applied. The most prevalent type of semiconductor diodes comprises a p-n junction. Their primary application lies in rectification, leading to the alternative terminology of "rectifiers" for diodes. These devices play a crucial role in various electronic circuits by enabling the conversion of alternating current (AC) to direct current (DC).

The concept of the single molecule diode was initially proposed by Arie Aviram and Mark Ratner in 1974 [26]. It involved a donor molecule (D) linking an

acceptor molecule (A) to simulate a semiconductor p-n junction. This was the first step towards using molecules to build functional molecular electronic devices. Specifically, this molecule is composed of tetrathiafulvalene (TTF) acting as the donor fragment, tetracyanoquinodimethane (TCNQ) acting as the acceptor fragment and a triple methylene bridge connecting them, as shown in Figure 2.4.

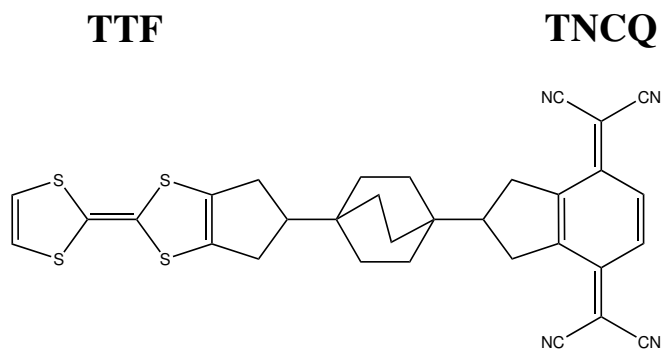


Figure 2.4: the first single molecule diode

A core indicator of the performance of molecular diodes is the rectification ratio (RR), which is the ratio of current under positive and negative bias. The larger the rectification ratio, the better it is for achieving conduction in one direction only. In recent decades, numerous experimental and theoretical studies have been conducted to enhance the rectification ratio (RR) of molecular rectifiers [29]. Arag3nes et al. notably achieved a remarkable resistance ratio surpassing 4×10^3 for 1,8-nonodiyne molecules, which were deposited on low-doped silicon electrodes, via an STM-break-junction method under ambient conditions[30]. The researchers further stated that the integration of single molecules with semiconductor materials, such as the highly mechanically stable silicon electrodes employed, would be compatible with traditional semiconductor circuitry. This compatibility aspect is a crucial consideration for the potential incorporation of molecular components into existing electronic systems and devices. Later in 2018, Atesci et al. demonstrated that the RR value of Ru-polypyridyl complexes is correlated to the surrounding humidity[31]. By simply adjusting the relative humidity between 5% and 60%, the RR of these complexes could be varied

across a wide range spanning three orders of magnitude, from 1 to 10^3 . This adjustable behavior is attributed to the presence of two localized molecular orbitals. Under high humidity conditions, the two degenerate orbitals present in dry environments become misaligned due to the displacement of (PF_6^-) ions, leading to the observed tunability of the rectification ratio.

Despite extensive research efforts in this field[32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 34], the majority of molecular rectifiers have only achieved rectification ratios (RR) ranging from 10^2 to 10^3 , whereas commercial diodes commonly exceed 10^5 to 10^8 in RR[42]. Consequently, molecular rectifiers remain inferior to current commercial diodes, and their practical application has yet to progress beyond the theoretical level. This performance gap underscores the continued challenges in developing molecular-scale electronic components that can compete with their conventional semiconductor counterparts.

Following Yuan's research which fabricated SAMs using ferrocene (Fc)[43], Chen et al. surpassed the rectification ratio (RR) limitation of molecular rectifiers, achieving a value of 10^5 by constructing a self-assembled monolayer (SAM) with $\text{Fc} - \text{C} \equiv \text{C} - \text{Fc}$ [44]. When a positive bias is applied, the positively charged Fc units repel each other and are attracted to the negatively charged top electrodes due to electrostatic interactions. Conversely, under negative bias, the neutral Fc units interact via van der Waals forces. Consequently, Fc units are more likely to contact the electrodes under positive bias than under negative bias, resulting in the significant RR enhancement.

2.2.2 Mechanisms for unimolecular rectification

The rectification ratio (RR) largely depends on the underlying rectification mechanisms. The majority of electronic diodes are designed based on three primary mechanisms: S-type, A-type, and U-type[45].

S (Schottky)-type:

The Schottky-type rectification mechanism stems from the work function difference of the metal electrodes commonly employed. In "metal-molecule-metal" sandwich junctions, distinct Schottky barriers at the two molecule-electrode interfaces induce rectification. These differences typically arise from the use of dissimilar metals for the electrodes, the linking spacers between metals and molecules, or even variations in the contacting geometry at the interfaces, all of which can lead to work function disparities. Thus, the Schottky-type mechanism relies on the asymmetry inherent in the device structure to achieve rectification.

It is evident that the rectification caused by the structural asymmetry of the device does not capture the essence of the rectification mechanism. Even if the device is scaled down to a single molecular layer, the underlying principle remains distinct from true molecular rectification, as the intrinsic properties of the molecule do not play a pivotal role in the rectification process. Rather, this rectification can be considered an error that arises during the manufacturing process. For instance, when using active metals as electrodes in the device, it is challenging to prevent the oxidation of these metals. As a result, disparate Schottky barriers are formed between the oxide layer and the pure metal or organic layers. Therefore, to avoid this type of spurious molecular rectification, the emphasis should be on using the same metals for both the top and bottom electrodes, as well as implementing measures to prevent electrode material oxidation when investigating genuine molecular rectification phenomena.

A ("Asymmetric") type

Another type of rectification mechanism stems from the different placements of an electrostatic conductive group within the molecular structure. This class of molecules comprises an electrostatic conductive group connected to alkane chains of varying lengths, which serve as barriers of different widths. The coupling between the left and right electrodes varies due to these various barrier

widths, leading to asymmetric current flows under positive and negative bias, respectively. The rectification arising from this asymmetric coupling with the electrodes is referred to as the A-type mechanism.

U (unimolecular type)

The rectification resulting from the asymmetry of the molecular backbone represents an inherent property of the transport characteristics of molecular junctions. The $D - \delta - A$ molecule, to which the $A - R$ diode belongs, represents a primary example of this mechanism. This type of molecule constitutes a diode where the highest occupied molecular orbital (HOMO) of the donor (D) fragment is close to the Fermi energy (EF) of the electrode connected, while the lowest unoccupied molecular orbital (LUMO) of the acceptor (A) fragment is close to the EF of the electrode to which it is connected. When the bias is applied in different directions, distinct orbitals are engaged within the bias window, resulting in disparate currents in the positive and negative directions, thereby achieving rectification.

In addition to the aforementioned HOMO and LUMO, the U type of rectification can also be triggered by the interaction of HOMO and HOMO-1. Perrin et al. [46] proposed an orbital resonance-based tunnelling single-molecule diode of this type of rectification in 2015, where the donor and acceptor are linked via $-CH_2CH_2-$ bridges. Through modulation of various chemical modification groups, the HOMO and HOMO-1 serve as the transport pathway. Such molecular junctions can exhibit rectification ratios as high as 10^3 , even in cases of symmetrical coupling to the same two electrodes.

2.2.3 NDR

The primary objective of molecular rectifiers is to maximize the rectification ratio (RR). However, they are unable to meet the demands for our electronic nose application. Another type of molecular electronic device is the molecular

resonant tunneling diode, which exhibits a significant feature known as negative differential resistance (NDR).

Negative differential resistance (NDR) denotes a phenomenon wherein the current passing through a device decreases as the applied bias increases[47]. This conduction behavior stands in contrast to the linear current variation usually observed in conventional devices in accordance with Ohm's Law, where the current increases in proportion to the applied bias.

The generation of NDR is often attributed to the interplay between two narrow energy states. Near zero bias, the gap between the HOMO and LUMO prevents them from aligning, resulting in a small current. However, as a positive bias is applied to the junction, the HOMO rises and the LUMO drops, following the chemical potential shift in the electrodes. Once a specific bias is reached, the HOMO and LUMO jump into resonance, leading to a current maximum. If the applied bias continues increasing, the HOMO and LUMO will eventually move out of resonance, and the conductive pathway generated by their resonance will disappear. Consequently, the current drops, leading to the characteristic NDR peak in the current-voltage (I-V) characteristic. This is the common underlying mechanism for the generation of NDR.

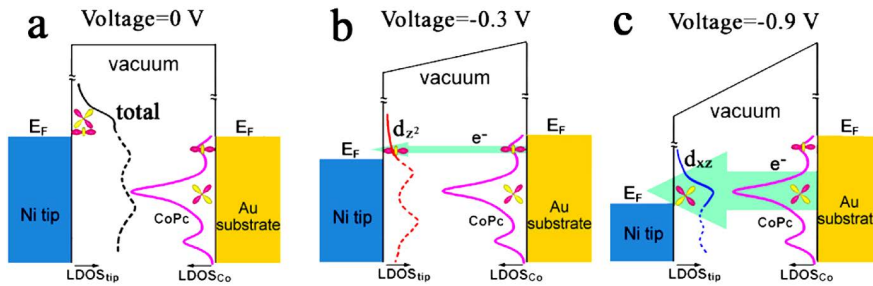


Figure 2.5: NDR mechanism put forward by Chen[48]

In 2007, Chen[48] proposed a novel mechanism demonstrating that even broad energy levels could generate an NDR feature. This was reported for a cobalt phthalocyanine (CoPc) molecule, which exhibited NDR when using a nickel (Ni) tip, as shown in Figure 2.5. Although the total density of states (DOS) of the Ni tip is continuous and broad, the spatial discreteness of the d_{xz} orbital resonates with

the CoPc, resulting in a sharp NDR peak in the current-voltage (I-V) characteristic. This finding complements the previously established mechanisms and suggests a potential simplification in the construction of molecular junctions.

2.2.4 Molecule resonant tunnelling diode

The electronic device that exhibits the NDR feature is known as a resonant tunneling diode (RTD)[49, 50, 51]. As the name suggests, the electron transport mechanism in this device is based on tunneling, which necessitates the presence of a barrier. In a molecular RTD, conjugated parts like phenyl and vinylene units are decoupled by a saturated carbon chain acting as the barrier. Electrons must tunnel from one conjugated site to another through this barrier. A typical molecular RTD, depicted in Figure 2.6, was calculated by Reed, revealing a distinct NDR peak[52]. The benzene molecule inserted between two CH_2 groups functions as a single quantum well. The successful synthesis of this molecule may mark a breakthrough in molecular orbital engineering [53].

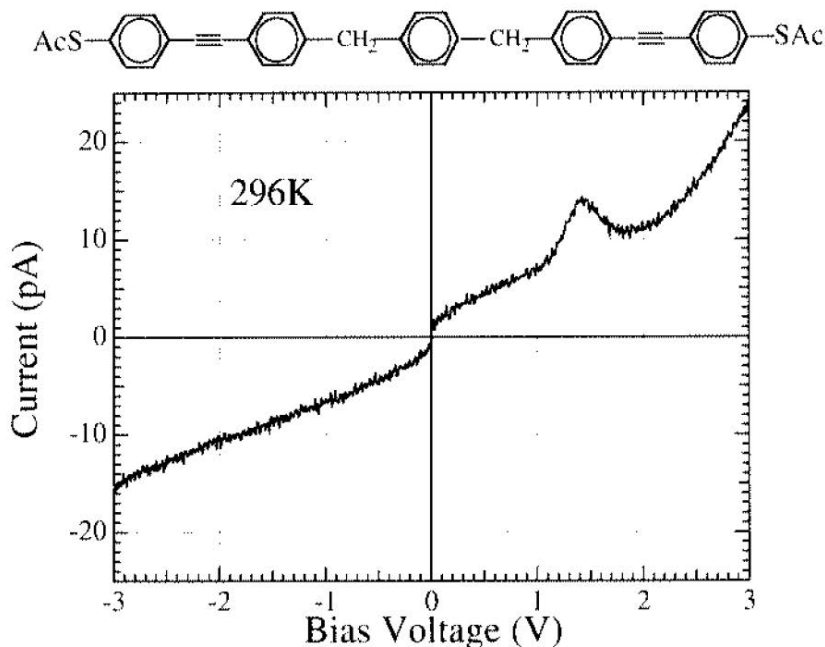


Figure 2.6: An illustration of vibrational theory. Adapted from [52]

To design a molecular RTD, the CH_2 group is not an absolute requirement, as an entirely conjugated molecule can also exhibit RTD-like features. For instance, π -conjugated oligo(phenylene ethynylene), which appears to lack any discernible barrier, still displays characteristics typical of an RTD[54]. As the applied bias increases, the charge on the molecule rises, and the molecular geometry becomes twisted. Initially, the LUMO, which serves as the conduction orbital, extends until the current reaches a peak, at which point the LUMO becomes localized once again. Liu has simulated this molecule using a model that incorporates quadratic electron-vibration coupling into vibration softening[55]. The resulting current curve closely matches the experimental data, suggesting that higher-order electron-vibration coupling plays a crucial role in the NDR behavior of the OPE- NO_2 system.

2.3 Molecule Engineering

Molecular engineering is a scientific field focused on the design and manipulation of molecules, which encompasses altering their structure, composition, or properties to achieve desired characteristics or functions [56, 57]. This field requires the integration of diverse techniques from various domains, including chemical engineering, materials science, bioengineering, electrical engineering, physics, mechanical engineering, and chemistry.

The concept of "molecular engineering" was first introduced in the work of Arthur Von Hippel in 1956 [58]. Von Hippel described it as "a new mode of thinking about engineering problems. Instead of taking prefabricated materials and trying to devise engineering applications consistent with their macroscopic properties, one builds materials from their atoms and molecules for the purpose at hand."

In this section, we will discuss in detail the various components of a typical molecular junction to elucidate their impact on its performance, drawing insights from the field of molecular engineering.

2.3.1 Electrodes

A molecular junction comprises two electrodes with a molecule inserted between them[59]. The electrodes are the crucial factors influencing the coupling between the molecules and the electrodes. At present, two primary types of materials are widely employed as the electrodes: metal and carbon-based materials.

Metal

Metals are utilized as electrodes due to their generally good inherent conductivity, with options including gold, platinum, silver, copper, and aluminum. The choice of metal depends on factors such as conductivity, stability, compatibility with the electrolyte, and cost. Among the available metals, gold is commonly

selected, considering its excellent conductivity, stability, compatibility with diverse electrolytes, and, most importantly, its resistance to corrosion. While gold may be more expensive compared to other metals, its superior properties often make it the preferred choice in applications where reliability and performance are in high demands.

The predominant approach in electrode-molecule contacts is the chemisorption of thiols onto gold surfaces[60, 61, 62, 63, 64]. This connection can be easily established due to the spontaneous growth from dilute thiol solutions[65, 66]. Despite the extensive history of use, molecular electronics with gold leads face substantial challenges, including the instability of S-Au bonds, structural transformations induced by electric fields, and the limited tunability of the electrical properties of gold electrodes, thereby constraining the widespread application of these junctions[67, 68]. In recent years, there has been a growing interest in exploring alternative suitable candidates for the electrodes of molecular electronics, such as semiconductors[69, 70, 71] or other metals.

In contrast to gold (Au), which belongs to group 11 of the periodic table, platinum (Pt) and palladium (Pd) exhibit stronger d-orbital interactions. Typically, the π -character of the bonds established by Pt and Pd offers an alternative pathway for electron transfer, leading to enhanced conductance[72]. A study of isothiocyanate-terminated alkanes found that the conductance of Pd and Pt junctions was 2–3 times greater than that of Au junctions, despite the similar work functions of Au and Pd[73]. In Pt-based molecular junctions, a strong hybridization between the Pt frontier orbitals and the dominant conducting molecular orbitals results in the broadening of molecular energy levels, producing a wide plateau of high transmission.

On the other hand, silver and copper exhibit reduced $d - \pi^*$ hybridization, resulting in a decreased metal–molecule coupling due to the lower density of states of d orbitals near the Fermi level compared to Au. This weaker interaction leads to a smaller conductance magnitude of 4,4–bipyridine if the molecule is inserted between Ag electrodes instead of Au electrodes[74].

Magnetic metals such as Ni[75, 76, 77] and Fe[78] have also been utilized as electrodes in molecular junctions. The spin-polarized orbital hybridization near the Fermi level of the electrode facilitates the observation of fascinating magnetic phenomena, like the gate-controlled Kondo effect[79, 80]. This effect depicted the precise manipulation of the spin degree of freedom through the application of gate voltage, providing valuable insights into the junction and holding potential for diverse device applications.

Carbon based materials

The practicality of metallic materials is constrained by atomic mobility and their mismatch of size and work function with single molecules. Carbon-based nanomaterials like carbon nanotubes and graphene could be seen as substitute electrode materials for molecular electronics. Among them, graphene is the shining star in the scientific field. Graphene is inherently rigid at the atomic level and highly compatible with single molecules, while its composition and atomic bonding configuration are relatively simple, featured by the honeycomb lattice structure formed by the sp^2 -hybridized carbon atoms.

In graphene–molecule–graphene junctions, the effect of molecular orbital gating at room temperature has been validated[81, 82]. This effect is undetectable in metal–molecule–metal junctions because the thick metal electrodes screen the gating effect. Therefore, by employing graphene as the electrodes, we can reduce the relatively complicated molecule junctions into a thin two-dimension junction.

In addition, carbon-based electrodes have other benefits, including flexibility in contact geometry, which can be formed by either covalent bonding or π – π stacking. When molecules are attached directly to graphene through covalent bonding via anchoring groups, the strong interaction extends the electronic structure to the molecules and impacts the functionality. In single-molecule junctions constructed using single-layer graphene as electrodes, the current scales as the cube of the voltage at low voltage levels, thus challenging Ohm's

law, as theoretically predicted and experimentally demonstrated by I Bâldea [83]. The lack of an ohmic regime is attributed directly to the distinctive band structure of single-layer graphene, where the disappearance of the density of states at the Dirac points inhibits electron flow between the electrodes under low biases.

On the other side, the molecules can also form a junction with graphene electrodes through the configurations of π - π stacking. Li discovered that the thermal conductance of the π - π stacking systems is approximately 95% less than that of a molecular junction with a covalent bonding geometry[84]. Phonon transmission in π -stacked systems experiences significant decline across the entire frequency spectrum, with most transmission occurring below 5 THz, a frequency range is usually not concerned. Consequently, the figure of merit ZT , as shown in the equation 2.1

$$ZT = S^2 \rho^{-1} \kappa^{-1} T \quad (2.1)$$

where S is the Seebeck coefficient (thermopower), ρ is the electrical resistivity, κ is the thermal conductivity and T is the temperature, for the π -stacked molecular junction is significantly improved due to the substantially reduced thermal conductance.

Recent focus has shifted towards exploring additional semiconductor materials that can function as the electrodes in single molecule junctions. GaAs[69] and Si[30] are two promising candidate electrodes which are ideal for investigating the charge distribution across the interface between electrodes and molecules in single molecule junctions. In contrast to metallic electrodes, these materials offer the advantage of easily adjustable Fermi levels by doping or tweaking the compositions, bringing new avenues to incorporate innovative functionalities into molecular junctions.

2.3.2 Anchoring group

Within covalent bonding, the thiol group (-SH) is considered to be the initial and the prevalent choice for anchoring groups, owing to the favourable binding energy and strong tendency to form junctions. However, various bonding configurations are available for covalent Au-S bonds, as shown in Figure 2.7, leading to a diverse array of single-molecule conductance behaviors.

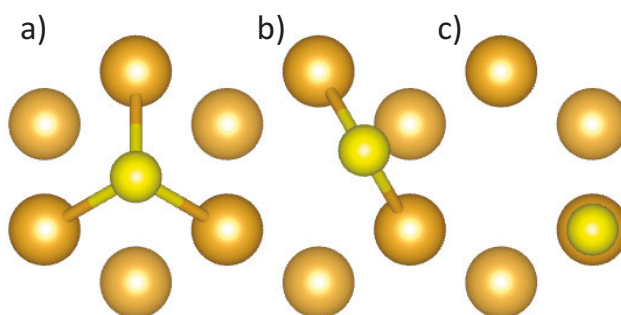


Figure 2.7: An illustration of different geometries of Au-S a) honeycomb-bridge structure; b) bridge structure; c) atop structure.

Flicker noise is a form of electronic noise characterized by a power spectral density that is inversely proportional to the frequency. This type of noise exists in nearly all electronic devices and is generated by various phenomena, including the presence of impurities within conductive channels[85]. Umar Rashid's finding demonstrated that the analysis of Flicker noise offers a distinct approach to differentiate between strong chemisorption interactions, such as Au-SR bonds, and weaker physisorption interactions like Au-SRR' configurations[86]. The investigation into Flicker noise indicates that the rearrangement of gold atoms within chemisorbed Au-SR junctions is similar to the behavior observed during the breaking of pure Au-Au metallic contacts, which is independent of the molecular backbone structure or the resulting conductance. Conversely, in the case of thioethers, which forms a weaker physisorbed Au-SRR' bond, the Flicker noise measurements indicate the changes occur at the interface between gold

and the anchoring group; however, they do not exhibit the characteristic Au-Au rearrangement observed in the Au-SR chemisorption case.

Another popular candidate with robust interface coupling is the covalent bond formed between gold (Au) and carbon atoms with sp hybridization, denoted as Au-C (sp). Compared to thiol anchoring groups, these Au-C (sp) bonds have a more significant hybridization of the molecular orbitals with the metal states, resulting in a larger shift of the energy peaks towards the Fermi level (E_F). Consequently, molecular junctions incorporating Au-C bonding exhibit enhanced mechanical stability and increased electrical conductivity. Furthermore, the conductance variations observed in Au-C bonds are substantially minimized due to the more stable bonding configuration.

Other than covalent bonding, donor-acceptor bonding involves electron transfer from either π -donors or lone pair donors to gold atoms. Frequently employed π -donors encompass fullerenes, along with other aromatic rings such as those found in pyrene molecules. Table 2.1 presents the commonly employed anchoring groups with π -electron donor or lone pair donor[87].

The formation of Au-N bonds have also been utilized extensively in the construction of single-molecule junctions. Among the three nitrogen-based donor anchoring groups (listed in Table 2.1), the order of decreasing stability is reported as follows: pyridine, amine, and nitrile[88]. However, the binding energy sequence differs, with pyridine exhibiting the highest value, followed by nitrile and then amine.

Beyond the lone pair donation from the nitrogen atoms, the delocalized π -character inherent to pyridine and nitrile moieties also plays a role in influencing the binding energy[89]. A novel π -conjugated anchoring group, thiazole, has been reported and used in Au-molecule-Au junctions[90]. Experimental findings reveal that the conductance of these junctions distinctly varies depending on the substitution position of the thiazole group, which is attributed to the changes in the coupling strength between the molecule and electrodes. Both Au-N and

Au- π interactions in the thiazole contribute as anchoring mechanisms, and the coupling between the thiazole anchor and electrodes can be effectively tuned, confirmed by XPS and DFT calculations.

Due to its extensive molecular interface with metals and strong affinity for precious metals, fullerene has been extensively utilized as an anchoring group in various applications. The incorporation of fullerene units in molecule junctions can lead to a relocation of the barriers for electron transfer, shifting them from the molecule-metal interface to the molecular core region, thereby facilitating direct charge injection into the molecular backbone[91].

Simon A. Svatek's study reveal that the value of the Seebeck coefficient of Metal-C60-Graphene exhibits up to a ninefold enhancement compared to previously employed Au-C60-Pt molecular junctions. Using conducting-probe atomic force microscope (c-AFM), he measured the thermoelectric properties of these systems and confirmed exceptional thermoelectric performance exhibited by C60 derivative systems. His work also highlighted the promising prospects of employing graphene electrodes to modulate thermoelectric properties of the C60-incorporated junctions[92].

2.3.3 Spacer

In cases where interface coupling is overly strong, adverse outcomes may arise, such as the impairment of intrinsic functionalities in single molecules and reduced gating effects in three-terminal structural devices. However, both mechanical stability and electronic coupling are positively correlated to the binding energy between the electrode and the anchoring moiety. Therefore, achieving an optimal interface between electrodes and molecules requires a balance between mechanical stability and electronic coupling. One approach to accomplish this decoupling effect is to incorporate methylene groups as insulating spacers between the central molecular backbone and the anchoring groups.

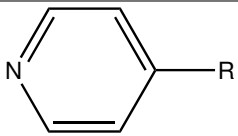
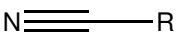
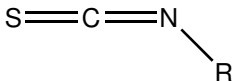
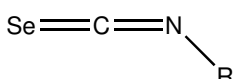
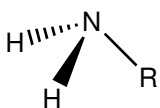
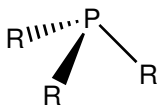
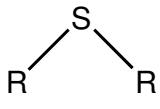
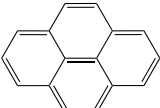
Type	Structure	Name
Lone pair		4-Substituted pyridine
		Nitrile
		Organothiocyanate
		Organoselenocyanate
		Primary amine
		Tertiary phosphine
		Thioether
π donor		C ₆₀
		Pyrene

Table 2.1: Typical anchoring groups[87]

The presence of methylene groups can significantly diminish the electronic coupling between the orbitals of the functional molecule and the electrodes by disrupting the delocalization of π -electrons, while still maintaining a strong enough mechanical connection.

G.R. Berdiyorov explored the electronic transport characteristics of diazatriptycene molecular systems, which exhibits distinct current rectification behavior arising from its structural asymmetry [93]. The degree of rectification is influenced by the nature of the anchoring group. By introducing an insulating methylene (CH_2) spacer between the thiol end group the adjacent phenyl ring, the current rectification of the system was amplified by more than a factor of two.

Other than influencing the electronic coupling of molecular junctions by adding spacers, anchoring groups can also impact the energy levels of frontier molecular orbitals. The impact is determined by the electronegativity of these anchoring moieties. Electron-donating anchoring groups, such as amines and thiols, typically transform the charge transport through the junctions into hole-dominated transport, predominantly occurring along the HOMO. This transformation is because those anchoring groups typically raise the energy of frontier molecular orbitals so that the HOMO is raised to be the closest in energy to the electrode's Fermi level. In contrast, charge transport in pyrene-based molecular junctions is preferentially governed by the LUMO, affected by the electron-withdrawing groups like pyridine and nitrile

2.3.4 Molecule length

The length of a molecular wire, a topic that has been extensively investigated across diverse molecular systems, is a critical factor that can significantly impact its single-molecule conductance. Fundamentally, the molecular length determines the distance that charge carriers must traverse between the two electrodes, thereby influencing the overall single-molecule conductance.

Two distinct mechanisms govern charge transport: temperature-independent coherent tunneling and temperature-dependent incoherent hopping processes. For short molecular wires (typically less than 4 nanometers in length), coherent tunneling is the prevailing and dominant charge transport mechanism. However, in non-resonant scenarios, the molecular conductance (G) demonstrates an exponential decay with increasing molecular length (L), following the relationship

$$G = G_0 \exp(-\beta L) \quad (2.2)$$

where G_0 represents an effective constant conductance term, and β is a decay constant.

For extended molecular wires, incoherent hopping is considered the dominant mechanism for charge carrier transport. According to Marcus theory, which elucidates the kinetics of electron transfer processes, the conductance exhibits an Arrhenius-type temperature dependence, as shown

$$G \propto \exp(-E_A/k_B T), \quad (2.3)$$

where E_A represents the activation energy associated with the hopping process. The rate of hopping-mediated charge transfer is primarily determined by the activation energy rather than the molecular length. This is why the decrease in conductance with the length of the molecular wire is gradual and not as significant as that in coherent tunneling. In general, if the molecular length increases beyond a certain threshold, the dominant charge transport mechanism transitions from coherent tunneling to incoherent hopping.

2.4 Summary

The central idea underlying the Turin mechanism in the vibrational theory involves the generation of an inelastic electron tunneling spectrum, positioning it as a promising candidate for the development of a physical chemical sensor for molecule recognition.

In a study exploring the potential of chemical sensors based on the vibrational theory of olfaction, Patil utilized a tight-binding Hamiltonian model with nearest-neighbor hopping to simulate the behavior of a molecular wire [94]. This wire was connected to two semi-infinite leads, forming a molecular junction. The resulting Inelastic Electron Tunnelling Spectroscopy (IETS) spectrum displayed a distinct peak at 0.15V, attributed to the presence of an external molecule, alongside the primary peak associated with the molecular wire. This secondary peak highlighted the sensor's capability to detect external molecules. Subsequently, in 2018, Patil replaced the molecular wire with a molecular Resonant Tunneling Diode (RTD) within the same framework [95]. This adaptation overcame the limitation of IETS operation, which requires cryogenic temperatures to mitigate thermal broadening of spectrum peaks, showcasing the potential of the molecular RTD as a sensor at room temperature. While Patil's research shows promise in this field, the sensors he examined were theoretical models rather than actual molecules. Expanding on Patil's work, Sahoo incorporated a real molecule RTD proposed by Perrin [96] into this sensor configuration and successfully identified Hydrogen Cyanide and Benzaldehyde through IETS [97]. However, the configuration of Sahoo's molecular junction and the relative position of the odorant seem not to be energetically favorable, an aspect that will be discussed in Chapter 7.

While the principle of vibration detection seems to be similar to that of Inelastic Electron Tunneling Spectroscopy (IETS), both involving inelastic electron tunneling, the sensor's recognition system isn't necessarily dependant on the

conventional IETS peaks observed in the second derivative of the current-voltage ($I(V)$) response.

Traditional IETS experiments typically employ metal-insulator-metal junctions, requiring operation at cryogenic temperatures to address the thermal broadening issues that impact peak resolution. This low-temperature condition is a strict operational requirement. Currently, the prevailing approach to enhance resolution at higher temperatures involves the utilization of machine-learning algorithms to differentiate between compounds based on raw sensor data [98, 99, 100, 101, 102, 103, 104, 105].

However, when the junction is downsized to the molecular scale, the orbitals become more energetically well-separated due to quantum confinement. As a result, the movement of electrons through the highly quantized orbitals, induced by the applied voltages, introduces peaks directly in the $I(V)$ curve, rather than in the d^2I/dV^2 spectrum as typically utilized in IETS.

Despite the substantial research on molecular electronics based on IETS [106, 107, 108, 109, 110, 111, 112, 113, 114], there has been relatively limited exploration of the application of IETS in molecular electronics for chemical sensing, particularly focusing on the $I(V)$ characteristic of the sensor device instead of its second derivative. In this work, we will investigate potential molecules that can serve as molecular sensors, potentially leaving a distinct fingerprint directly in the $I(V)$ curve. The methods to investigate the elastic and inelastic behaviors of electron transport through these molecules will be elaborated in the next chapter.

CHAPTER 3

METHODS

3.1 Density functional theory

Density functional theory (DFT) is a method that determines the ground state energy of a system using the electron density as the sole variable, significantly reducing the computational cost. This approach originated in the early days of quantum mechanics. In 1927, Thomas and Fermi proposed a homogeneous electron gas model[115, 116], in which the kinetic energy of an atom, the electron-nuclei interaction, and the electron-electron interaction were all expressed in terms of the electron density. However, the formula they provided to describe the kinetic energy using electron density was not accurate enough, and the correlation energy of electrons was not considered. As a result, this model did not adequately describe the actual system.

In 1964, after studying the Thomas-Fermi homogeneous electron gas model, Hohenberg and Kohn formulated their famous theorem - the Hohenberg-Kohn theorem, which laid the theoretical foundation for density functional theory [117]. However, the theorem did not provide a practical method to find the exact form of the electron density. The following year, Kohn and Sham proposed the Kohn-Sham equation, a specific method for obtaining various properties of

systems using electron densities [118]. The general idea behind this method is to introduce non-interacting orbitals with the same electron density and energy as the actual system. Using this set of orbitals, the Kohn-Sham equations can be transformed into a series of single-electron equations through the variational principle. The problem is then solved by solving these single-electron equations.

3.1.1 Hohenberg-Kohn theorems

The two Hohenberg-Kohn theorems form the fundamental framework of density functional theory:

Theorem 1: The external potential $V(\mathbf{r})$ of any N -electron system is uniquely determined by the electron density $n(\mathbf{r})$. In other words, the external potential $V(\mathbf{r})$ is a unique functional of the electron density $n(\mathbf{r})$.

Proof: Assume that two wavefunction Ψ' and Ψ can generate the same electron density while they correspond to the different Hamiltonians $\hat{H}'$ and $\hat{H}$. As Ψ' does not correspond to the ground state of $\hat{H}$, then due to the variational principle

$$\begin{aligned} E_0 &< \langle \Psi' | \hat{H} | \Psi' \rangle \\ &< \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &< E'_0 + \int n_0(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (3.1)$$

As Ψ also does not correspond to the ground state of $\hat{H}'$, then from the variational principle we have

$$\begin{aligned} E'_0 &< \langle \Psi | \hat{H}' | \Psi \rangle \\ &< \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\ &< E_0 + \int n_0(\mathbf{r}) [V'_{\text{ext}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r})] d\mathbf{r} \end{aligned} \quad (3.2)$$

Adding Eq. 3.1 and 3.2 lead to the contradiction which is $0 < 0$

$$E_0 + E'_0 < E_0 + E'_0 \quad (3.3)$$

Hence, the above equation demonstrate that there cannot be two different wavefunction that correspond to different $\hat{H}$ but generate the same electron density. Thus the ground state of $\hat{H}$ is determined by the electron density.

Theorem 2: The ground state energy of a system is a functional of the electron density $n(\mathbf{r})$. The electron density that minimises the total energy is the actual electron density of the system.

Proof: The functional $F[n(\mathbf{r})]$ is defined as follows

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\text{int}}[n(\mathbf{r})] \quad (3.4)$$

$T[n(\mathbf{r})]$ is the kinetic energy and $E_{\text{int}}[n(\mathbf{r})]$ is the interaction energy between the particles in the system. According to the variational principle, the energy corresponding to wavefunction Ψ'

$$E[\Psi'] \equiv \langle \Psi' | \hat{T} + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} | \Psi' \rangle \quad (3.5)$$

reaches its minimum value when Ψ' is the ground state wavefunction Ψ^0 . According to Hohenberg-Kohn theorem 1, the wavefunction Ψ' has a unique correspondence to the electron density $n'(\mathbf{r})$ and $E[\Psi']$ is also uniquely determined by $n'(\mathbf{r})$

$$\begin{aligned} E[\Psi'] &\equiv \langle \Psi' | \hat{T} + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} | \Psi' \rangle \\ &= E[n'(\mathbf{r})] \\ &= \int n'(\mathbf{r}) V'_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[n'(\mathbf{r})] \end{aligned} \quad (3.6)$$

According to the variational principle, if the wavefunction Ψ' is not the ground state wavefunction Ψ_0 then

$$\begin{aligned} E[\Psi'] &> E[\Psi_0] \\ &= \int n_0(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + F[n_0(\mathbf{r})] \\ &= E[n_0(\mathbf{r})] \end{aligned} \quad (3.7)$$

Therefore, by finding the lowest energy of system, we can determine the ground state wavefunction Ψ_0 and the ground state density $E[n_0(\mathbf{r})]$

3.1.2 Kohn-Sham equation

According to the Hohenberg-Kohn theorem, the total energy of a multi-electron system at an external potential $V(\mathbf{r})$ can be expressed as

$$E[n] = T[n] + U[n] + \int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r}) \quad (3.8)$$

where $T[n]$ is the electron kinetic energy term, $U[n]$ is the electron-electron interaction term and $\int d\mathbf{r} V(\mathbf{r}) n(\mathbf{r})$ is the energy contributed by the external potential. However, as aforementioned, it has not been possible to accurately describe the kinetic energy and the electron-electron interaction terms using the electron density so far. For this reason, Kohn and Sham propose an ingenious strategy: the kinetic energy term $T[n]$, which is initially determined by the electron density, is replaced by the kinetic energy of the non-interacting electrons; the electron-electron interaction $U[n]$ is approximated by a mean field Coulomb interaction potential (Hartree energy). The errors from the approximations are all subsumed in the exchange-correlation energy.

According to the strategy proposed by Kohn and Sham, the electron density at any point $\mathbf{r}$ for a multiparticle system consisting of N electrons is

$$n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2 \quad (3.9)$$

and the relationship between the electron density and the total number of electrons is

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad (3.10)$$

A single particle Hamiltonian is introduced with the form

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \quad (3.11)$$

The Kohn-Sham (K-S) equations can then be derived, giving

$$\left(-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad (3.12)$$

and

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \quad (3.13)$$

where V_H is the hartree potential

$$\begin{aligned} V_H(\mathbf{r}) &= \frac{\delta E_H[n(\mathbf{r})]}{\delta n(\mathbf{r})} \\ &= \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \end{aligned} \quad (3.14)$$

and V_{xc} is the exchange correlation potential

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (3.15)$$

The non-interacting kinetic energy is

$$T_{KS}[n(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^N \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} \quad (3.16)$$

Theoretically, the Kohn-Sham equation provides a strictly accurate description of the system, owing to the existence of the exchange-correlation energy term. This term includes the error between the genuine kinetic energy and the non-interacting kinetic energy, as well as the electron-electron interaction energy

and the Hartree energy E_H in the system.

$$E_{XC}[n(\mathbf{r})] = T[n(\mathbf{r})] - T_{KS}[n(\mathbf{r})] + E_{int}[n(\mathbf{r})] - E_H[n(\mathbf{r})] \quad (3.17)$$

Unfortunately, obtaining an exact universal exchange-correlation functional remains a significant challenge and can only be addressed through various approximations depending on the specific case. The popular approximations for the exchange-correlation functional are the local density approximation (LDA) and the generalized-gradient approximation (GGA).

To be noted, KS eigenvalues do not have a rigorous physical meaning.

The procedure to solve the KS equations is illustrated in Figure 3.1. First, a set of KS orbitals is selected, and the initial electron density is obtained. After computing the Hartree and exchange-correlation potentials, all the required quantities are substituted into the KS equation to obtain a new set of KS orbitals. If the new orbitals are the same as the previous ones within the expected tolerance, the calculation is considered converged, and the resulting electron density is accurate enough to calculate further physical quantities. Otherwise, the previous set of orbitals is replaced by the new one, and the KS equation is solved again until the target tolerance is reached.

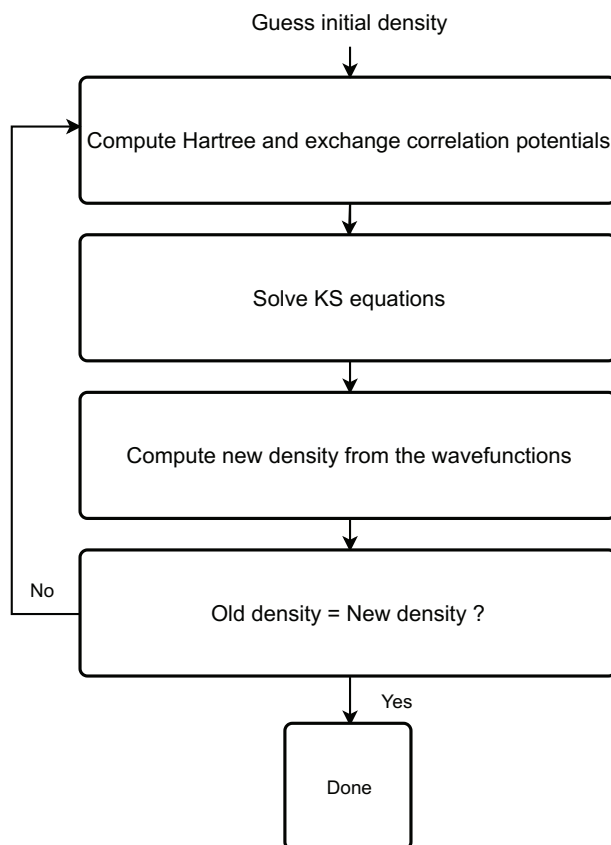


Figure 3.1: Procedure for KS calculations

3.2 Vibrational mode

3.2.1 Hamiltonian

The previous Hamiltonian describes the interaction between electrons under the assumption that the atomic nuclei stay static, which is quite reasonable as the movement of the atomic nuclei is quite slow compared with the movement of the electrons. To calculate the energy of the whole system which includes the vibration of the atoms, the Hamiltonian is expanded to

$$\hat{H} = \hat{H}_e^0 + \hat{H}_{ph}^0 + \hat{H}_{e,ph} \quad (3.18)$$

where $\hat{H}_e^0$ is the electronic Hamiltonian under the assumption that the positions of the atomic nuclei remain fixed. If we introduce the electron raising and lowering operators $\hat{c}_i^\dagger$ and $\hat{c}_j$ we can represent the Hamiltonian in second quantized notation in terms of the matrix elements H_{ij}^0 as

$$\hat{H}_e^0 = \sum_{i,j} H_{ij}^0 \hat{c}_i^\dagger \hat{c}_j \quad (3.19)$$

Similarly, for free phonons we have the Hamiltonian $\hat{H}_{ph}^0$

$$\hat{H}_{ph}^0 = \sum_{\lambda} \hbar \omega_{\lambda} \hat{b}_{\lambda}^\dagger \hat{b}_{\lambda} \quad (3.20)$$

where, for phonon mode λ , ω_{λ} is the vibrational angular frequency, and $\hat{b}_{\lambda}^\dagger$ and $\hat{b}_{\lambda}$, the phonon raising and lowering operators.

Finally, the Hamiltonian $\hat{H}_{eph}$ that describes the interaction between the electrons and phonons to first order in the phonon displacements is given by

$$\hat{H}_{eph} = \sum_{\lambda} \sum_{i,j} M_{ij}^{\lambda} \hat{c}_i^\dagger \hat{c}_j (\hat{b}_{\lambda}^\dagger + \hat{b}_{\lambda}), \quad (3.21)$$

where M_{ij}^{λ} is the matrix of electron-phonon interactions.

3.2.2 Dynamical Matrix

The dynamical matrix is used to compute the vibrational modes of a collection of interacting atoms. The starting point is Newton's second law of motion

$$M_I \frac{\partial^2 \mathbf{R}_I}{\partial t^2} = \mathbf{F}_I(\mathbf{R}) = - \frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} \quad (3.22)$$

where M_I is the mass of atom I , $\mathbf{F}_I$ is the force acting on atom I , and is the negative of the first derivative of the energy E with respect to the atomic displacements. We assume that displacements of atomic nuclei from the equilibrium positions $\mathbf{R}_0$ are small and we can take a Taylor expansion in powers of the displacements

for the energy around $\mathbf{R}_0$, giving

$$E(\mathbf{R}) = E(\mathbf{R}_0) + \sum_{I\alpha} \left. \frac{\partial E}{\partial R_{I\alpha}} \right|_{\mathbf{R}=\mathbf{R}_0} Q_{I\alpha} + \frac{1}{2} \sum_{I\alpha, J\beta} \left. \frac{\partial^2 E}{\partial R_{I\alpha} \partial R_{J\beta}} \right|_{\mathbf{R}=\mathbf{R}_0} Q_{I\alpha} Q_{J\beta} + O(Q^3) \quad (3.23)$$

where $Q_{I\alpha} = R_{I\alpha} - R_{0,I\alpha}$. The matrix of the second derivative of E is defined as $C_{I\nu, J\mu}$, which is usually called the Hessian matrix or dynamic matrix

$$C_{I\nu, J\mu} \equiv \left. \frac{\partial^2 E(\mathbf{R})}{\partial R_{I\nu} \partial R_{J\mu}} \right|_{\mathbf{R}=\mathbf{R}_0} \quad (3.24)$$

As we are looking for vibrational modes characterised by a frequency, we let the displacement of the atoms from their equilibrium positions have the following time dependence

$$\mathbf{Q}_I(t) = \mathbf{Q}_I e^{i\omega t} \quad (3.25)$$

If we insert the dynamical matrix and the displacements into Newton's second law we obtain

$$-\omega^2 M_I Q_{I\nu} = - \sum_{J\mu} C_{I\nu, J\mu} Q_{J\mu} \quad (3.26)$$

where we have used the fact that at equilibrium the atomic forces are zero, and hence that

$$\left. \frac{\partial E}{\partial R_{I\alpha}} \right|_{\mathbf{R}=\mathbf{R}_0} = 0$$

We can reorganise equation 3.26 into a matrix equation to give

$$(\omega^2 \mathbf{1} - \mathbf{W}) \mathbf{v} = 0 \quad (3.27)$$

where $\mathbf{W}$ is the mass-scaled dynamic matrix

$$W_{I\nu, J\mu} \equiv \frac{C_{I\nu, J\mu}}{\sqrt{M_I M_{J\mu}}} \quad (3.28)$$

and $\mathbf{v}_I = \sqrt{M_I} \mathbf{Q}_I$.

In most prevalent DFT software packages we can readily access the forces, which are the first derivative of the energy, through a basic self-consistent calculation. Thus, instead of directly calculating the second derivative of energy directly we calculate the first derivative of the forces to obtain the dynamic matrix.

$$W_{I\mu,J\nu} = -\frac{1}{\sqrt{M_I M_J}} \frac{\partial F_{I\mu}}{\partial R_{J\nu}} \quad (3.29)$$

The first derivative of the force can be approximated by a forward finite difference calculation

$$\frac{\partial F_{I\mu}}{\partial R_{J\nu}} \approx \frac{F_{I\mu}(Q_{J\nu}) - F_{I\mu}(0)}{Q_{J\nu}} \quad (3.30)$$

or more accurately by a centred finite difference calculation

$$\frac{\partial F_{I\mu}}{\partial R_{J\nu}} \approx \frac{F_{I\mu}(Q_{J\nu}) - F_{I\mu}(-Q_{J\nu})}{2Q_{J\nu}} \quad (3.31)$$

3.3 NEGF

The computational model of molecular device transport is an infinitely large non-periodic open system consisting of molecules or clusters of molecules embedded between semi-infinite length electrodes on the left and right sides. A particular bias is applied across both electrodes so that the whole system is a non-equilibrium and non-periodic open system. A suitable method for dealing with electron transport in this system is density functional theory combined with the non-equilibrium Green's function Method (NEGF-DFT)[119, 120, 121, 122, 123].

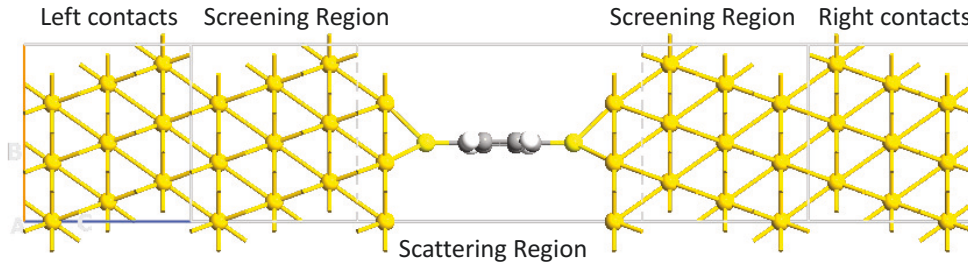


Figure 3.2: molecular device model for NEGF calculations

Figure 3.2 shows the molecular device model, where the molecules are coupled to two semi-infinite left and right electrodes, L and R. The molecules and some of the atoms in the electrode region form a scattering region so that the molecules have a negligible effect on the electronic structure inside the left and right electrodes. For the whole L S R system, the Hamiltonian matrix H and overlap matrix S can be written as

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}_L & \mathbf{H}_{LS} & 0 \\ \mathbf{H}_{SL} & \mathbf{H}_S & \mathbf{H}_{SR} \\ 0 & \mathbf{H}_{RS} & \mathbf{H}_R \end{pmatrix} \quad (3.32)$$

$$\mathbf{S} = \begin{pmatrix} \mathbf{S}_L & \mathbf{S}_{LS} & 0 \\ \mathbf{S}_{SL} & \mathbf{S}_S & \mathbf{S}_{SR} \\ 0 & \mathbf{S}_{RS} & \mathbf{S}_R \end{pmatrix} \quad (3.33)$$

Where subscript S means the scattering region, L means the left electrode and R means the right electrode. It should be noted that the size of a scattering region of should be selected so that the direct interactions between left and right electrodes can be ignored.

Considering the existence of the left and right contacts, the independent particle Schrödinger equation can be expanded from $\mathbf{E} \mathbf{S} \psi = \mathbf{H} \psi$ to include the inflow and outflow electrons

$$\mathbf{E} \mathbf{S} \psi = \mathbf{H} \psi + \Sigma \psi + s \quad (3.34)$$

where $\Sigma \psi$ is the outflow term and s is the source term. The wavefunction can be found from

$$\psi = [\mathbf{E} \mathbf{S} - \mathbf{H} - \Sigma]^{-1} s \quad (3.35)$$

The Green's function for the entire L S R system is defined as

$$[\mathbf{E} \mathbf{S} - \mathbf{H} - \Sigma] \mathbf{G}(\mathbf{E}) = \mathbf{I} \quad (3.36)$$

where $\mathbf{E}$ is the energy, $\mathbf{S}$ is the overlap matrix, $\mathbf{G}(\mathbf{E})$ is the Green's function matrix, $\mathbf{I}$ is the identity matrix, and Σ is the self-energy matrix which introduces the effect of the electrodes. The corresponding broadening matrix Γ is defined by

$$\Gamma = i(\Sigma - \Sigma^+) \quad (3.37)$$

Γ is a measure of how easily electrons can transfer between the electrodes and the device region.

As long as we know the self-energy terms for both electrodes, we can compute the retarded Green's function for the scattering region

$$G_s(E) = [(E + i\eta)S_s - H_s - \Sigma_L - \Sigma_R]^{-1} \quad (3.38)$$

where η is an infinitesimal real number which makes the matrix numerically stable for every energy. Knowing all the physical quantities, we can obtain different quantities related to the device region like the density of the state (DOS)

$$\text{DOS}(E) = -\frac{1}{\pi} \text{Tr}[G_s(E)S_s] \quad (3.39)$$

The other quantities we can compute are the transmission from the left electrode to the right electrode

$$T(E) = \text{Tr}[G_s(E)\Gamma_L G_s^+(E)\Gamma_R] \quad (3.40)$$

and the steady-state current

$$I = \frac{1}{2\pi} \int T(E)[f(E - \mu_L) - f(E - \mu_R)] dE. \quad (3.41)$$

Here μ_L is the chemical potential of the left electrode, μ_R is the chemical potential of the right electrode and f is the Fermi function

$$f(E - \mu) = \left[\exp\left(\frac{E - \mu}{k_b T}\right) + 1 \right]^{-1} \quad (3.42)$$

where k_b is the Boltzmann constant and T is the temperature

Figure 3.3 shows the block scheme of the (DFT-NEGF) approach used to calculate electron transport. The initial electron density P is first used to calculate the Hamiltonian H of the system, which then provides a new electron density P using the non-equilibrium Green's function (NEGF) method. The electron

density P is computed using the term of the lesser Green's function $G_S^<(E)$

$$P = \frac{1}{2\pi i} \int_{-\infty}^{\infty} G_S^<(E) dE \quad (3.43)$$

and then, a comparison is made to determine whether convergence has been achieved. If not, an updated electron density is calculated using the NEGF-DFT approach, and the iterations are repeated until the self-consistency requirement is met. Once self-consistency is achieved, the relevant physical properties of the system, such as the density of states (DOS), transmission, and current, can be calculated.

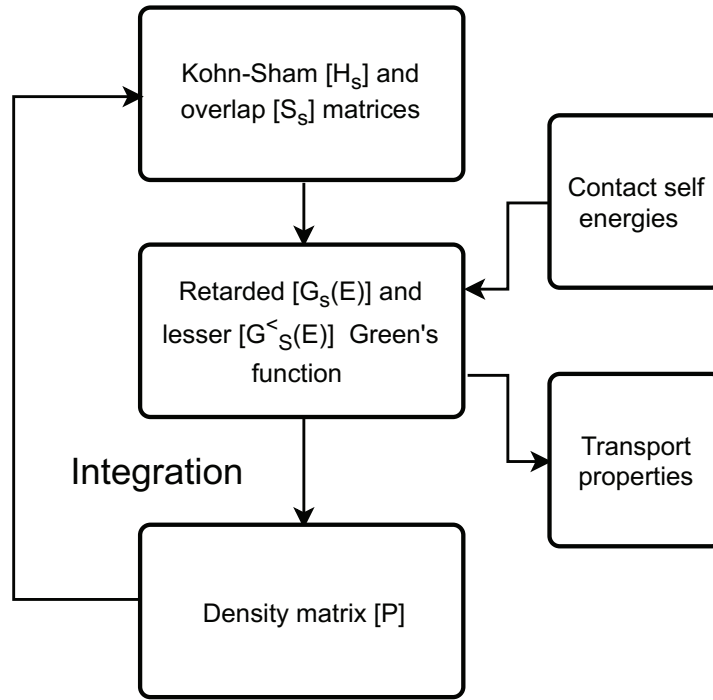


Figure 3.3: block-scheme of (DFT-NEGF).

When no bias is applied, the electron density P is consistent with the electron density obtained from ground state DFT. Conversely, when an external potential is applied to the electrodes it induces a current flow that alters the electron density within the scattering region. This means that the initial Hamiltonian

matrix becomes inconsistent with the actual density, which will go through a self-consistent procedure to iteratively refine the Hamiltonian matrix.

3.4 IETS

To calculate the inelastic electron tunneling spectrum, two essential quantities are needed: the dynamical matrix and the matrix of Hamiltonian derivatives. The phonon frequencies ω_λ and eigenvectors v_λ can be obtained from the dynamical matrix as discussed above. Once we have the phonon frequencies and eigenvectors we can sum up the displacement vectors and obtain $Q_{I\nu}$ in each direction for each atom using

$$Q_{I\nu}^\lambda = v_{I\nu}^\lambda \sqrt{\frac{\hbar}{2M_I\omega_\lambda}} \quad (3.44)$$

If we know the displacement vector $Q_{I\nu}^\lambda$, we can compute the electron-phonon coupling matrix using the matrix of Hamiltonian derivatives.

$$M_{ij}^\lambda = \sum_{I\nu} \left\langle i \left| \frac{\partial \hat{H}}{\partial R_{I\nu}} \right| j \right\rangle Q_{I\nu}^\lambda \quad (3.45)$$

3.4.1 Hamiltonian Derivatives

In DFT, the Hamiltonian derivatives are defined as the first derivative of the Hamiltonian with respect to the small displacements of the atoms, providing a correction to the adiabatic approximation of the Born-Oppenheimer approximation.

$$\hat{H} \approx \hat{H}^0 + \sum_{I\nu} \left. \frac{\partial \hat{H}}{\partial R_{I\nu}} \right|_{R=0} \hat{Q}_{I\nu} \quad (3.46)$$

Thus, the Hamiltonian $\hat{H}$ can be replaced by the derivatives of the effective potential V_{eff} , as the kinetic term of electrons is not affected.

$$\left\langle i \left| \frac{\partial \hat{H}}{\partial R_{I,\alpha}} \right| j \right\rangle = \left\langle i \left| \frac{\partial V_{\text{eff}}}{\partial R_{I,\alpha}} \right| j \right\rangle \quad (3.47)$$

Again, the Hamiltonian derivatives can be computed using the centred finite difference method:

$$\left\langle i \left| \frac{\partial V_{\text{eff}}}{\partial R_{I,\alpha}} \right| j \right\rangle \approx \frac{\langle i | V_{\text{eff}}(R_{I,\alpha} + \delta) - V_{\text{eff}}(R_{I,\alpha} - \delta) | j \rangle}{2\delta}. \quad (3.48)$$

3.4.2 Self-consistent Born approximation

To compute the inelastic current, we begin with the Meir-Wingreen current formula [124].

$$I = \frac{-2e}{\hbar} \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} t_{\alpha}(\varepsilon) \quad (3.49)$$

$$t_{\alpha}(\varepsilon) = \text{Tr}[\Sigma_{\alpha}^{<}(\varepsilon)G_D^{>}(\varepsilon) - \Sigma_{\alpha}^{>}(\varepsilon)G_D^{<}(\varepsilon)]$$

where $G^{<,>}$ is the lesser(greater) Green's functions for the device region and $\Sigma_{\alpha}^{<,>}$ is the lesser(greater) self energy of lead α . This current formula is different from the previous current formula above. However, if we ignore the electron-phonon self-energies, which is reasonable in all the elastic cases, the current formula will return to the Landauer formula, which is familiar.

To use the Meir-Wingreen current formula we need the self energy of the phonons

$$\Sigma_{ph,\lambda}^{<,>}(\epsilon) = i \int_{-\infty}^{\infty} \frac{d\epsilon'}{2\pi} M^{\lambda} D_0^{<,>}(\lambda, \epsilon - \epsilon') G^{<,>}(\epsilon') M^{\lambda} \quad (3.50)$$

In the self-consistent Born approximation (SCBA) [125, 126] the Green's functions are calculated using those electron-phonon coupling self-energies. Solving the SCBA equations becomes a challenging numerical endeavor when dealing with systems containing more than just a few atoms. To calculate the inelastic electron tunneling spectroscopy (IETS) efficiently, an approximation will be taken for systems with weak electron-phonon coupling and a density of states that changes gradually with energy.

3.4.3 Lowest order expansion

The primary computational challenge of the SCBA arises from the calculation of the current expression, which requires numerically integrating over energy, as shown in equation 3.49. In systems where the density of states changes slowly with energy, the Lowest Order Expansion (LOE) [127] approximation makes the reasonable assumption that the retarded and advanced single-particle Green's functions, as well as the lead self-energies, are energy-independent. In this case, by expanding the current to the second order in electron-phonon couplings, the energy integrations can be performed analytically.

$$\begin{aligned}
 I^{\text{LOE}}(V, T) = I^{\text{elastic}} \\
 + \sum_{\lambda} I_{\lambda}^{\text{sym}}(V, T, \langle n_{\lambda} \rangle) T_{\lambda}^{\text{sym}} \\
 + \sum_{\lambda} I_{\lambda}^{\text{asym}}(V, T) T_{\lambda}^{\text{asym}}
 \end{aligned} \tag{3.51}$$

There are three items in the current expression of the LOE approximation:

1. The current of the elastic electron transport as mentioned before.
2. A term for which the conductance step is symmetric at the vibration energy, where I_{λ}^{sym} is

$$I_{\lambda}^{\text{sym}}(V, T, \langle n_{\lambda} \rangle) = \frac{e}{\pi \hbar} \left(2eV \langle n_{\lambda} \rangle + \frac{\hbar \omega_{\lambda} - eV}{e^{(\hbar \omega_{\lambda} - eV)/k_B T} - 1} - \frac{\hbar \omega_{\lambda} + eV}{e^{(\hbar \omega_{\lambda} + eV)/k_B T} - 1} \right) \tag{3.52}$$

$$T_{\lambda}^{\text{sym}} = \text{Tr} \left[G^r \Gamma_L G^a \{ M^{\lambda} A_R M^{\lambda} + \frac{i}{2} (\Gamma_R G^a M^{\lambda} A M^{\lambda} - \text{H.C.}) \} \right] \tag{3.53}$$

3. A term for which the conductance step is not symmetric corresponding to the dips and peaks in the conductance, where $I_{\lambda}^{\text{asym}}$ is

$$I_{\lambda}^{\text{asym}} = \frac{e}{\hbar} \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} [f(\epsilon) - f(\epsilon - eV)] \times \mathcal{H}_{e'} \{f(\epsilon' + \hbar\omega_{\lambda}) - f(\epsilon' - \hbar\omega_{\lambda})\}(\epsilon) \quad (3.54)$$

$$T_{\lambda}^{\text{asym}} = \text{Tr} [G^a \Gamma_L G^r \{\Gamma_R G^a M^{\lambda} (A_R - A_L) M^{\lambda} + \text{H.C.}\}] \quad (3.55)$$

where $\mathcal{H}_{e'}$ is the Hilbert transform, f is the fermi function and the inelastic transmission functions are T_{λ}^{sym} and $T_{\lambda}^{\text{asym}}$. The notation H.C. signifies the hermitian conjugate and the spectral function is given by

$$A_{L,R} = G^r \Gamma_{L,R} G^a \quad (3.56)$$

$$A = i(G^r - G^a) = A_L + A_R \quad (3.57)$$

3.4.4 XLOE

In systems where the electron-vibration (e-vib) coupling is relatively weak and the density of states (DOS) changes gradually with energy (compared with typical vibration energies), employing the Lowest Order Expansion (LOE) alongside the wide-band approximation (LOE-WBA) enables significantly simplified calculations. However, the use of the wide-band approximation (WBA) fails to capture IETS signals near electronic resonances or band edges, which often contain essential information.

The LOE was initially designed for examining molecular junctions featuring a molecule positioned between metallic electrodes. In cases where there are no molecular states in close proximity to the Fermi energy, employing the LOE alone will suffice. When there are states situated near the Fermi energy, the extended lowest order expansion (XLOE) provides a more accurate depiction[128], as it permits some variation in the density of states, capturing the information

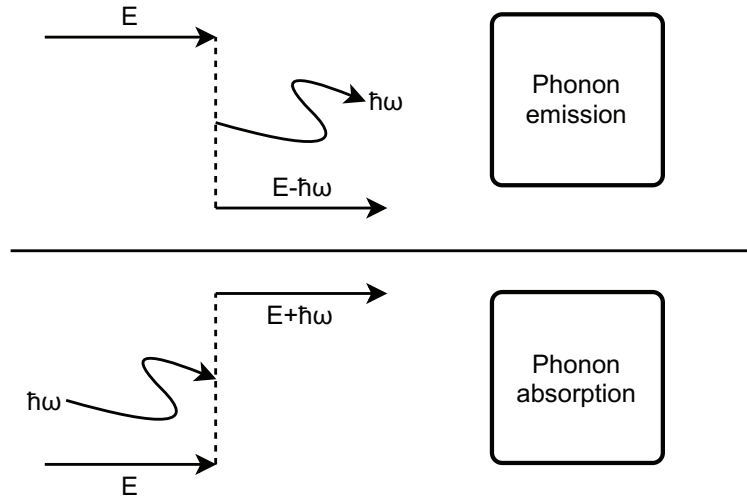


Figure 3.4: Difference between loe and xloe

contained in the tips of DOS. Additionally, XLOE is also available for situations where transport takes place in proximity to semiconductor band edges.

In XLOE, the phonon emission and phonon absorption processes are distinguished, as illustrated in Figure 3.4. In the upper panel, we observe a phonon emission process where an electron entering from the left electrode emits a phonon and exits the right electrode with reduced energy. At low temperatures, such an occurrence is restricted to positive bias voltages. In the lower panel, a phonon absorption process is depicted where the electron exits with greater energy in the right electrode compared to the left.

3.5 Software packages

3.5.1 CP2K

CP2K[129] is a famous quantum chemistry software package able to conduct density functional theory simulations. Unlike other quantum codes, CP2K employs a combination of Gaussian and plane waves methodology. Gaussian functions handle the wavefunction representation and the Kohn-Sham matrix, while plane waves are utilized for density calculations. Moreover, CP2K incorporates various algorithms tailored for tackling large systems or large basis sets, such as the orbital transformation method. It also pioneers the integration of cutting-edge techniques like CP-like and Metadynamics methods, making it one of the select few codes to do so. Notably, the NEGF sections of CP2K have been validated for accuracy and demonstrate good efficiency.

3.5.2 QuantumATK

QuantumATK[130], developed since 2003 by a team of professional software engineers and academic researchers, constitutes an integrated suite of atomic-scale modeling tools. It incorporates a variety of simulation techniques, from ab initio Density Functional Theory (DFT) to semi-empirical and classical force field analyses.

3.5.3 Gaussian

Gaussian[131] uses DFT with a gaussian basis set, as well as wavefunction based methods, to provide predictions for energies, molecular structures, vibrational frequencies, and a range of molecular properties.

CHAPTER 4

4TPA-C60

4.1 Introduction

There is a controversial theory of how we smell molecules, based on the idea that we identify them by their vibrational frequencies. Luca Turin in 1996 first proposed a mechanism by which we could do this, which was refined in 2007 by Brookes et al[18]. The core idea is that an electron can only jump between two energy levels that differ in energy by an amount equal to $\hbar\omega$ if there is a molecule vibrating in the neighbourhood with angular frequency ω . As Figure 1.4 shows, this process of electron transfer is called inelastic tunnelling, which introduces a peak corresponding to $V_0 + \hbar\omega$. Regardless of the controversy, it is a plausible theory that we can refer to in designing sensors that behave like animal noses.

This chapter builds on previous work carried out by Dr. Aaron Thong in Prof. Andrew Horsfield's group, who explored one molecule, 4TPA-C60, as an alternative material for the electronic device[132]. This molecule consists of a benzene ring acting as an electron donor, a fullerene acting as an electron acceptor and a bridging nitrogen atom connecting them. When the frontier orbitals of the two fragments are in resonance, a path for electron transport is

generated and the current flowing through the path reaches the maximal value. If the orbitals jump out of the resonance, the path disappears and the current drops. This process is called Negative Differential Resistance (NDR), and is signalled by a peak in the bias vs current figure. However, it was found that the NDR peak is too broad for high resolution and that the additional peak introduced by odours will be hidden by this broad peak. Thus, it is impossible to recognize the odours, which is the fundamental function of an electronic nose. More computational work needs to be done such as modifying the original molecule to sharpen its NDR peak and identifying other molecules with a sharp NDR peak

4.2 Results

4.2.1 Di-thiol-benzene

With the sample input provided by CP2K, we successfully reproduced the I(V) curve and transmission figure of di-thiol-benzene using Pade approximation for the LDA exchange functional [133] and 500 Ry plane wave cutoff, as Figure 4.1 shows. We used SZV-MOLOPT-SR-GTH basis set for gold atoms and TZVP-MOLOPT-GTH basis set for all the other atoms. It is noteworthy that NEGF in CP2K does not support k-points calculations for the device region because gamma point calculation is generally enough for the transport calculation. Also, we would like to study the transport property of a single molecule rather than a group of molecules interacting with each other. The results are in good agreement with previous calculations [134, 135], except for the transmission curve around -2 eV, which may be a result of the finer energy interval we sampled during the calculations for the transmission plot.

To further test the reliability of our approach we decided to use CP2K to reproduce previous work carried out by Dr. Aaron Thong who explored one

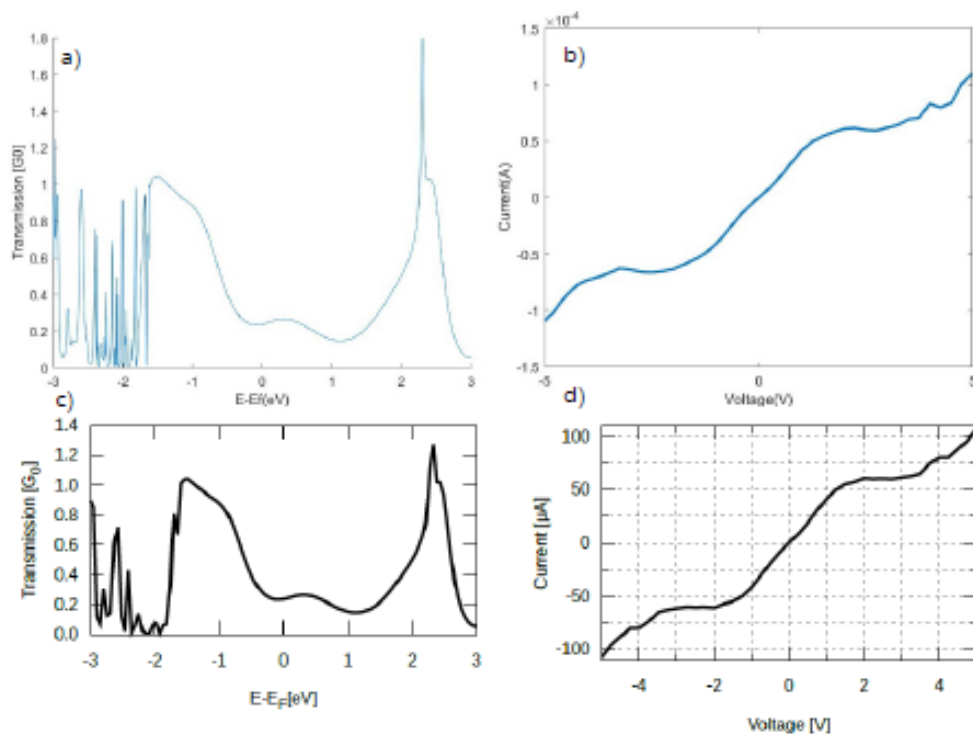


Figure 4.1: a) The calculated transmission plot of di-thiol-benzene b) the corresponding I(V) figure of di-thiol-benzene c) the reference transmission plot d) the reference I(V) figure in paper

molecule 4TPA-C60, using the Atomistix ToolKit[130], as an alternative material for the electronic device.

The structure, I(V) and transmission curve are shown in Figure 4.2. Unlike the calculations for di-thiol-benzene where we get good agreement with previous calculations, the obtained current of 4TPA-C60 values differ from those calculated by Thong [132]. However, the shapes of the current curve and transmission curve are similar. Most importantly, we can see a clear NDR peak. Considering that we used a finer bias interval which made the curve smoother, our results should also be reliable.

4.2.2 4TPA-C60

Thong calculated the properties of 4TPA using 700 Ry cutoff energy, single- ζ polarised basis sets for gold atoms and double- ζ polarised basis sets for the others. To make sure the difference between the results does not originate from

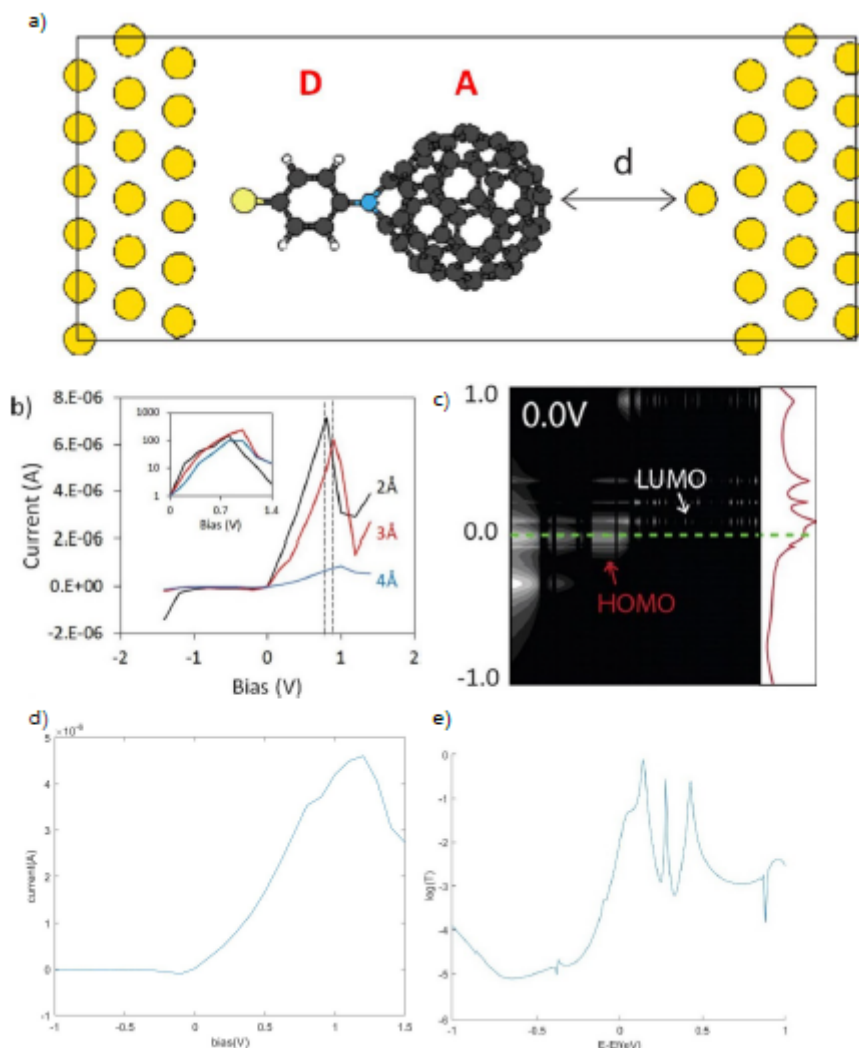


Figure 4.2: a) the structure of 4TPA-C60 b) the I(V) figure in paper(18) c) the transmission in paper(18) d) calculated I(V) figure e) calculated transmission figure

the different choices of calculation parameters, we did a series of calculations with similar parameters to Thong's calculation, such as DZVP basis sets for all atoms except gold, and 700 Ry cutoff. The results shown in Figure 4.3 suggests that a different choice of calculation parameters does not make the results more similar and we have thus retained our original calculation parameters.

Our calculations on di-thiol-benzene and 4TPA-C60 show that the implementation of NEGF in CP2K can generate reliable results. The next step is to modify 4TPA-C60 to sharpen its NDR peak.

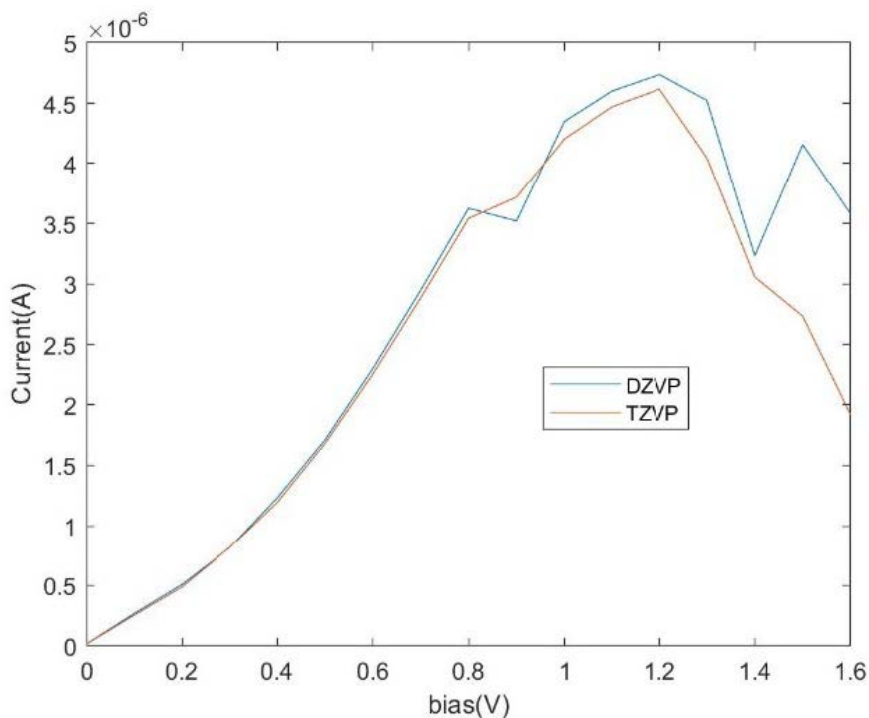


Figure 4.3: the I(V) figure calculated using DZVP and TZVP basis set

4.2.3 Anchoring group modification

A broad NDR peak results from level pinning in a big bias range. In contrast to the frontier orbitals in Figure 1.4, the HOMO and LUMO in the real system are much broader. Once the HOMO and LUMO reach resonance, it is harder for broader levels to jump out of the resonance, called level crossing, than thinner levels because the tails of broad levels still enable resonant tunnelling. The current increase due to an increased bias offsets the current decrease due to the main parts of frontier orbitals slowly moving out of the resonance.

Level broadening results from strong coupling between the anchoring groups and the gold electrodes. To reduce the strong coupling interaction of the sulfur atom, two methods to modify the anchoring group are investigated here: replacing the thiol with a weak linker, and inserting CH₂ groups after the thiol.

Replacing anchoring group

The thiol anchoring was replaced with an NH_2 anchoring group as the coupling between the gold and NH_2 is weaker. In contrast to a study which showed that an N atom tended to form bonds with electrodes[136], the N atom tends to escape from the electrode after geometry optimisation. Meanwhile, the $I(V)$ curve is too noisy compared with that with a thiol anchoring group and we could not see a clear trend, as shown in Figure 4.4 d). We decided to abandon this method and stick to the thiol anchoring group.

inserting CH_2 groups after the thiol

As the coupling between the molecule and the electrode is too strong, we can insert a CH_2 group into the anchoring group. The presence of methylene groups can significantly diminish the electronic coupling between the orbitals of the functional molecule and the electrodes by disrupting the delocalization of π -electrons, while still maintaining a strong enough mechanical connection. Thus, CH_2 groups, functioning as a spacer, increase the distance between the benzene and the electrode, weakening the coupling and sharpening the frontier orbitals. As expected, a sharper NDR peak appeared in the $I(V)$ figure, as shown in Figure 4.4 a).

However, if we split the NDR peak into two parts, the right part (higher voltage) is sharp while the left (lower voltage) is still broad. We suspect this broad left part is a result of the strong coupling to the bridging area. Although, the twisted π structure is also a decoupling moiety that prevents the overlap of frontier orbitals with the twisted structure, we suspect that the lone electron pair of the N atom might still be a path connecting the donor and acceptor fragment to some extent. This electron pair might make it easier for the electron to be transported than a conventional σ bridge used in most rectifiers. To test this hypothesis we added a CH_2 group into the bridging group.

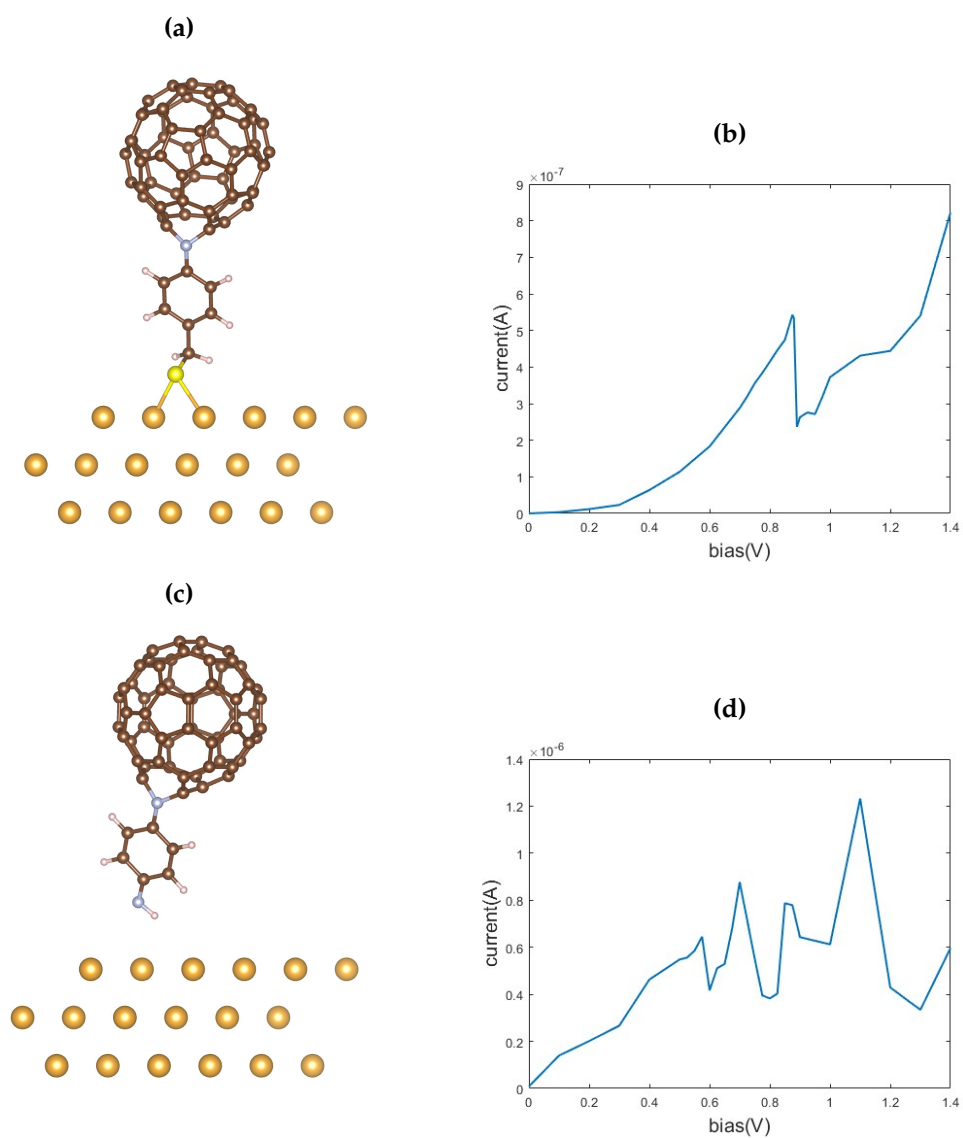


Figure 4.4: a) the structure of the molecule with Au-S-CH₂ contact and b) its corresponding I(V) figure c) the structure of the molecule with Au-N contact and d) its corresponding I(V) figure

Bridging group modification

The geometry after geometry optimisation is shown in Figure 4.5. We inserted CH₂ groups on the both sides of the N atom to fully decouple the benzene and the C60. In this case, it is the conventional σ bridge rather than the twisted π that functions as the decoupling unit. Moreover, the inserted CH₂ groups further separates the two fragments, which makes the decoupling unit more effective.

Several unprecedented and extremely sharp NDR peaks appeared in the I(V) figure as shown in Figure 4.5 b), and which might make it possible to meet our demands for an ideal sensor. However, upon constructing a supercell which repeats the molecular junction periodically over space, we discovered that our simulation was effectively representing a network of strongly interacting molecules adsorbed onto the gold surface, as shown in Figure 4.5 c). It seems the size of the electrode is not enough that the existence of the lateral interaction between molecules cannot be ignored. This network geometry contradicts our initial intention of simulating an isolated molecule absorbed on the electrode. Therefore, it is necessary to investigate the impact of the electrode size.

4.2.4 The effect of Au electrode size

To determine the appropriate size of the electrode, we ran a k-points convergence test on the 3×3 Au 111 electrode. The calculations converged after k-point mesh was larger than 13×13×1, as Figure 4.6 a) shows. If the cell size becomes larger, the k-points needed to get the converged results are smaller. For example, 13 × 13 × 1 k-point scheme was used for the electrode with 9 atoms per layer while for the one with 16 atoms, the k-points scheme was 11 × 11 × 1. With the converged k points parameter for the 3×3, we could easily transform the choice of k points scheme with different sizes of the electrodes.

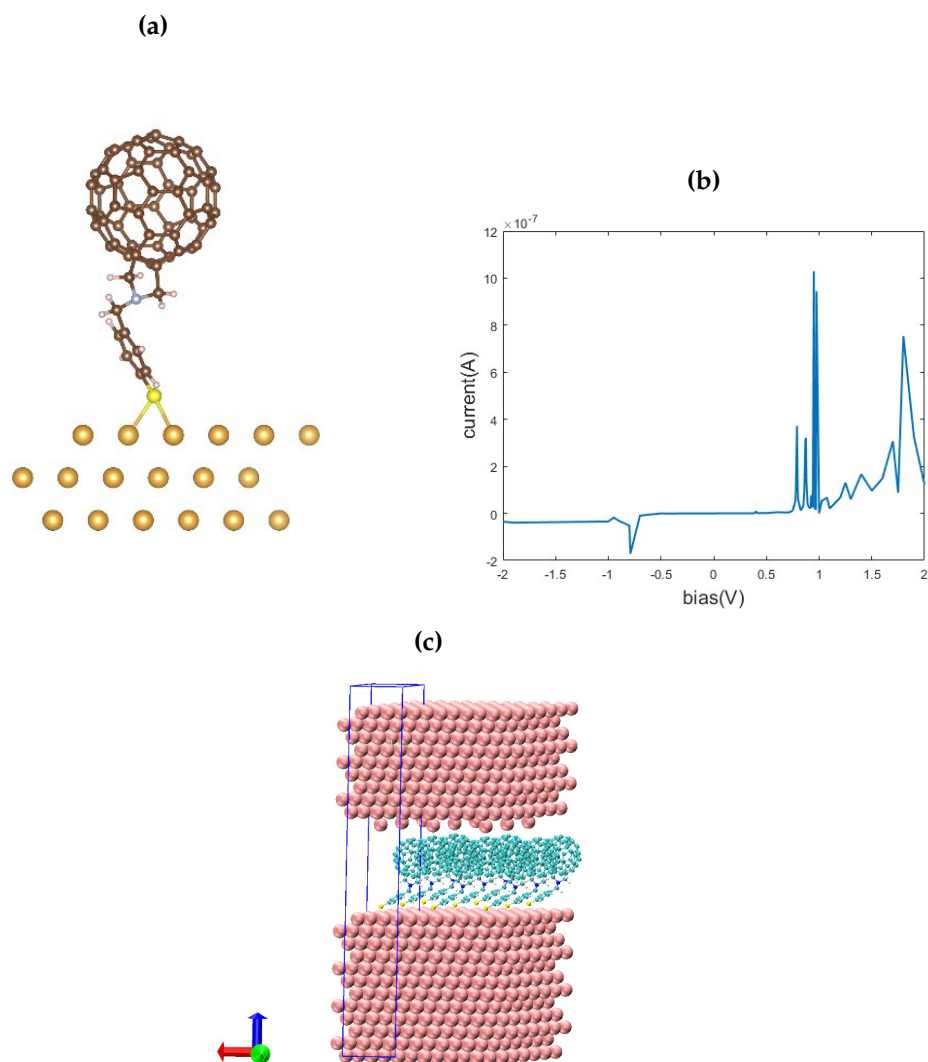


Figure 4.5: a) bridging area modified 4TPA-C60 and b) its $I(V)$ figure c) the network of this molecule

Then, we calculated the total energy of different sizes of electrodes with and without a molecule and computed the absorption energy using equation 4-1:

$$E_{\text{absorption}} = E_{\text{withmolecule}} - E_{\text{withoutmolecule}} - E_{\text{molecule}} \quad (4.1)$$

The absorption energy with different sizes of electrodes using converged k-points is shown in Figure 4.6. It turns out that the electrode has a negligible effect on the absorption energy if the atoms per layer in the electrode are more than 16. However, as CP2K only supports gamma point calculations for NEGF, we cannot ignore the error between k-point converged and gamma point calculations. The differences of red and blue bars in Figure 4.6 show that the error between k-point converged calculations and gamma point calculations is acceptable once the size of electrode reaches 30 atoms per layer or larger.

We also calculated the work function of different sizes of electrodes and the results are shown in Figure 4.6 c). The work function calculated with just the gamma point is similar to that obtained with multiple k-points and we can draw the same conclusion that the electrode with 30 atoms per layer is a reasonable choice. Therefore, the electrode with 30 gold atoms will be utilized in the subsequent calculations.

It is noted that the NEGF calculation using a larger electrode consumes more memory. NEGF calculations in CP2K use adaptive integration algorithms, which leads to high memory consumption as lesser Green function matrices are kept in memory to increase the number of integration points and to refine the final density matrix later. Thus, in the case of a scattering region with 10240 basis functions and 128 integration points, CP2K needs 16 bytes/matrix-element $\times 10240^2$ matrix-elements $\times 128$ points = 200 GiB of memory to cache matrices. These cached matrices are distributed among all compute nodes. Typically, an NEGF calculation using electrodes with 30 atoms per layer consumes 500 to 600 Gib of memory.

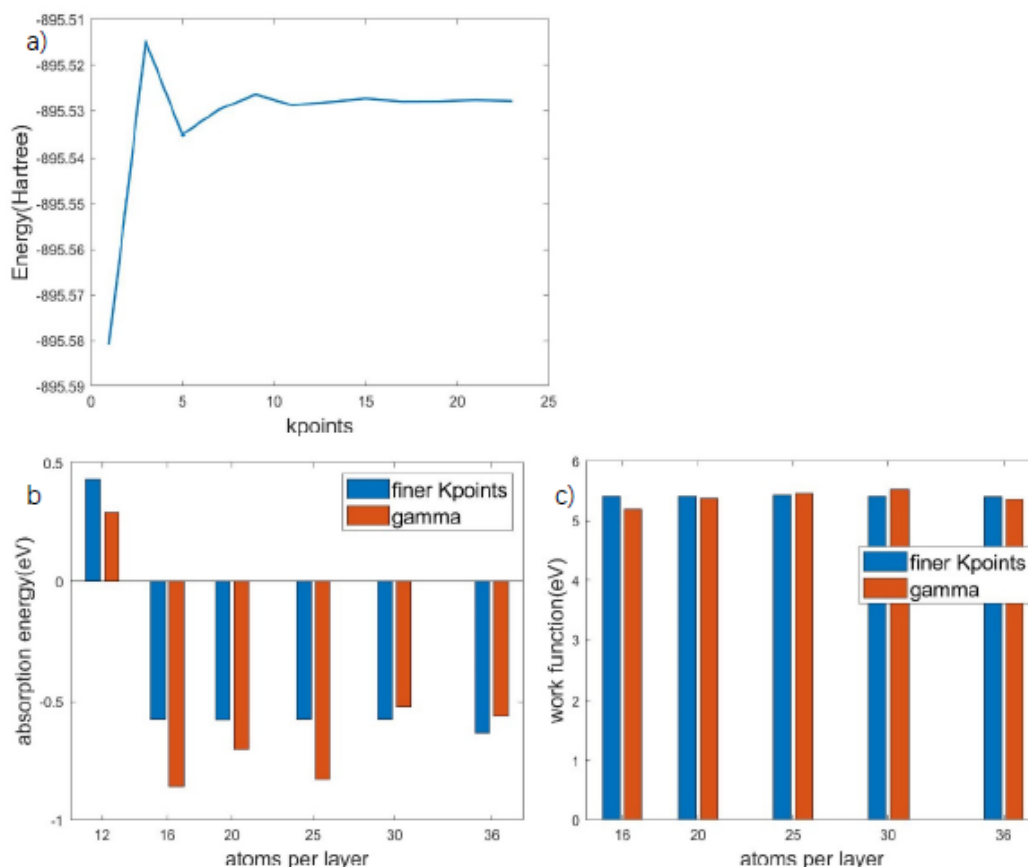


Figure 4.6: a) k-points convergence tests on Au 111 3x3 electrodes b) absorption energy with different sizes of electrodes c) work function with different sizes of electrodes

4.3 Strengths, Weaknesses, and Experimental Relevance

This chapter explores the electronic properties of molecular junctions of the 4TPA-C60 system. The strengths of this work lie in the comprehensive computational examination of critical design compositions of a molecular junction, including molecular structure, electrode dimensions, and coupling interactions. By extending the original 4TPA-C60 frameworks, the study establishes a solid foundation for understanding how molecular systems can be optimized for sensing technologies. The findings offer broad implications, generating insights that can guide the development of molecular sensors across various configurations.

However, the scope of this chapter is inherently foundational. While the research optimizes existing configurations, it focuses primarily on validating and refining established principles rather than discovering novel mechanisms. Consequently, the contribution is incremental, serving as a crucial stepping stone for the following chapters' research rather than presenting an innovative solution to current challenges.

The work's relevance to experimental research is particularly straightforward. The findings provide clear guidance for optimizing the 4TPA-C60 molecular design, a molecule comprising a benzene ring donor, a fullerene acceptor, and a nitrogen bridging atom. The study demonstrates that the modifications to anchoring groups and electrode configurations can significantly enhance the molecule's electronic properties. For example, introducing a CH₂-mediated S anchoring group effectively moderates molecule-electrode coupling, resulting in more pronounced Negative Differential Resistance (NDR) peaks. Such modifications offer direct insights for experimental approaches aimed at achieving specific NDR characteristics for systems based on 4TPA-C60.

Furthermore, the research provides insights into electrode size and its critical impact on molecular performance, offering practical guidelines for experimental setups. The computational analysis reveals how electrode dimensions influence coupling strength and molecular adsorption, underscoring the importance of electrode optimization to achieve consistent and targeted current-voltage (I-V) characteristics. These computational predictions are directly applicable to experimental techniques like scanning tunneling microscopy (STM) break-junction experiments, where precise control and evaluation of electrode-molecule interactions are essential.

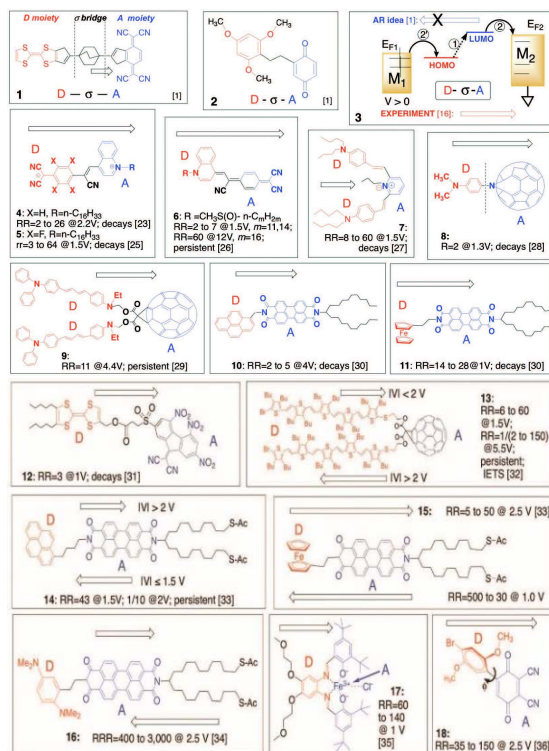


Figure 4.7: Molecule diodes studied in the last few decades[29]

4.4 Summary

An ideal electronic nose should be small, fast and inexpensive. To find the alternative materials that meet these demands, this project is split into two parts: modifying 4TPA-C60 and identifying other donor-acceptor pairs. Most of the work done in this chapter has been focused on the first part:

1. Inserting a CH_2 group after the thiol significantly weakens the coupling between the electrodes and the molecule, generating a sharper NDR peak. In contrast, replacing the thiol with a weak anchoring group, $-\text{NH}_2$, is not effective and the $I(V)$ curve is noisy after substitution.
2. Inserting CH_2 groups in the bridge to prevent the donor and acceptor fragments from coupling is a good way to sharpen the NDR peak, reaching a resolution of 0.1 V.

Despite the promising progress on sharpening the NDR peak, we have not developed a design rule that guarantees a molecule junction with a sharp NDR peak. Also, the computational cost to determine whether or not a specific molecule has a sharp NDR peak is very high. Thus, as we have thousands of donor-acceptor pairs to consider, as shown in Figure 4.7, instead of using trial and error we need to have a clearer design strategy and investigate simpler and faster calculations to screen materials initially before performing full NEGF calculations. For example, we could use simpler models such as a Tight-Binding model or continue to use DFT calculations but on less complicated systems.

An abstract but instructive model is a wire with scatterers based on tight binding calculations. The position, width and number of scatterers have a huge effect on the transmission curve of this model. The best combination of these three factors generates sharp transmission peaks. Then, we can replace the wire and the scatterers with real acceptor units, donor units and decoupling groups and do full NEGF calculations on the real molecules.

4.5 Methodology

The calculations was implemented using the CP2K DFT code [137], version 7.1. The combination of Goedecker, Teter, and Hutter (GTH) norm-conserving pseudopotentials[138] and triple zeta valence polarized basis sets was used, except for the gold atoms, for which a single zeta polarized basis set was used. As the electrodes consist of hundreds of atoms and the calculations are quite time-consuming, the use of a single zeta basis was necessary to reduce the computational resources required while still maintaining sufficient accuracy.

The cutoff energy for the density mesh was set to 500 Ry. We didn't implement a k points calculations for the device because we are more interested in the transport behaviors of an isolated device system rather than a group of identical devices close to each other. Also, the size of device is usually large enough to eliminate the effect of K points. We have compared the effect of the electrode size on the molecule absorption energy and $5 \times 5 \times 1$ is determined to be the appropriate electrode size to be used in the subsequent calculations.

NEGF calculations for transport properties, including current and transmission spectrum, were conducted using the implementation in CP2K version 7.1 [139]. Dr. Chulkov has previously demonstrated the reliability of the NEGF formalism in CP2K by computing the I(V) curve of dithiol benzene with gold electrodes [139] and comparing the results with those reported in earlier studies [135], conforming consistency between the results.

CHAPTER 5



TIGHT-BINDING MODEL FOR ELASTIC TRANSPORT CALCULATION

5.1 Introduction

The tight-binding (TB) model is a popular approach for studying the behaviour of electrons in computational materials science and condensed matter physics [140]. It offers a less computationally demanding alternative to more rigorous electronic structure methods like Density Functional Theory (DFT). By focusing on the most significant electronic interactions, the tight-binding model simplifies calculations, making it especially valuable for studying large systems and complex materials.

In this chapter, we employ a simple 1D tight-binding model to simulate molecular junctions. By tweaking the energy parameters and hopping integrals we are able to investigate the correlation between the inter-molecular or metal-molecular coupling strength and the current curves without heavy computational costs. Our findings built a concrete foundation and provide instructive guidance for when we employ Density Functional Theory calculations to study the behavior of actual molecules in the junction.

5.2 Theory

Here, we introduce a straightforward transport model to support our exploration of Inelastic Electron Tunneling Spectroscopy (IETS) as a potential mechanism for chemical sensing[141].

5.2.1 System

Let's consider a one-dimensional chain of atoms, where each atom is described by a single s orbital. The Hamiltonian describing the electrons in this system has the following form:

$$H_{ij} = \begin{cases} a_i & j = i \\ b_i & j = i - 1 \\ b_{i+1} & j = i + 1 \\ 0 & \text{otherwise} \end{cases} \quad (5.1)$$

Suppose the atoms with $i < 1$ and $i > 2$ function as the left and right electrodes, respectively. Correspondingly, the onsite energies and hopping integrals of the atoms in the left (right) electrodes are $a_L(a_R)$ and $b_L(b_R)$. The system is illustrated in Figure 5.1

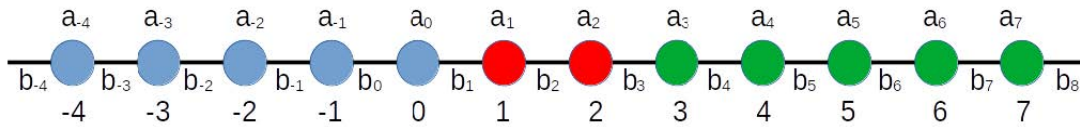


Figure 5.1: the 1D chain showing the system with the onsite energies (a_i) and hopping integrals (b_i). The blue atoms form the left lead, the green atoms for the right lead, and the red atoms form the device

5.2.2 Wavefunction

Schrödinger's equation for this system can be written as a matrix equation as follows:

$$\sum_j H_{ij} c_j = E c_i \quad (5.2)$$

where the coefficients c_i are the expansion coefficients for the wave functions and appear as the elements of an eigenvector in Eq. 5.2. The electron energy E appears as an eigenvalue in Eq. 5.2. If we substitute the terms for H_{ij} from equation 5.1 into Eq. 5.2 we get the following recurrence relation for the wavefunction coefficients:

$$c_{i+1} = \frac{1}{b_{i+1}} ((E - a_i) c_i - b_i c_{i-1}) \quad (5.3)$$

The wavefunction in the left electrode corresponds to an incoming traveling wave and a reflected wave. This can be described by the following equation with the reflection coefficient R and the wave vector k :

$$c_p^{(L)} = e^{ikp} + R e^{-ikp} \quad (5.4)$$

On the other hand, the wavefunction in the right electrodes corresponds to a transmitted traveling wave, with the transmission coefficient T , and can be described by the following equation:

$$c_p^{(R)} = T e^{iq(p-3)} \quad (5.5)$$

We now need to find the values of T and R . The eigenvectors C depend on the reflection coefficient R . Assuming the dependency is linear in R , we can express the eigenvectors as $A + BR$ where A and B are the expansion coefficients. Thus, the eigenvector can be written as a combination of A and B coefficients

$$c_i = A_i + B_i R \quad (5.6)$$

If we introduce the results from Eq. 5.5 we then get

$$c_3 = A_3 + B_3 R = T \quad (5.7)$$

$$c_4 = A_4 + B_4 R = T e^{iq} \quad (5.8)$$

We can now solve these equations to find a solution for T , which can then be used to calculate the current:

$$T = \frac{B_4 A_3 - B_3 A_4}{B_4 - B_3 e^{iq}} \quad (5.9)$$

If we substitute for c_i in Eq. 5.3 with Eq. 5.6 we obtain the following equations that allows us to find A and B :

$$A_{i+1} + B_{i+1} R = \frac{1}{b_{i+1}} ((E - \alpha_i) (A_i + B_i R) - b_i (A_{i-1} + B_{i-1} R)) \quad (5.10)$$

The equation stands true whatever the value of R is, which means the coefficients before each power of R must be the same on the left and right sides of Eq. 5.10:

$$A_{i+1} = \frac{1}{b_{i+1}} (E - \alpha_i) A_i - b_i A_{i-1} \quad (5.11)$$

$$B_{i+1} = \frac{1}{b_{i+1}} ((E - \alpha_i) B_i - b_i B_{i-1}) \quad (5.12)$$

The elastic current through the system is found from the following integral[141]:

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} [f(E - \mu_L) - f(E - \mu_R)] |T(E)|^2 \frac{b_R \sin q}{b_L \sin k} dE \quad (5.13)$$

where the Fermi function, f , is given by

$$f(E - \mu) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)} \quad (5.14)$$

5.3 Results

According to the theory, we have coded a simplified tight-binding model to simulate a 1D metal chain, where two sites, atom 1 and atom 2, are in the device region, and the remaining sites function as the electrodes. The code is shown in Appendix A.

5.3.1 A 1D metal chain

A uniform metal chain without internal resistance, subjected to a consistent external voltage, serves as an ideal test case for evaluating the accuracy of our basic computational model.

A perfect metal chain

To simulate a metal chain, we assign parameters as follows. The hopping integral b_i , representing the coupling strength between adjacent atoms, is uniform throughout the chain and has a value of [GIVE VALUE]. For the electrodes, we assign onsite energies of $-\frac{1}{2}V$ and $\frac{1}{2}V$ to the left (a_L) and right (a_R) electrodes, respectively. In the device region, we assume a linear voltage drop due to the chain's perfect metallic nature. Consequently, we assign $-\frac{1}{6}V$ and $\frac{1}{6}V$ to a_1 and a_2 , respectively.

The resulting current-voltage (I-V) relationship, depicted in Figure 5.2 a), exhibits a linear variation of current with applied bias, which aligns with Ohm's law, validating the model's representation of a perfect metal chain.

A broken metal chain

If we adjust the hopping integral between the two central atoms, the behavior of the metal chain will resemble adding an adjustable resistance between them. For instance, setting $b_1 = -0.1$ eV introduces a high resistance to current flow as -0.1 eV is significantly smaller than the hopping integrals in the electrodes,

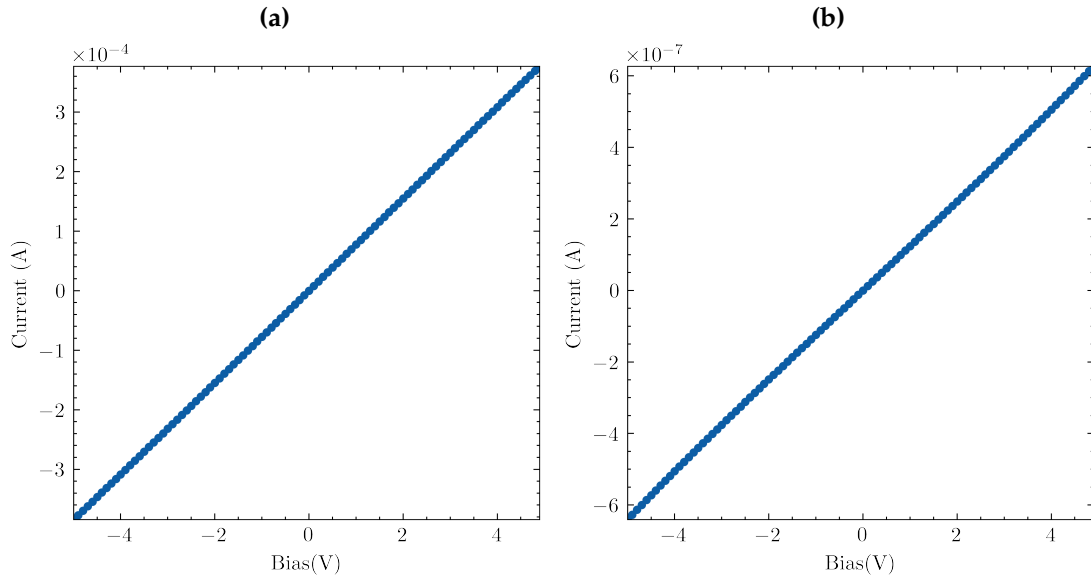


Figure 5.2: The I(V) curves for the tight binding models used to simulate a) a metal chain b) a broken metal chain. The current of a broken metal chain is notably lower compared to that of the perfect metal chain

thereby blocking electron transport between them. The corresponding I(V) figure is shown in Figure 5.2b). As anticipated, while the relationship between current and voltage remains consistent with Ohm's law, the current is notably lower compared to that of the perfect metal chain.

These examples illustrate the credibility and practicality of our simple model. We can now expand the model to simulate Metal-Molecule-Metal junctions by varying combinations of a_1 , a_2 and b_0 , b_1 , b_2 .

5.3.2 Metal-Molecule-Metal junction

To simulate a molecule inserted between electrodes, what we can do is to tweak the hopping integral b_0 , b_1 , b_2 . Specifically, b_0 represents the coupling between the site 1 (the left molecule fragment) and the left electrode. b_1 represents the coupling between the site 1 (the left molecule fragment) and the site 2 (the right molecule fragment). b_2 represents the coupling between the site 2 (the right molecule fragment) and the right electrode. All of these 3 parameters have important but different roles in the electron transport. They can be categorised to

inter-molecular coupling and molecule electrode coupling. By modifying these values, we can simulate various molecular configurations and their interactions with the electrodes, allowing us to explore different aspects of electron transport in molecular junctions.

Inter-molecular coupling

To eliminate the effect of molecule-electrode coupling and focus on the inter-molecular coupling, we kept b_0 and b_2 fixed to -0.1 eV while adjusting b_1 with two values, -0.1 eV and -1 eV, representing weak and strong inter-molecular coupling. We set the value of a_1 and a_2 as $0 - \frac{1}{2}$ V and $0 + \frac{1}{2}$ V. The corresponding $I(V)$ figure is shown in Figure 5.3 and Figure 5.4.

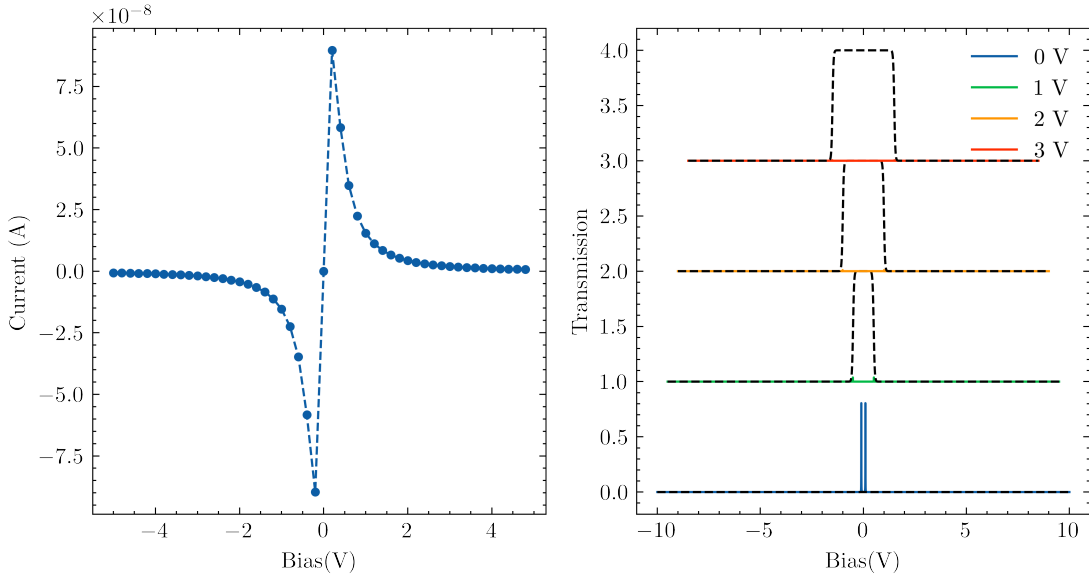


Figure 5.3: The results for the tight binding model used to simulate a molecule pair with weak inter-molecular coupling a) the $I(V)$ curve for a bias range of -5 V to 5 V b) the transmission plot at 0 V, 1 V, 2 V, 3 V

Both figures display Negative Differential Resistance (NDR) peaks near 0 V. These peak positions are influenced by the onsite energies of site 1 and site 2. Given our setup of onsite energies as $0 \pm \frac{1}{2}$ V, the energy levels of the two sites are initially close at low bias. However, they quickly separate as the applied bias increases. Consequently, an electron transport channel forms near 0 V when the energy levels align. This channel then vanishes at higher biases as the levels

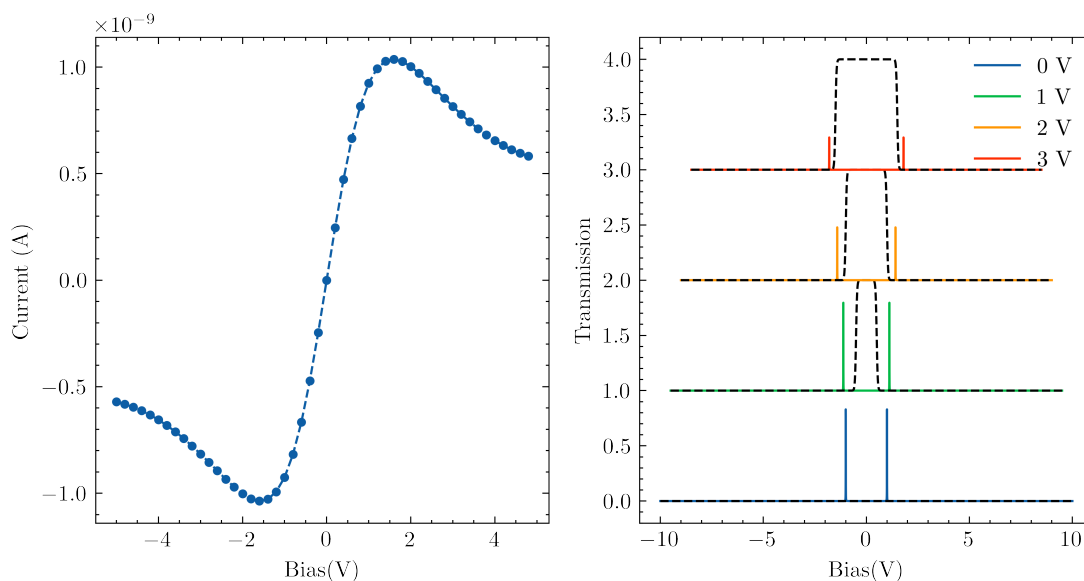


Figure 5.4: The results for the tight binding model used to simulate a molecule with strong inter-molecular coupling a) the I(V) curve for a bias range of -5 V to 5 V b) the transmission plot at 0 V, 1V, 2V, 3V

move apart. This mechanism explains the observed NDR effect, where current initially rises but then decreases with increasing voltage in a specific range.

The transmission plots in Figure 5.3 clearly illustrate this process. At 0V, two distinct peaks are visible. As the bias increases, these peaks gradually disappear, indicating the blockage of current. This disappearance strongly suggests that the two energy levels have become decoupled.

In contrast, Figure 5.4 shows a different behavior. Here, the hopping integral is set to -1, representing much stronger coupling than before. Despite increasing bias, transmission peaks persist even at higher voltages. This strong inter-site coupling makes the energy levels more resistant to bias-induced separation, maintaining some degree of connection. As a result, the I-V curve shows broader peaks, and the current doesn't drop as rapidly. The strong coupling allows electrons to continue flowing through the maintained channel, even at higher biases.

This comparison highlights how the strength of inter-molecular coupling can significantly influence electron transport characteristics in molecular junctions, particularly in terms of NDR behavior and overall conductance.

molecule electrode coupling

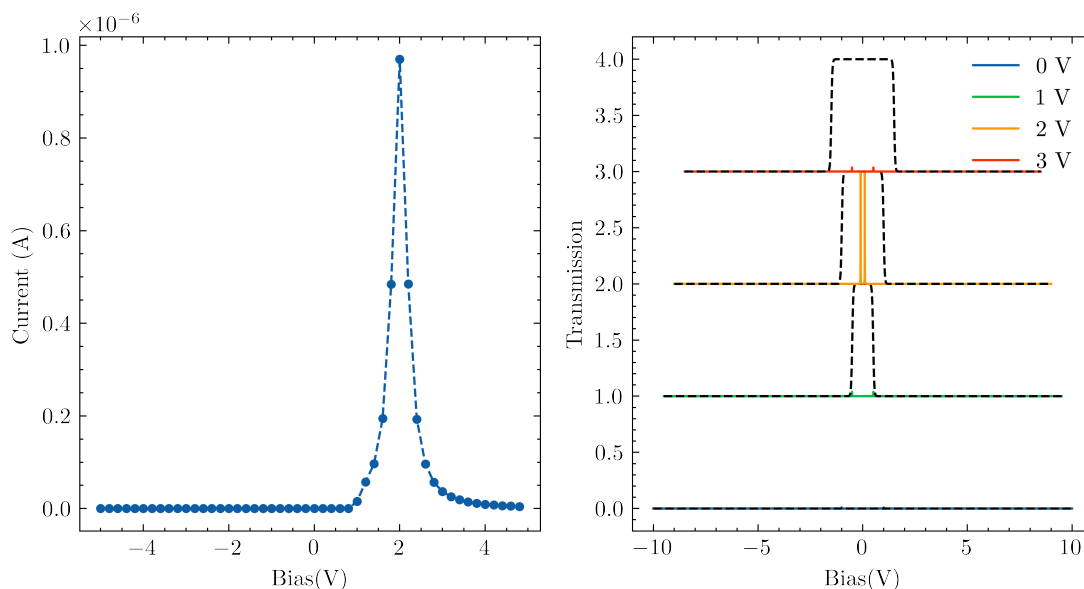


Figure 5.5: The results for the tight binding model used to simulate a donor-acceptor pair with weak molecule-electrode coupling a) the I(V) curve for a bias range from -5 V to 5 V b) the transmission plot at 0 V, 1V, 2V, 3V

While the inter-molecular coupling is an intrinsic property of the molecule, molecule-electrode coupling is another property affecting the electron transport, and is determined by the anchoring groups connecting the molecule and the electrodes. To explore the effect of molecule electrode coupling using our simple model we will adjust the parameters b_0 and b_2 while keeping b_1 fixed. As aforementioned, we will set b_1 to -0.1 eV to keep the inter molecular coupling weak so that the resistance to the bias-induced separation is negligible. Utilising 1 eV and -1 eV for α_1 and α_2 , the two sites in this model are capable of simulating a donor with a 1 eV LUMO paired to an acceptor with a -1 eV HOMO.

The I(V) curves of the models used to simulate a donor acceptor pair with weak and strong molecule electrode coupling are shown in Figures 5.5 and 5.6. These two figures share the commonality of a NDR peak observed at 2 V. This 2V

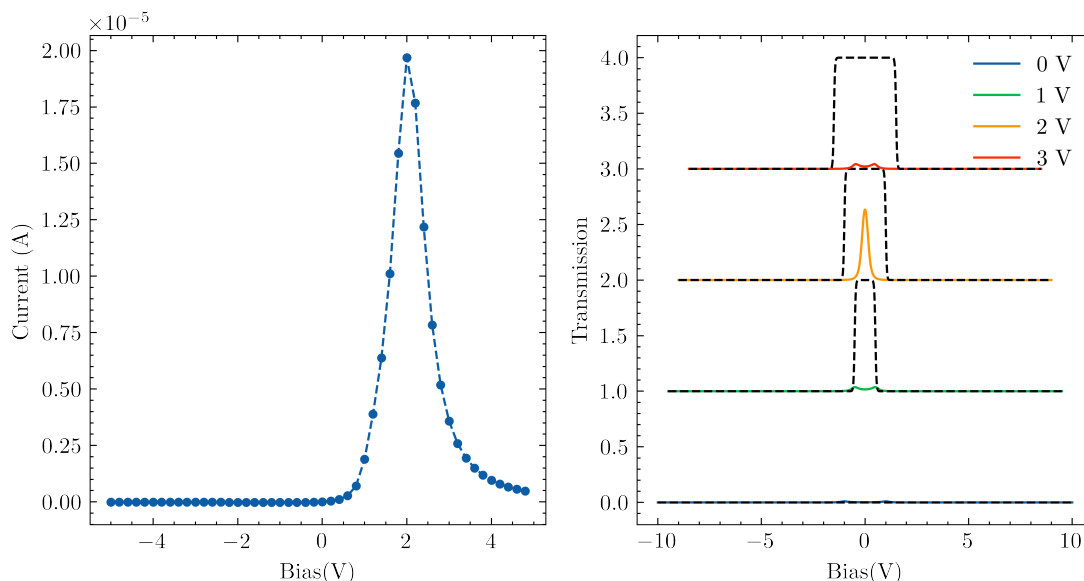


Figure 5.6: The results for the tight binding model used to simulate a donor-acceptor pair with strong molecule electrode coupling a) the $I(V)$ curve for a bias range from -5 V to 5 V b) the transmission plot at 0 V, 1V, 2V, 3V

peak is obvious since the difference between the level energy is 2 eV and it requires exactly 2 V for the levels to become equivalent if the voltage drop on the electrode are transferred to the level 100%. This assumption was made when constructing the model for simplicity, and we assume it holds true for all cases. In reality, this assumption is plausible when the molecule-electrode coupling is strong, but possibly not when the molecule-electrode coupling is weak.

Another obvious observation is that the peak in Figure 5.6 is broader than that in Figure 5.5. This broadness is a direct consequence of the stronger molecule electrode coupling. The stronger coupling expands the electron transport channel, allowing electrons across a wider energy range to flow through the junction. This effect is even more obvious in the transmission plot. Figure 5.6 exhibits a broad peak in the transmission spectrum while Figure 5.5 shows two narrow lines. These transmission characteristics vividly illustrate how the strength of molecule-electrode coupling affects the energy range of electrons involved in transport through the molecular junction.

5.4 Strengths, Weaknesses, and Connection

This chapter explores the electronic transport properties of molecular systems using tight-binding calculations, offering a simplified yet insightful approach to understanding fundamental transport mechanisms. A key strength of this work is its ability to abstract complex quantum mechanical interactions into computationally efficient models, allowing for a systematic analysis of molecule-electrode coupling and inter-molecular interactions. The tight-binding framework provides a clear and intuitive approach for more sophisticated systems while consuming affordable computational resources.

The primary limitation of this chapter lies in the inherent simplicity of the tight-binding model. While it captures the general trends and qualitative behavior of molecular transport, it relies on approximations that may ignore the detailed quantum mechanical effects present in real systems. Parameters such as coupling strength and electronic structure are treated in a simplified manner for convenience, limiting the model's accuracy in predicting highly specific transport phenomena.

The significance of this chapter is in its role as a conceptual and computational bridge to the density functional theory (DFT)-based calculations presented in Chapter 6. By identifying key parameters and trends, such as the effects of coupling strength and molecular geometry on I-V characteristics, the tight-binding approach informs the design and interpretation of more complex DFT studies. The insights gained here lay the foundation for the formulation of design rules in Chapter 6, where the results and discussions are also split to inter-molecular coupling and molecule electrode coupling.

5.5 Summary

In this chapter we developed a simplified tight-binding model to explore elastic electron transport in a 1D atom chain. By manipulating the onsite energy

(a_i) and hopping integral (b_i) we simulated both a metal chain and molecular junctions containing a donor-acceptor pair.

Our findings reveal that both inter-molecular coupling and molecule-electrode coupling significantly influence the shape of the $I(V)$ curve. This simple model has provided valuable insights into screening criteria for molecules with sharp NDR peaks, which could potentially serve as sensor molecules.

Building upon this 1D model, the next chapter will replace the theoretical sites with actual molecules. We will discuss the conditions necessary to generate sharp NDR peaks for molecular sensors, expanding our understanding of these systems in more details.

CHAPTER 6



DESIGN RULE

6.1 Introduction

One particular challenge for the $I(V)$ characteristics of such sensor devices is that their selectivity is determined by the shape of the NDR peak. If the NDR peak is excessively broad, the additional peak introduced by external molecules will be obscured, making the process of recognition difficult and decreasing the overall sensitivity of the chemical sensor.

To address this challenge of NDR peak broadening, in this work we design a simple molecular sensor model and investigate the relationship between the features of the molecular sensor and the shape of the NDR peaks in the $I(V)$ curve. We develop three key conditions to control the device sensitivity and demonstrate how our simple models meet these three conditions. Our research highlights the viability of a single-molecule chemical sensor in which the recognition system is based solely on the $I(V)$ curve, and provides valuable insights into molecular transport mechanisms and molecular electronics engineering. However, the limitations of our models and calculations are discussed in later sections. This chapter is reproduced from Ref. Li M, Cucinotta C S, Horsfield A P. A

computational model for a molecular chemical sensor[J]. *Nanoscale*, 2024, 16(10): 5334-5342 with permission from the Royal Society of Chemistry.

6.2 Results

We propose a simplified molecular model for a resonant tunneling diode sensor, comprising the molecular junction depicted in Figure 6.1. To establish optimal design principles, the molecular junction is partitioned into five functional domains: a bottom anchoring group, a donor site (bottom site), a bridging group, an acceptor site (top site), and a top anchoring group. Initially, benzene molecules were employed as the donor and acceptor, while a saturated carbon chain served as the decoupling unit. By systematically varying the lengths of the bridging and anchoring groups, we quantitatively evaluated the impact on the intensity and peak shape of the current-voltage ($I(V)$) curve, attributable to the coupling strength between the molecular moieties and between the molecules and electrodes. Note that the proposed model illustrated in Figure 6.1 solely represents the sensor molecule and does not incorporate the odorant.

Based on this analysis, we propose three design guidelines to control the sensitivity of the molecular resonant tunneling diode designed as a chemical sensor:

1. Weak coupling between the molecular donor and molecular acceptor.
2. Weak coupling between the molecules and the electrodes.
3. Proximity of the highest occupied molecular orbital (HOMO) of the acceptor to the Fermi energy of the electrodes.

Before walking into the design guidelines in details, it is crucial to comprehend the "pinning" mechanism, which involves electron interaction between two orbitals. When two partially occupied orbitals come into contact and reach equilibrium, any increase in the energy of one orbital leads to an electron flow from it to the other. This flow causes the first orbital to lower its energy due

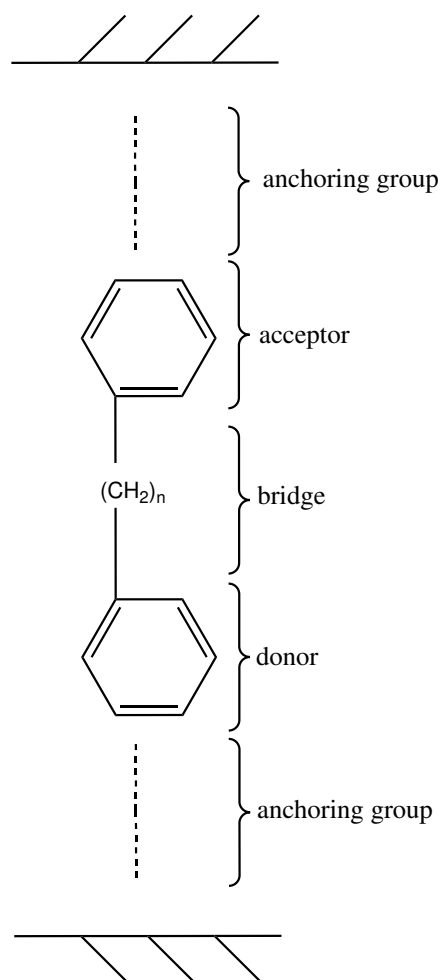


Figure 6.1: The simplified model composed of a bottom anchoring group, a donor site (bottom site), a bridging group, an acceptor site (top site), and a top anchoring group. The left and right boundaries represent for the bottom and top electrodes.

to reduced electron repulsion, while the second orbital raises its energy due to increased electron repulsion. Consequently, the two levels realign, although with different charges. However, if the electron flow between the orbitals is insufficient to keep them aligned, the two orbitals move out of alignment, and the pinning is broken. This electronic interaction exists not only between orbitals localized on electrodes and molecules but also between different molecular moieties within the system.

6.2.1 First condition: weak coupling between molecular donor and molecular acceptor

The appearance of negative differential resistance (NDR) arises due to the interaction between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), localized at the donor site (bottom aromatic group) and acceptor site (top aromatic group), respectively, within our molecular junction. These frontier orbitals are each pinned to distinct electrodes. When resonance is attained at a specific potential, the HOMO and LUMO become interconnected, extending across the entire molecular junction. This widespread orbital overlap manifests as broad peaks, consequently diminishing the sensor's sensitivity. Our primary design guideline to ensure optimal sensitivity and selectivity of the sensor is to minimize the coupling between the donor and acceptor sites within the junction.

We introduced a saturated carbon chain of increasing length in the bridging region to decouple the donor and acceptor sites. The length of this carbon chain determines the coupling strength between the donor and acceptor. Reduced coupling minimizes conjugation between these two moieties, restricting the energy range for electron transmission. Consequently, this weak coupling narrows the negative differential resistance (NDR) peak, enhancing sensor performance in line with our primary design objective.

These molecular junctions are denoted as ben-ben0X0, where X represents the number of CH₂ groups in the bridging region, varying from 1 to 4 CH₂ groups. It's important to clarify that in this context, (CH₂)_n denotes the group in a saturated chain, in contrast to the ethyne molecule. Figure 6.2 illustrates the resulting I(V) curves. Analyzing the figure reveals two distinct types of I(V) behavior: for chains with less than three CH₂ groups, the corresponding I(V) curves display NDR peaks near 2 V, albeit broad. The appearance of an NDR peak around 2 V can be attributed to the anchoring of the molecular orbitals of the sensor to the electrodes under applied bias. Specifically, the HOMO_{bottom}

does not fall within the bias window until reaching 2V, at which point the current attains its maximum value. Beyond this threshold, the HOMO_{top} and $\text{HOMO}_{\text{bottom}}$ levels shift in opposite directions with increasing bias, exiting the resonant state and resulting in a decline in the current. When the chain length exceeds 3 CH_2 groups, the NDR peak diminishes, and only minor fluctuations are observed in the $I(V)$ curve.

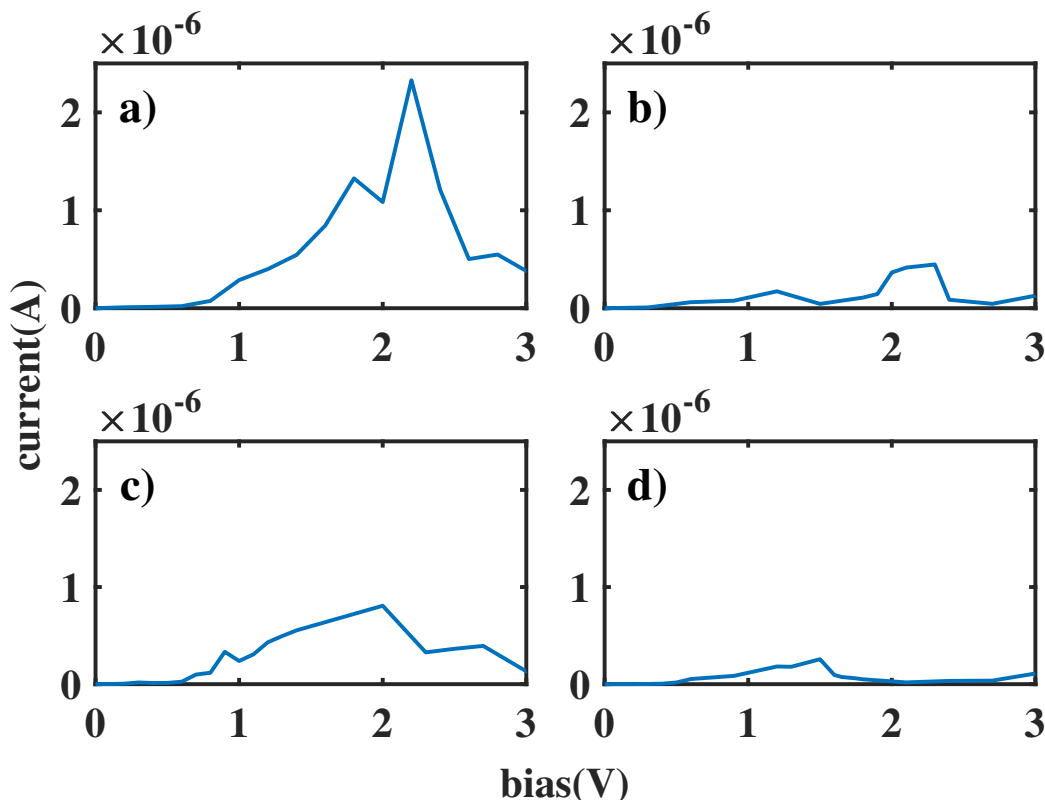


Figure 6.2: The current through the double benzene molecule as a function of applied bias voltage for the following models: a) ben-ben010; b) ben-ben020; c) ben-ben030; d) ben-ben040.

This length-dependent characteristic can be elucidated by examining the density of states projected over the two molecules (PDOS), illustrated in Figure 6.3 for each bridge length under a bias of 2 V. When the bridge length consists of three or fewer CH_2 groups, the coupling between the HOMO of the top (HOMO_{top}) and bottom ($\text{HOMO}_{\text{bottom}}$) benzene molecules remains strong, causing them to stay pinned and resulting in a broad peak. Specifically, $\text{HOMO}_{\text{bottom}}$ remains close to the lower boundary of the bias window at -1 eV. However, with an increase

in bridge length to four CH_2 groups, the intermolecular coupling diminishes, and $\text{HOMO}_{\text{bottom}}$ becomes anchored to the potential of the bottom electrode. Consequently, $\text{HOMO}_{\text{bottom}}$ moves quickly to a higher energy position as a positive bias is applied to the bottom electrode. Given the reduced coupling between donor and acceptor in this scenario, we consider four CH_2 groups as the optimal bridge length. Therefore, ben-ben040 is selected as the reference bridge length for subsequent calculations and discussions.

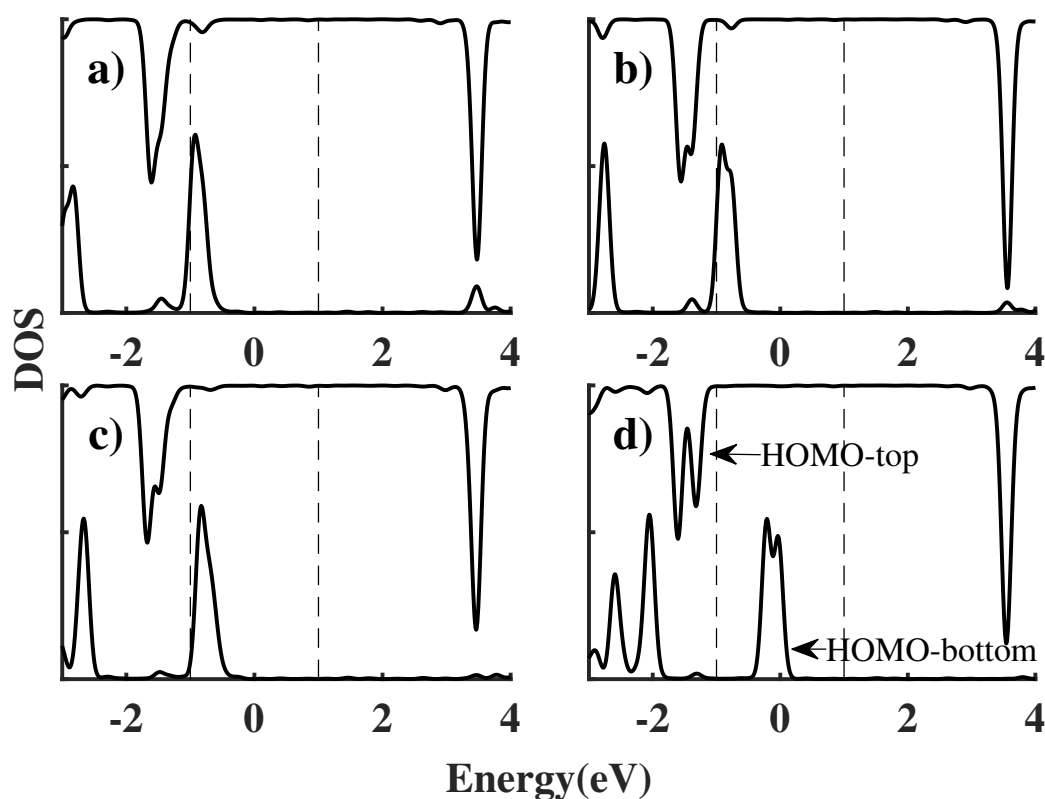


Figure 6.3: The PDOS of ben-ben models at 2 V a) ben-ben010 b) ben-ben020 c) ben-ben030 d) ben-ben040. The black dotted lines indicate the boundaries of the bias window, which spans from -1 to 1 eV at 2 V. The highest energy peaks in the upper and lower curve represent the HOMO of the top (HOMO_{top}) and bottom ($\text{HOMO}_{\text{bottom}}$) benzene molecules, respectively.

An additional critical observation is that the current in our molecular junction decreases with an increasing number of CH_2 groups in the bridging region. This can be attributed to the fact that, in addition to decoupling the donor and acceptor, the saturated carbon groups act as insulators between the bottom and top contacts. Consequently, the resistance of the entire molecule rises, leading to

a decline in current. For this reason, it is crucial to strike a balance in the length of the bridge: if the bridge is excessively long, the resistance of the molecular sensor becomes too high, rendering the current undetectable.

It should be noted that the nonlinear decrease in current with increasing chain length, especially noticeable in ben-ben020 and ben-ben030, stems from the distinct geometries of the sensor molecule with an odd and even number of CH_2 groups in the bridge. This geometric variation impacts the electron transport, as elucidated and depicted in Figure 6.4.

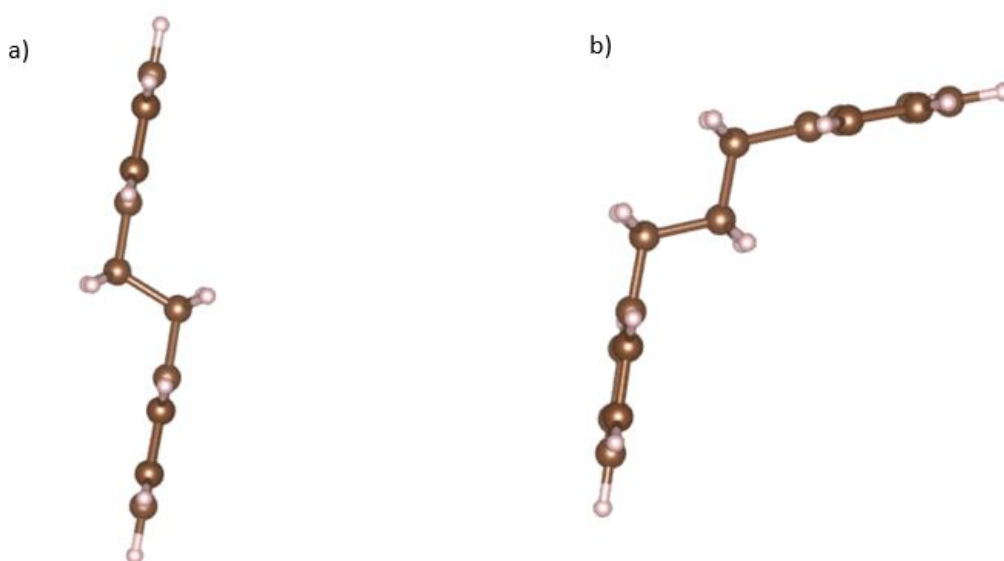


Figure 6.4: The geometry of a) ben-ben020 b)ben-ben030 The geometries of the models with an even number of CH_2 groups are different to those with an odd number of CH_2 groups. Different geometries affect electron transport, therefore we would not expect a linear relation between reduction of current and chain length.

The difference between ben-ben020 and ben-ben030 is also evident in the transmission plots, as shown in Figure 6.5 Within the bias window, the transmission peak for the ben-ben030 molecule surpasses that of ben-ben020. This larger transmission peak in ben-ben030 corresponds to an enhanced electron flow at the same bias, consequently resulting in a higher current.

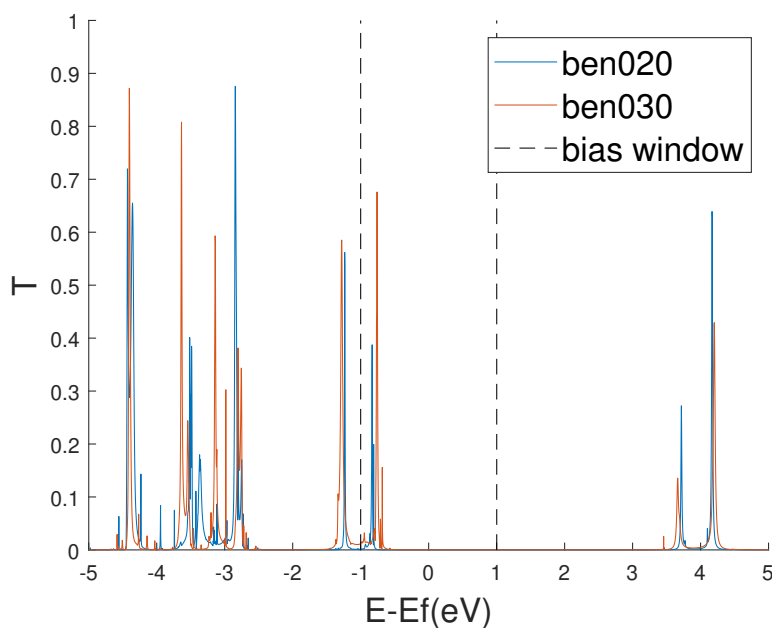


Figure 6.5: The transmission plot of ben-ben020 and ben-ben030. Within the bias window the transmission peak for the ben-ben030 molecule is larger than that of ben-ben020. The larger transmission peak in ben-ben030 correlates with greater electron flow at the same bias, resulting in a higher current.

6.2.2 Second condition: weak coupling between the molecules and the electrodes

An anchoring group serves as a linker, connecting the molecule and the electrodes in a molecular junction. The way in which the metal contacts are connected to the sensor molecule also impacts broadening: strong coupling facilitates greater transmission of the metal states through the molecule, resulting in increased broadening. In the previous calculations, we inserted a 3 Å vacuum gap between the molecule and the gold electrodes, roughly corresponding to contact with a scanning tunneling microscope (STM) tip. To investigate the effect of anchoring groups, thiols were appended to both ends of the template molecule and integrated into the junction, denoted as ben-ben040s.

The current-voltage ($I(V)$) characteristic in the presence of the thiol groups is illustrated in Figure 6.6 a). A peak emerges at 5.2 V, which is approximately the HOMO-LUMO gap (HLG) of benzene. This peak arises when the $\text{HOMO}_{\text{bottom}}$

and LUMO_{top} orbitals are in resonance, as shown in Figure 6.7. However, this peak exhibits considerable broadening due to the newly inserted thiols, which serve to bridge the gap between the molecule and electrodes. This bridging effect enhances the coupling between the molecule and electrodes, consequently broadening the frontier orbitals and facilitating electron transport. In other words, the current increases even as $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} move out of resonance, as the extended tails of these broadened levels still contribute to the coupling between the moieties, resulting in a current increment.

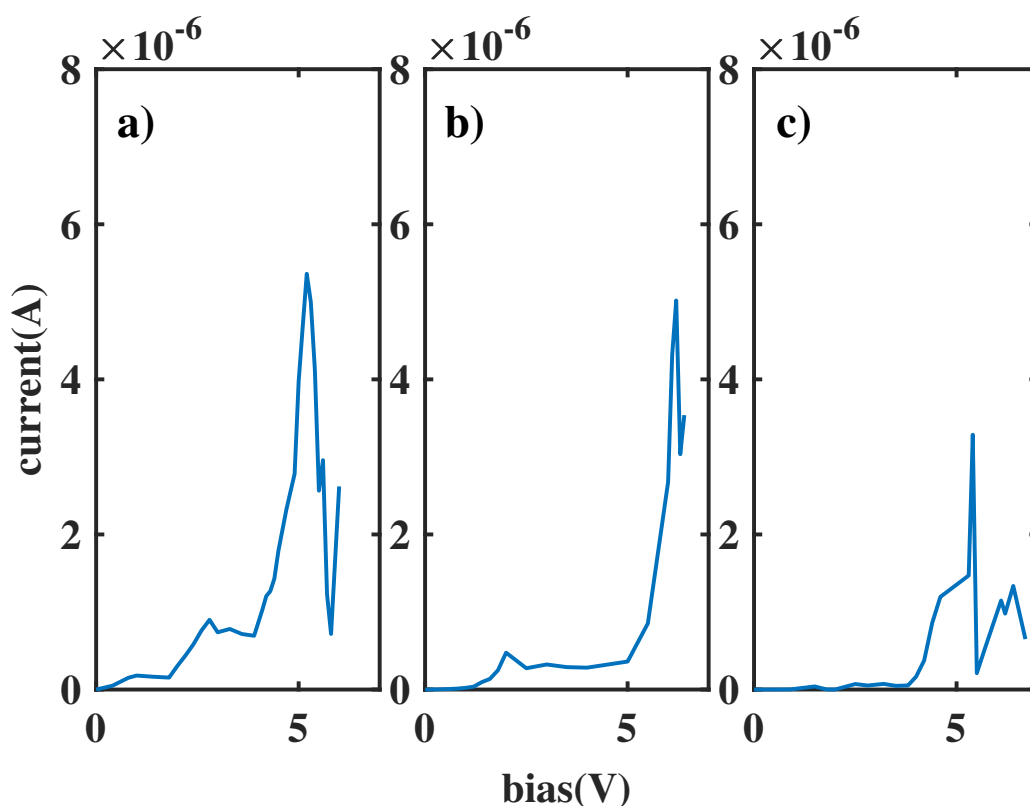


Figure 6.6: The current of ben-bens models a) ben-ben040s b) ben-ben141s c) ben-ben242s

The coupling strength between the molecule and the electrode can be adjusted by modifying the anchoring group. One approach to decrease the coupling strength and achieve a narrower peak is by incorporating CH_2 groups into the anchoring groups, as saturated carbon atoms serve as effective decoupling units. Specifically, one CH_2 group and two CH_2 groups were introduced at both ends of the prior thiol model, forming the S-CH_2 and $\text{S-CH}_2\text{-CH}_2$ linkers, respectively.

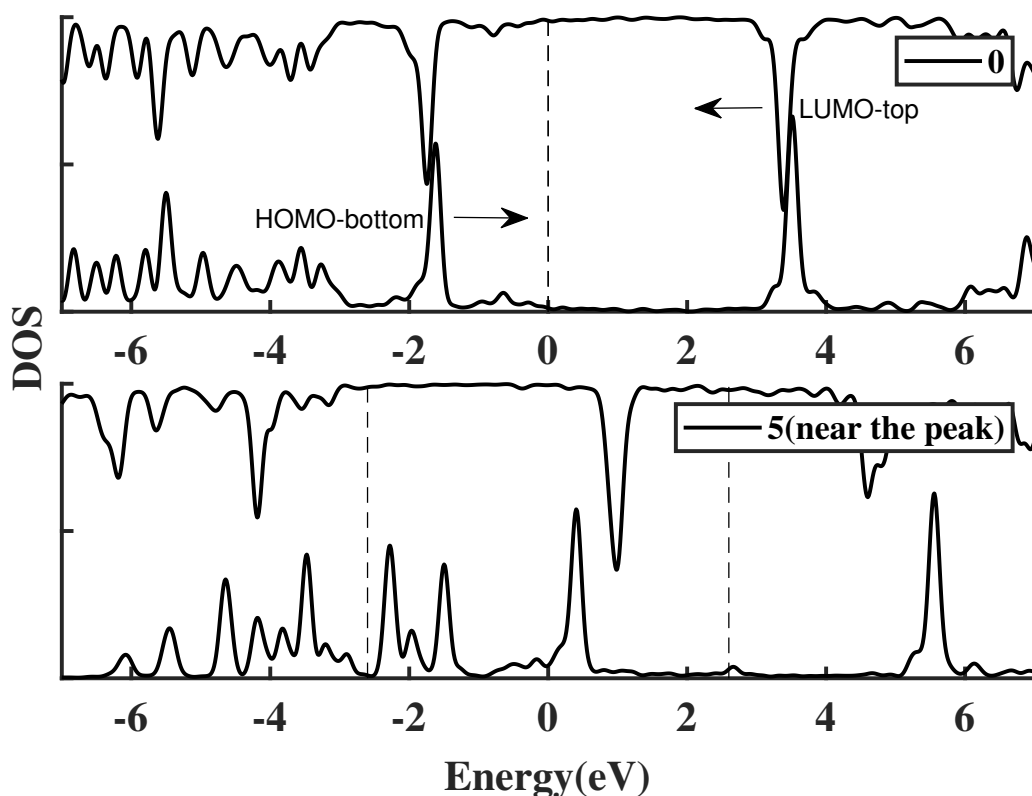


Figure 6.7: The PDOS of ben-ben040s model at 0 V and 5 V. $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} which generate the NDR peak are labelled. The arrows show how the orbitals move when a positive bias is applied

The $I(V)$ curves for these two new models, denoted as ben-benX4Xs, where X represents the number of CH_2 groups in the anchoring groups ($X=1$ or 2), are illustrated in Figure 6.6; notably, their corresponding peaks exhibit sharper profiles compared to those of the previous thiol model.

While the NDR peaks observed are sharp, their positions are shifted to even higher biases compared to those of ben-ben040s. This shift towards higher bias voltages arises due to the reduced molecule-electrode coupling resulting from the insertion of the CH_2 groups. Consequently, the electrodes diminished control over the relevant molecular orbitals, requiring a higher bias for these orbitals to attain resonance, as elucidated in the following explanation.

To elucidate this concept and quantify the pinning of molecular orbitals to the electrode across the molecular system, we introduce the efficiency factor, E .

This factor denotes the ratio between the shift of frontier orbitals relative to their positions at 0 V and the shift of the electrode potential, as depicted in the following equation.

$$E = \frac{\Delta E_{\text{orbitals}}}{\Delta E_{\text{electrode potential}}} \quad (6.1)$$

The efficiency factor provides a measure of how effectively the electrode potential influences the molecular orbital energies, thereby facilitating the interpretation of the observed bias dependence on the resonance condition. The efficiency factor (E) ranges from 1, representing extremely strong coupling where orbitals are pinned to the electrode potential, to 0, indicating no coupling, where orbital energies remain unaffected by the electrode potential shift. Table 6.1 lists the efficiency factors for ben-ben040s, ben-ben141s, and ben-ben242s. Models with extra CH_2 groups inserted exhibit smaller efficiency factors compared to ben040s, indicating reduced molecule-electrode coupling. A smaller efficiency factor implies a smaller shift in the orbitals compared to a larger efficiency factor under the same applied bias. Consequently, a higher bias is necessary for the orbitals of the aromatic groups with a smaller efficiency, $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} , to achieve resonance, thereby shifting the negative differential resistance (NDR) peak to higher biases. It is noteworthy that the efficiency of ben-ben242s is comparable to that of the vacuum models.

Model	E
ben-ben040s	93.1%
ben-ben141s	70.2%
ben-ben242s	63.3%
ben-ben040	59.3%

Table 6.1: The efficiency E of different models

6.2.3 Third condition: Proximity of the HOMO of the acceptor to the Fermi energy of the electrodes

While a pronounced negative differential resistance (NDR) peak is observed in Figure 6.6 b) and c) of our simplified sensor model, the voltage at which this sharp NDR peak occurs is too high to be realized experimentally in a molecular junction. Specifically, a voltage of 5.2 V or more, corresponding to the location of the sharp NDR peak in our model, risks compromising the stability of the molecular contacts or even causing the molecular junction to break down[142]. Consequently, it is necessary to explore measures to shift the position of the NDR peak to a more suitable voltage range for practical device applications.

To shift the position of the negative differential resistance (NDR) peak, one approach is to substitute the top benzene molecule with a different acene molecule, such as naphthalene, anthracene, or tetracene. These acenes exhibit a smaller HOMO-LUMO gap compared to benzene, thereby positioning their frontier orbitals closer to the Fermi level. This difference results in a disparity between the HOMO levels of the bottom and top moieties. On the basis of this difference, it is the $\text{HOMO}_{\text{bottom}}$ and HOMO_{top} , rather than the $\text{HOMO}_{\text{bottom}}$ and the LUMO_{top} , that resonate within the bias window. This shift leads to a significant reduction in the voltage required for resonance, as the energy gap between the two HOMO levels is considerably smaller than the highest-lying occupied molecular orbital (HLG) of benzene, as illustrated in Figure 6.8.

We replaced the top benzene group of ben-ben040 with an anthracene and computed the resulting molecule's $I(V)$ curve, as depicted in Figure 6.9. A distinct negative differential resistance (NDR) peak is evident near 1.65 V. Upon examining the corresponding projected density of states (PDOS) in Figure 6.10 for this new molecule, denoted as ben-ant, we observed that this sharp NDR peak arises exactly from the interaction between the HOMO of the benzene (depicted in black) and the HOMO of the anthracene (depicted in red), instead of involving the LUMO_{top} , as observed in the ben-ben case.

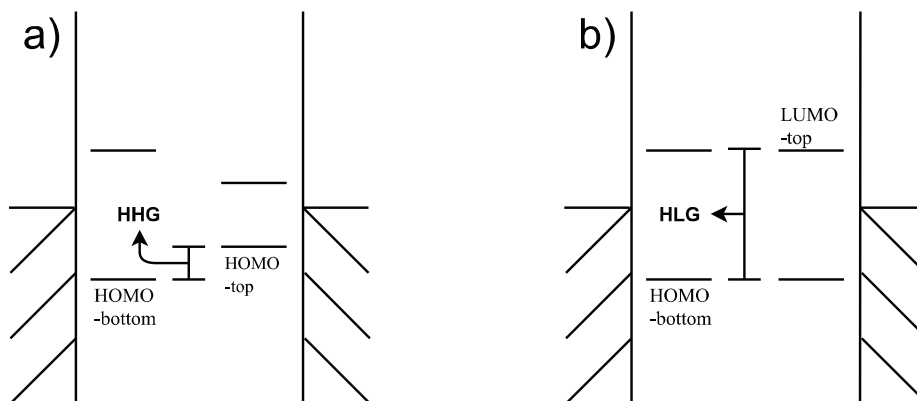


Figure 6.8: a) $\text{HOMO}_{\text{bottom}}\text{-HOMO}_{\text{top}}$ coupling. The $\text{HOMO}_{\text{bottom}}$ and HOMO_{top} belong to the benzene moiety and the anthracene moiety respectively b) $\text{HOMO}_{\text{bottom}}\text{-LUMO}_{\text{top}}$ coupling. The $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} belong to the bottom benzene moiety and the top benzene moiety respectively.

The emergence of this distinct negative differential resistance (NDR) peak involves the movement of the HOMO_{top} into and out of the bias window. The PDOS shift under bias vividly illustrates these dual movements of the HOMO_{top} , as depicted in Figure 6.10. At 0 V, the HOMO_{top} lies quite close to the Fermi level of the electrodes. Following a decrease in the potential of the top electrode due to the applied positive bias, the energy of the HOMO_{top} also decreases, resulting in a narrowing $\text{HOMO}_{\text{bottom}}\text{-HOMO}_{\text{top}}$ gap. At a bias of 1V, the HOMO-HOMO gap closes to 0, yet we would only anticipate a minor increase in current at this point because the majority of both HOMOs lie outside the bias window, as illustrated in Figure 6.10 g). However, once the entire $\text{HOMO}_{\text{bottom}}$ enters the bias window, the HOMO_{top} abruptly becomes conductive, allowing for charge accumulation, and returns to its former position with higher energy within the bias window. In this scenario, the resonance of the $\text{HOMO}_{\text{bottom}}$ and HOMO_{top} occurs within the bias window, generating a channel for electron transmission, thereby enhancing the current at 1.65 V, as demonstrated in Figure 6.10 i).

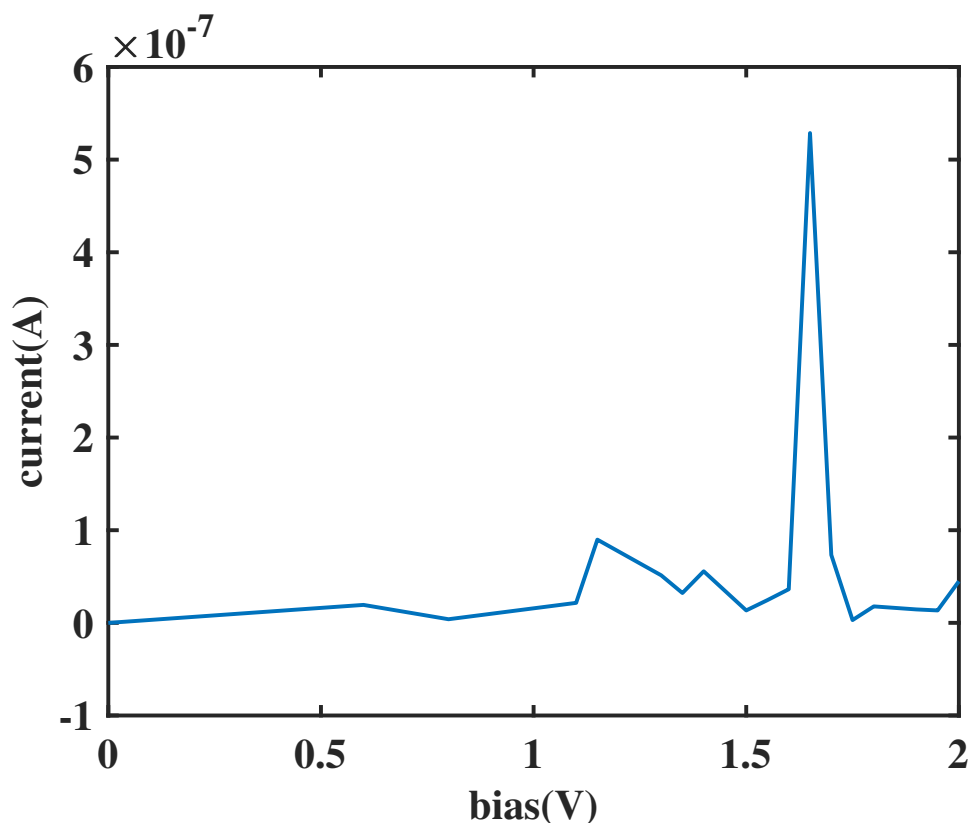


Figure 6.9: The variation with voltage of the current through the sensor molecule with the top benzene replaced by anthracene.

The distinct resonance occurring at 1.65 V is also evident in the charge distribution of the model, as depicted in Figure 6.11. As the applied bias increases, the charges on the benzene (anthracene) fragment increase (decrease) as the fragment approaches the bottom (top) electrode until reaching 1.65 V. At this bias, the resonance between $\text{HOMO}_{\text{bottom}}$ and HOMO_{top} occurs, and the charges on these two fragments undergo redistribution. The negative charges on the benzene migrate to the anthracene, facilitating the electron transport and thereby enhancing the current. This redistribution process manifests as a peak or a valley at 1.65 V in the charges versus bias figure.

The sudden entry and exit of the HOMO_{top} within the bias window requires two further key conditions to be met. The coupling between the electrode and the molecule must not be excessively strong. Also, the HOMO_{top} should be

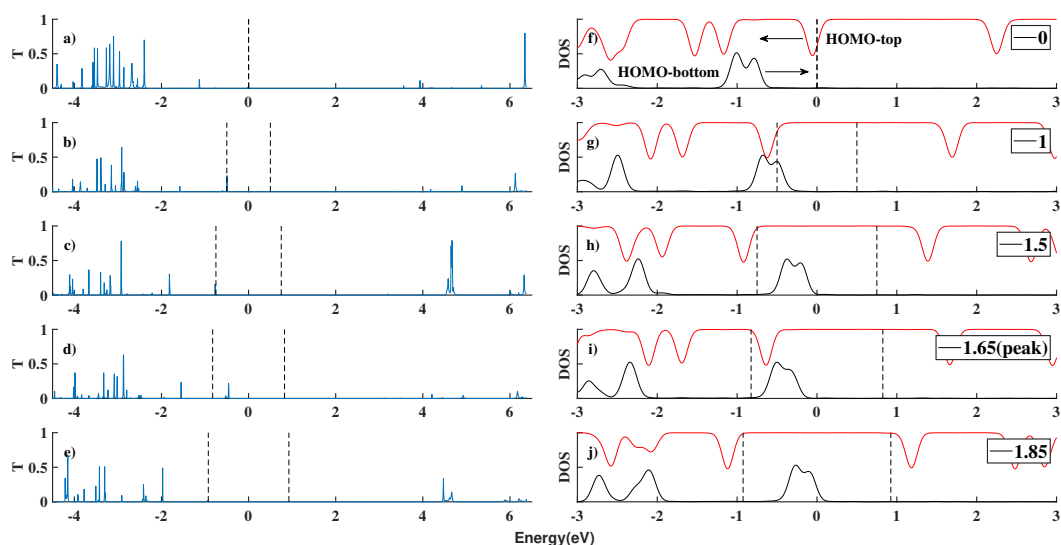


Figure 6.10: The transmission plot and the PDOS of ben-ant models under different voltages a) f) 0 V b) g) 1 V c) h) 1.5 V d) i) 1.65 V (the position of the NDR peak) e) j) 1.8 V. The pdos of the anthracene moiety is in red and the pdos of the benzene is in black. The orbitals that are concerned has been labelled as $\text{HOMO}_{\text{bottom}}$ and HOMO_{top} which belong to the benzene moiety and the anthracene moiety respectively. The arrows show how the orbitals move when a positive bias is applied.

positioned close to the Fermi energy of the top electrode, which is the third condition.

Regarding the second condition, when the coupling is strong, the energy of the HOMO_{top} is predominantly dictated by the electrode, leading to the HOMO being pinned to the electrode. As a result, the energy level would continue decreasing, tracking the shift in the electrode Fermi energy. This phenomenon is observed when the ben-ant groups are strongly linked to the electrode through a thiol group, as depicted in Figure 6.12.

For the third condition, the HOMO_{top} should be situated in close proximity to the Fermi energy of the electrodes. This condition ensures that the energy difference between the HOMO_{top} and the electrode Fermi energy is small when the $\text{HOMO}_{\text{bottom}}$ enters the bias window, as depicted in Figure 6.13 a). Consequently, the coupling between the $\text{HOMO}_{\text{bottom}}$ and HOMO_{top} can prompt the excitation of the HOMO_{top} by the flow of current-carrying electrons, as illustrated in Figure 6.10 i).

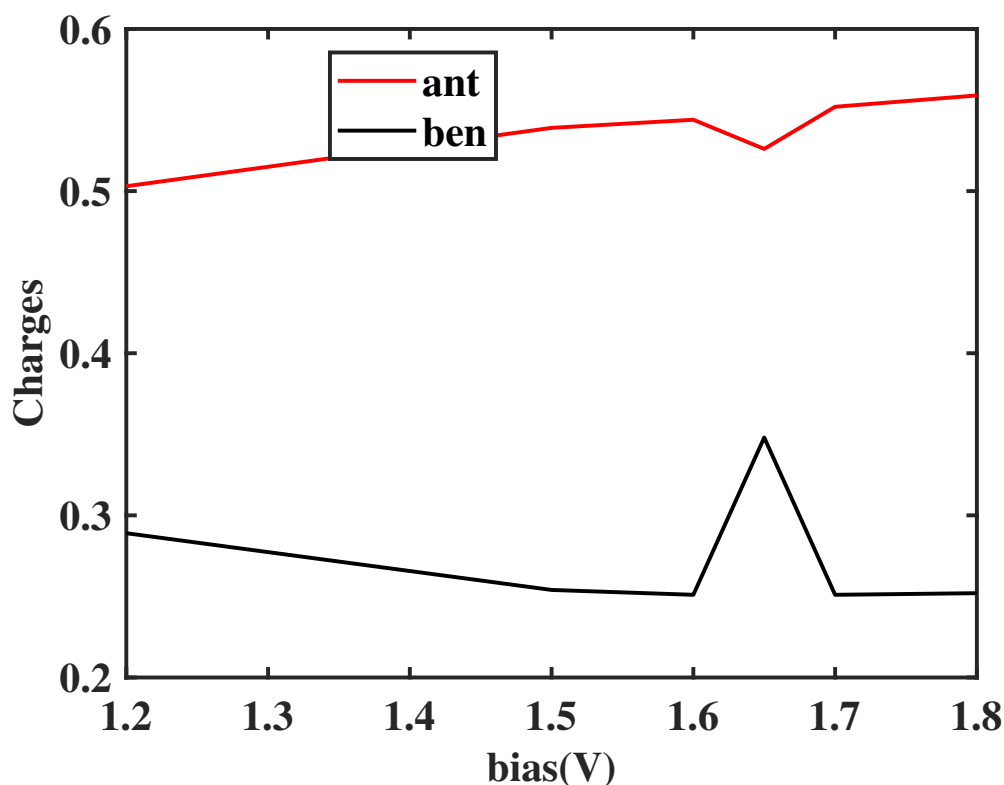


Figure 6.11: The charge distribution of the ben-ant model. Black: the Hirshfeld charge on the benzene fragment. Red: the Hirshfeld charge on the anthracene fragment.

In contrast, when there exists a significant energy gap between these two moieties, the $\text{HOMO}_{\text{bottom}}$ entering the bias window fails to bridge this gap so that the orbital is incapable of conducting current, as depicted in Figure 6.13 b). It is noteworthy that the robust coupling between the molecule and the electrode compresses the HOMO-LUMO gap of the molecule to a much narrower value compared to its isolated state, owing to the pinning effect [143]. However, this approach of reducing the energy difference between the molecule's HOMO and the electrode's chemical potential is impractical, as the strong interaction between the molecule and the electrode violates the second criterion.

In the previous discussion, we noted that the excitation of the HOMO_{top} appears to be triggered by the coupling between the molecular moieties, which seemingly contradicts the requirement of weak coupling between these moieties. However, it is precisely the weak intermolecular coupling that enables the

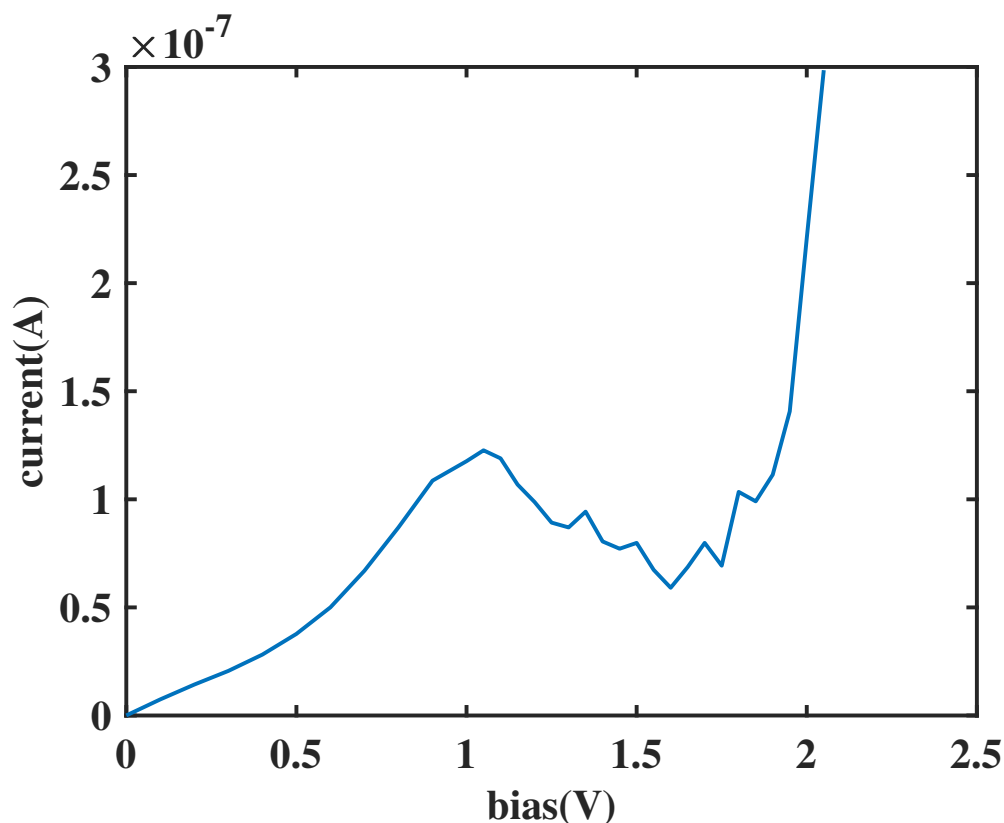


Figure 6.12: The I(V) figure of the ben-ant-S model

abrupt displacement of the HOMO_{top} . Otherwise, if the molecule-molecule coupling were strong, the orbital would remain firmly pinned in position rather than moving freely.

An NDR peak occurring at a lower voltage is not only due to a reduced gap but also to the suppression of the coupling of the electrode Fermi energy to the molecular orbitals. The movement of the HOMO_{top} occurs in two stages. In the initial stage (depicted in Figure 6.14 a), the shift of the HOMO_{top} is insignificant compared to the shift of the electrode Fermi energy induced by the bias, given the weak coupling between the molecule and electrode. Consequently, the gap between the HOMO_{top} and the corresponding electrode Fermi energy is expected to decrease. Subsequently, the energy level of the HOMO_{top} aligns with the Fermi energy of the electrode, marking the transition to the second stage (illustrated in Figure 6.14 b).

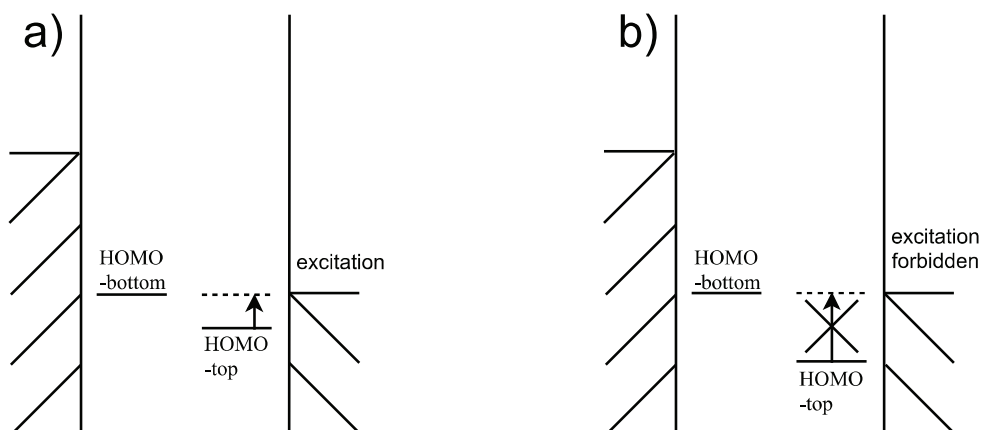


Figure 6.13: The HHG is a) small b) big when the HOMO – bottom enters the bias window

During the second stage, the movement of the HOMO_{top} accelerates. As the electrode Fermi energy diminishes, electrons from the adjacent HOMO readily transition from the moiety to the electrode, as the HOMO is the sole electron-rich pathway above the electrode potential. This electron drainage leads to a reduction in the energy level due to electron-electron interactions within the orbital. Consequently, the contribution of this level to electron transport is suppressed by the shift in the electrode Fermi energy. In other words, the movement of the level aligns with the shifting electrode potential, thereby enhancing the rate of change of orbital energy.

If we were to substitute the acceptor site with a moiety that aligns with the LUMO, meaning its LUMO is in close proximity to the Fermi level of the electrodes and its HOMO is lower than that of benzene, the NDR peak would arise from the coupling between $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} . Despite the LUMO_{top} energy being significantly lower than that of benzene's LUMO, the movement of LUMO_{top} remains relatively slow in the absence of strong coupling between the molecule and the electrode, especially the suppression of the electrode potential. Given that the LUMO_{top} consistently resides above its

corresponding electrode Fermi energy and no electrons reside on the LUMO_{top} , fluctuations in the electrode potential would have minimal impact on the orbital, resulting in a gradual shift with low efficiency.

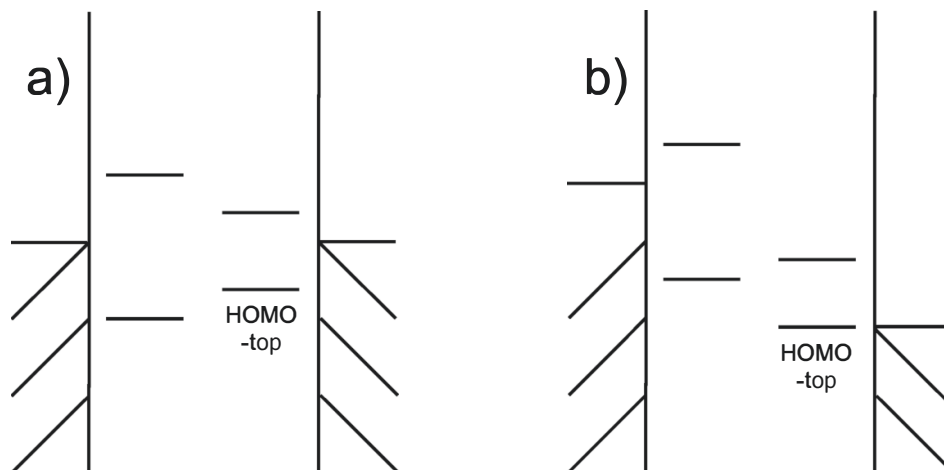


Figure 6.14: The movement of the HOMO_{top} a) slow shift b) fast shift, catching up with the shift of the electrode and reaching an efficiency of 100%

We also explored an alternative approach to adjust the gap between $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} by introducing electron-extracting groups, -F, to the top benzene molecule in the model. Conceptually, these electron-extracting groups function similarly to n-type dopants in semiconductors, shifting conduction bands towards the Fermi level. The projected density of states on the top and bottom benzene rings of these modified molecules are illustrated in Figures 6.15 and 6.16. However, we find that the impact of the added functional groups is relatively limited. The magnitude of the reduction in the $\text{HOMO}_{\text{bottom}}$ and LUMO_{top} gap is small compared to the large HOMO-LUMO gap (HLG) of the unmodified benzene, which is 5.2 eV.

To create a more practical sensor, rather than just an STM experiment, an anchoring group was introduced to either side of the ben-ant model to establish a connection between the molecule and the electrode, similar to the approach used for the ben-ben models. To satisfy the second condition, we specifically utilized $-\text{SCH}_2\text{CH}_2$ as the additional anchoring group. Previous studies on the

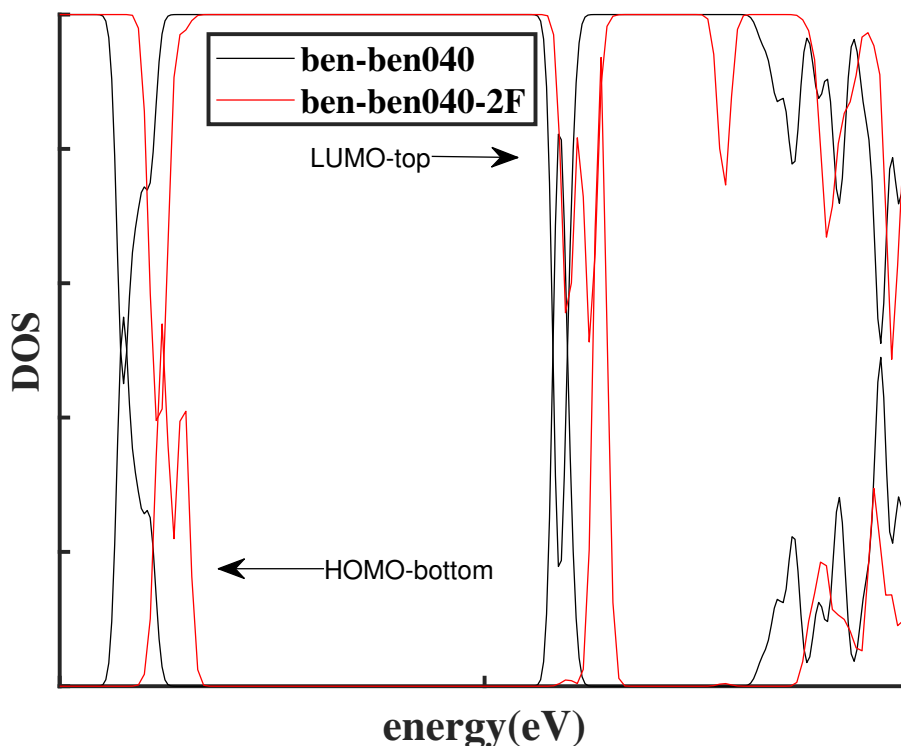


Figure 6.15: The pdos figure of modified ben-ben040. Black: original ben-ben040 Red: ben-ben040-2F. We have aligned the vacuum level energy of these two molecules. The orbitals that we determine the $\text{HOMO}_{\text{bottom}}\text{-LUMO}_{\text{top}}$ gap are labelled as HOMO-bottom and LUMO-top

ben-ben models have demonstrated that the inclusion of extra CH_2 groups tends to weaken the coupling between the molecule and the electrode. This effect was evident in the comparison between the efficiency factor (E) of ben-ben242s and ben-ben040, as detailed in Table 6.1.

Figure 6.17 displays the $I(V)$ curve of the ben-ant model featured by weak anchoring groups. As anticipated, a pronounced NDR peak is observed at 2.5 V, consistent with the behavior seen in the models with vacuum. Additionally, the previously mentioned $\text{HOMO}_{\text{bottom}}\text{-HOMO}_{\text{top}}$ crossover, which occurs beyond the bias window, is also evident in the PDOS figure and transmission curve, followed by the HOMO_{top} subsequently entering the resonance region between the two moieties. The successful reproduction of the sharp NDR peak using solid anchoring groups reinforces our hypothesis and makes the three

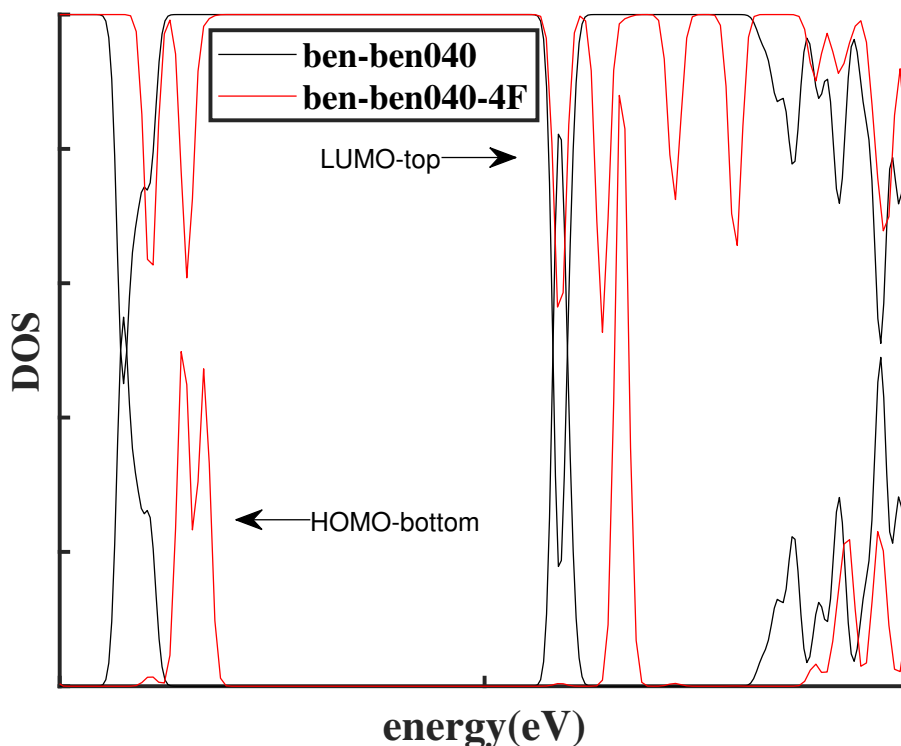


Figure 6.16: The pdos figure of modified ben-ben040. Black: original ben-ben040 Red: ben-ben040-4F. We have aligned the vacuum level energy of these two molecules. The orbitals that we determine the $\text{HOMO}_{\text{bottom}}\text{-LUMO}_{\text{top}}$ gap are labelled as HOMO-bottom and LUMO-top

proposed conditions more feasible and realizable for a practical chemical sensor application.

6.3 Strengths, Weaknesses, and Experimental Relevance

This chapter focuses on the development of design rules for optimizing molecular junctions through density functional theory (DFT) calculations. The results of these calculations are well translated into actionable principles for the design of molecular sensors. By systematically exploring molecular coupling, electrode interactions, and energy alignment, this chapter provides a clear guidelines for achieving optimal transport properties in molecular junctions. The insights

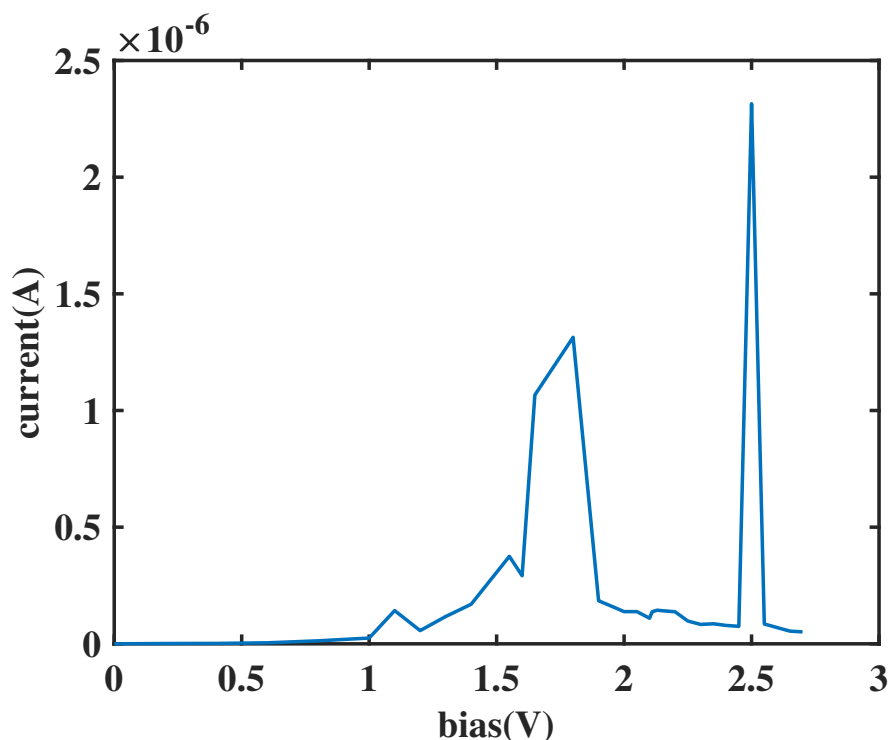


Figure 6.17: The current of ben-ant242

gained are both theoretically rigorous and practically applicable, bridging the gap between computational predictions and molecular sensor design.

We acknowledge that there are certain limitations to our models and calculations. While our findings support the feasibility of a single-molecule molecular sensor utilizing sharp NDR peaks in $I(V)$ curves for external molecule detection, we remain uncertain about the potential impact of additional interactions on this NDR peak. The electron-phonon interactions are outside the scope of this chapter as we have solely focused on the elastic condition for sensing. However, as the electron-phonon interaction between molecules and receptors is central to the vibrational theory of smell mechanisms, it will need to be explored to fully assess the performance of our sensors, and this will be addressed in later chapters. Moreover, our models are primarily simulated in a vacuum environment to isolate the fundamental electronic properties of the sensor material from external interference. In reality, components like O_2 and other atmospheric gases may affect sensor performance by altering odourant concentrations, engaging in

inelastic interactions with the sensor, and contributing to background noise in the $I(V)$ characteristic. The impact of environmental factors will also be explored in future work.

The experimental relevance of this chapter is obvious, as the design rules derived here provide clear templates for the synthesis and modification of molecular sensors. For instance, the finding that weak coupling between molecular donor and acceptor groups enhances selectivity directly informs the choice of the bridging areas in the molecular structures for experimental studies. Similarly, the analysis of electrode coupling and its influence on transport properties offers insights for optimizing electrode-molecule configurations in practical devices.

By highlighting the importance of energy alignment between molecular orbitals and electrode Fermi levels, this chapter provides a template for tailoring molecular systems to specific sensing applications. The donor and acceptor fragments in the template can be replaced with other aromatic rings to achieve specific current shapes and mediated NDR peaks' locations.

Finally, the synthesis of the suggested model molecule, ben-ant242, is considered highly feasible, as its donor and acceptor fragments, benzene and anthracene, are readily accessible as raw materials. While connecting these fragments using CH_2 groups may present some challenges, potentially impacting production yield and purity, minor impurities with longer bridges are unlikely to compromise the accuracy reliability of experimental measurements. This is due to the fact that the design rules still stand when the CH_2 bridge length exceeds four units.

6.4 Conclusions

In this study, a straightforward model comprising five functional sites has been developed, including a bottom anchoring group, a bottom moiety, a bridge, a top moiety, and a top anchoring group. Through adjustments to the number of CH₂ groups in the bridge sites and between the molecule and the contacts, we explored the impact of molecule-electrode coupling and molecule-molecule coupling on the current of the molecular junction. A sharp NDR peak, arising from the shift of the HOMO, was identified when both coupling interactions were relatively weak.

Three key design rules are proposed to realize a successful sensor:

1. Weak coupling between the molecular donor and molecular acceptor.
2. Weak coupling between the molecules and the electrodes.
3. Proximity of the highest occupied molecular orbital (HOMO) of the acceptor to the Fermi energy of the electrodes.

Our findings offer valuable insights for molecular engineering and could pave the way for a new type of single-molecule sensor. This sensor would rely solely on the I(V) characteristics, rather than the traditional IETS spectrum based on the second derivative of the current with respect to the bias. This approach represents a departure from the conventional sensing methods and could enable more practical and reliable chemical detection.

One note to consider when applying our three rules is that the strength of the current flowing through the junction and the sharpness of the NDR peaks are inversely affected by the strength of the couplings. Reducing the coupling of the molecule to the contact decreases the overall current magnitude, while simultaneously sharpening the resonance features. However, if the couplings become too weak, the current could diminish to a level that is too small to detect, and the meaningful NDR peak would become obscured by background noise.

Striking the right balance in coupling strength is imperative to ensure both detectable current and well-defined NDR peaks that can be reliably leveraged for sensing applications.

6.5 Methodology

The geometry optimization for all the structures was conducted using the CP2K DFT code [137], version 8.2. We employed Goedecker, Teter, and Hutter (GTH) norm-conserving pseudopotentials[138] and triple zeta valence polarized basis sets, except for the gold atoms, for which a single zeta polarized basis set was used. Since our system includes a 5×5 atom slab of gold as an electrode, the use of a single zeta basis was necessary to reduce the computational resources required while still maintaining sufficient accuracy. The cutoff energy for the density mesh was set to 500 Ry, and a $9 \times 9 \times 1$ k-point mesh was utilized. All the convergence parameters were determined through a series of convergence test calculations, achieving an error of less than 0.001 eV/atom.

The relaxed geometry was determined through the following procedure. Initially, an isolated molecule was optimized to establish the relaxed distance between the top and bottom atoms. Subsequently, electrodes were added above and below the outermost atoms, with a 3 Å vacuum gap between the electrode and the outermost atoms. This vacuum gap reduces the interaction between the molecule and the electrodes, allowing us to focus on the effect of the bridging group length between the two aromatic molecules on the current through the molecular junction. This setup roughly mimics an experiment using an STM tip as a contact. If the vacuum is replaced with a thiol, fixing the distance between the gold electrode and the top or bottom sulfur at 1.7 Å. In this scenario, the distance between the top and bottom electrodes becomes 2×1.7 Å plus the distance between the top and bottom atoms of the molecule obtained in the isolated molecule optimization stage. Finally, the molecule-electrode junction was optimized until the forces fell below 10^{-4} atomic units.

NEGF calculations for transport properties, including current and transmission spectrum, were conducted using the implementation in CP2K version 8.2 [139]. Subsequent post-processing analyses, such as the projected density of states under finite bias conditions, were performed using a modified version of CP2K

8.2 developed by Dr. Sergey Chulkov. Dr. Chulkov has previously demonstrated the reliability of the NEGF formalism in CP2K by computing the $I(V)$ curve of dithiol benzene with gold electrodes [139] and comparing the results with those reported in earlier studies [135], confirming consistency between the results.

CHAPTER 7



PHONON AND INELASTIC TUNNELLING

7.1 Introduction

In our previous chapters we simplified our molecular model by replacing a C60 fragment with a benzene ring to study the relationship between molecular structure and NDR peaks. By further modifying the top benzene to anthracene, we successfully shifted the model's NDR peaks to 1.65 V and established design principles for generating sharp peaks at low bias ranges.

However, there exist some limitations within our current calculations. The situation to which NEGF can be applied in this study is ballistic tunnelling which does not include electron-phonon interactions. Since electron-phonon interactions are fundamental to the vibrational theory of olfaction incorporating them is crucial for enhancing the credibility and completeness of our sensor performance models.

In this chapter, we aim to address this limitation by including electron-phonon interactions in our calculations using the QuantumATK software [130]. We assume that odours influence $I(V)$ characteristics through inelastic interactions with the sensor. To validate this hypothesis, we will perform calculations with external molecules present and compare the results to our previous

findings that didn't account for electron-phonon interactions. This approach will provide a more comprehensive understanding of molecular sensor behavior and potentially offer insights into the mechanisms of olfaction at the molecular level.

7.2 Results

7.2.1 IR Spectrum

A key factor in the vibrational theory of olfaction is the vibrational energy of the odourants. The prevailing gas characterization technique is Infrared (IR) spectroscopy, which measures the interaction of infrared radiation with the odourant. We aim to calculate the IR spectrum of our sensor molecules with some small polar molecules to determine whether they can be identified.

It is noteworthy that in the IR experiment, silica is utilized as the substrate to allow light to travel through and be absorbed by the sample matter. Similarly, our sensor molecule is analogous to the silica in the IR experiment, functioning as the substrate for the small polar molecules.

The sensor molecule

We take ben-ant242 from the previous models as the template. The corresponding IR spectrum is shown in Figure 7.1, computed by Gaussian[131]. The primary peaks are located between 3000 cm^{-1} and 3100 cm^{-1} , which are mainly attributed to C-H characteristic peaks. The majority of the secondary peaks are located between 1000 cm^{-1} and 1500 cm^{-1} , corresponding to the stretching mode of C=C in the benzene. From the IR spectrum, we can confirm that the molecule is composed of carbon and hydrogen and contains benzene rings, which is exactly the composition of ben-ant242.

with odorant

After obtaining the IR spectrum of ben-ant242 for reference, a group of molecules, including HCl, HCN, H₂S, NH₃, CO, and H₂O, has been inserted into the system. These molecules were selected because they are relatively small compared to our sensor molecules. The presence of these small molecules should not affect the vibrational modes of the sensor molecules so much that the peaks shift significantly. Additionally, all of these molecules are polar, and their corresponding vibrational modes are infrared active. For a vibrational mode to be infrared active, the molecule's dipole moment must change periodically during vibration.

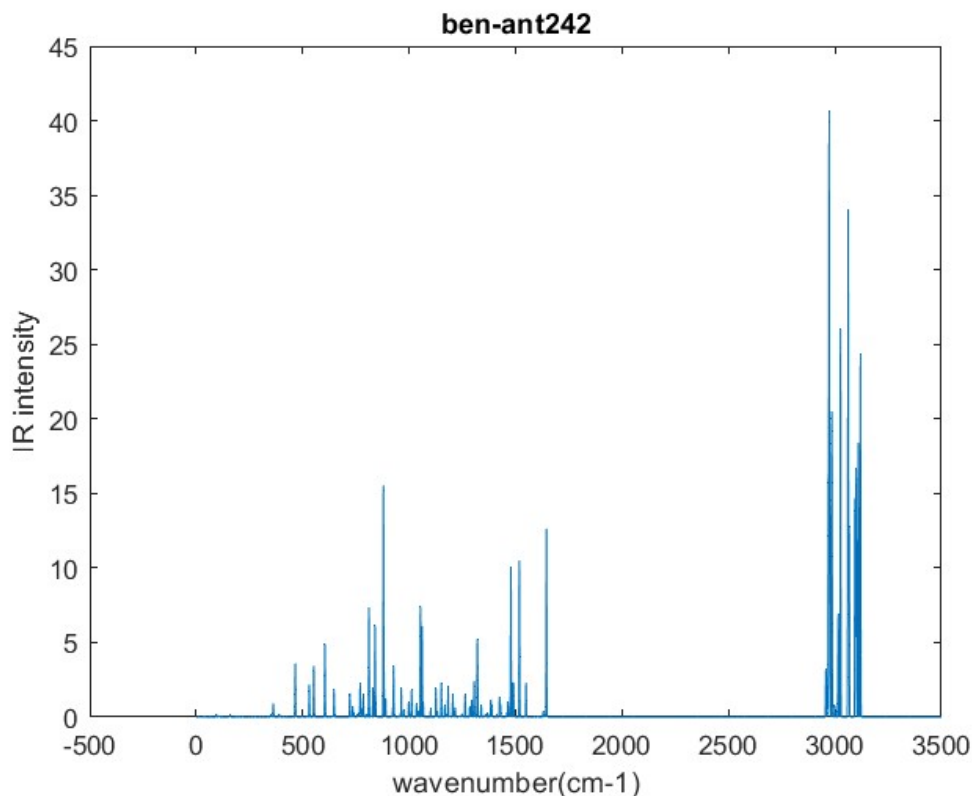


Figure 7.1: The IR spectrum of ben-ant242 composed of C and H atoms which form aromatic rings. The primary peaks are located between 3000 cm^{-1} and 3100 cm^{-1} , which are mainly attributed to C-H characteristic peaks. The majority of the secondary peaks are located between 1000 cm^{-1} and 1500 cm^{-1} , corresponding to the stretching mode of C=C in the benzene.

The IR spectrum of our model with these six small polar molecules is shown in Figure 7.2. All the peaks belonging to the small molecules can be found in the IR spectrum of the mixture containing ben-ant²⁴² and the odorant. The existence of these peaks demonstrates that the vibrational modes of these molecules are not masked by the sensor molecule. This is a prerequisite for detecting the electron-phonon interaction between the external molecules and the sensor molecule inelastically.

Among these six molecules, HCl exhibits the most IR activity, as shown in Figure 7.2b. The peak corresponding to the stretching mode of HCl around 2700 cm^{-1} surpasses all the peaks belonging to the substrate and becomes the primary peak in the spectrum. The outstanding performance of HCl in the IR spectroscopy makes sense, as only those vibrational modes that cause a change in dipole moment can be detected. We acknowledge that the peak is almost invisible for the isolated HCl, in sharp contrast to the the outstanding performance of HCl in the mixture but the reasons remain unclear.

HCl is a diatomic molecule with a linear structure. The primary vibrational mode in HCl is the stretching mode, which involves a clear, periodic change in the dipole moment. This singular, strong mode leads to prominent IR absorption. Additionally, HCl has a significant dipole moment because chlorine is much more electronegative than hydrogen, resulting in a polar bond. During the vibrational motion (specifically stretching), the distance between hydrogen and chlorine changes, causing a periodic change in the dipole moment. This makes the vibrational mode strongly IR active. The simple structure and highly polar bond enable HCl to outperform the other molecules in IR spectroscopy. Due to its outstanding performance, HCl is selected as the odorant in the subsequent calculations for the inelastic tunneling spectrum.

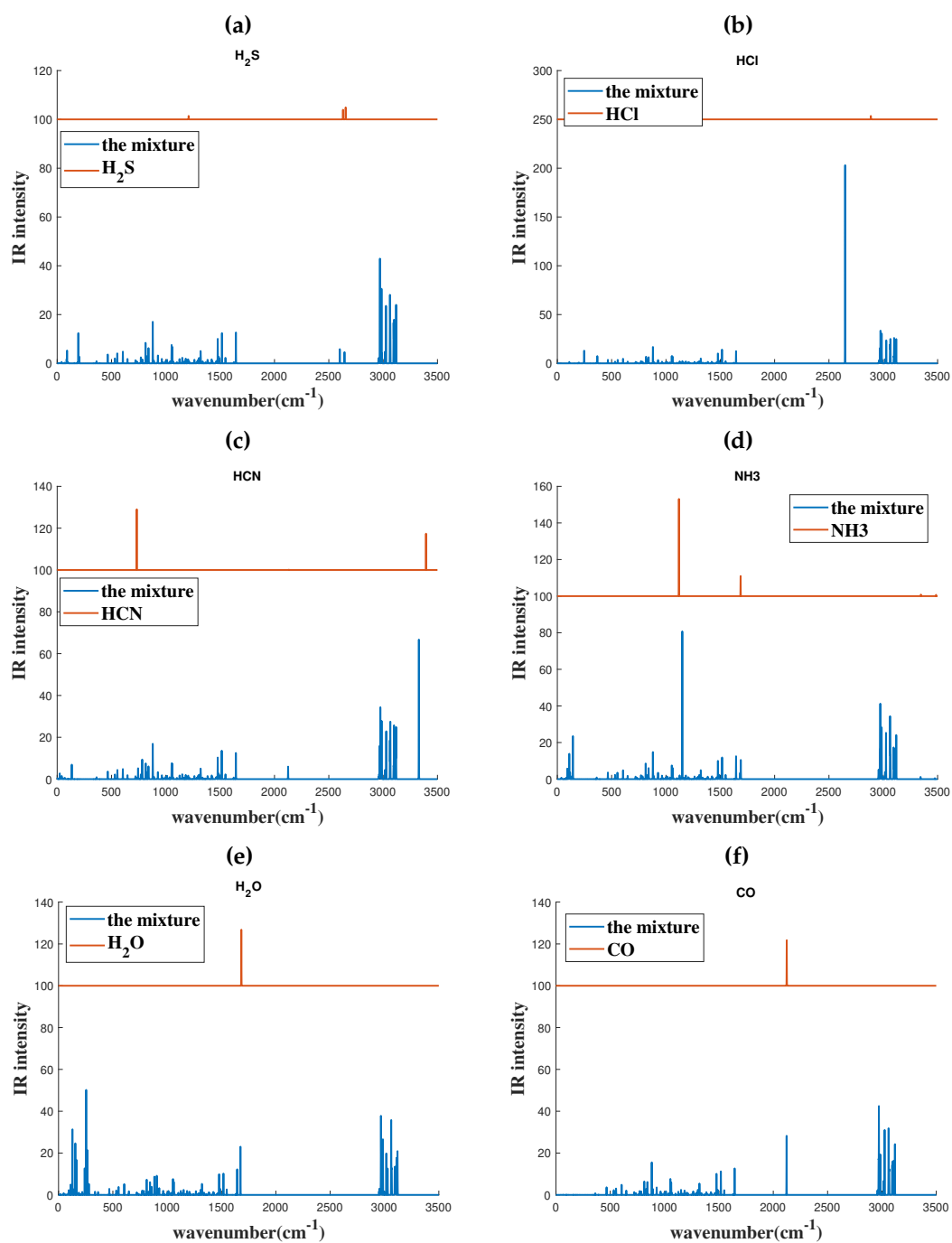


Figure 7.2: The IR spectrum of the mixture of ben-ant242 and the odourant a) H₂S b) HCl c) HCN d) NH₃ e) H₂O f) c) CO. For comparison, the IR spectrum of the odourant alone is presented at the top of each graph in red.

7.2.2 Inelastic Tunneling Spectrum with bridging areas

Thanks to QuantumATK integrating the calculations of inelastic tunneling, we can obtain the inelastic tunneling spectrum of a molecular junction without consuming significant computational resources. To test the reliability of this method, we will start with the di-thiol benzene junction and compare the result with the IR spectrum of benzene.

Benzene

The inelastic tunneling spectrum of the dithiol benzene junction is shown in Figure 7.3. From the figure, three main peaks, 0.09 eV, 0.13 eV, and 0.19 eV, are observed corresponding to the three peaks in the IR spectrum. Despite the difference in the strength of the peaks, the position of the peaks matches between the inelastic tunneling spectrum and the IR spectrum. The consistency between IETS and IR spectra suggests that those vibration modes detectable in the IR spectrum may also be observed in the inelastic tunneling spectrum, which is promising for the application of our sensor.

We also compared our results with those in reference [128]. In the paper, the authors calculated the IETS of the dithiol benzene junction using both LOE and X-LOE methods. All the peak positions in the paper are consistent with our results, which reassures us that the calculation methods are reliable. Additionally, both LOE and X-LOE methods produce similar results, while X-LOE is much more time-consuming. Therefore, we will use LOE as the primary method to obtain the IETS of a molecular junction.

ben-ant242

The inelastic tunneling spectrum of the sensor molecule ben-ant242 is shown in Figure 7.4. Comparing it with the IR spectrum in Figure 7.1 we can draw the same conclusion: the positions of the peaks match despite differences in peak strength, demonstrating the reliability of IETS calculations in QuantumATK.

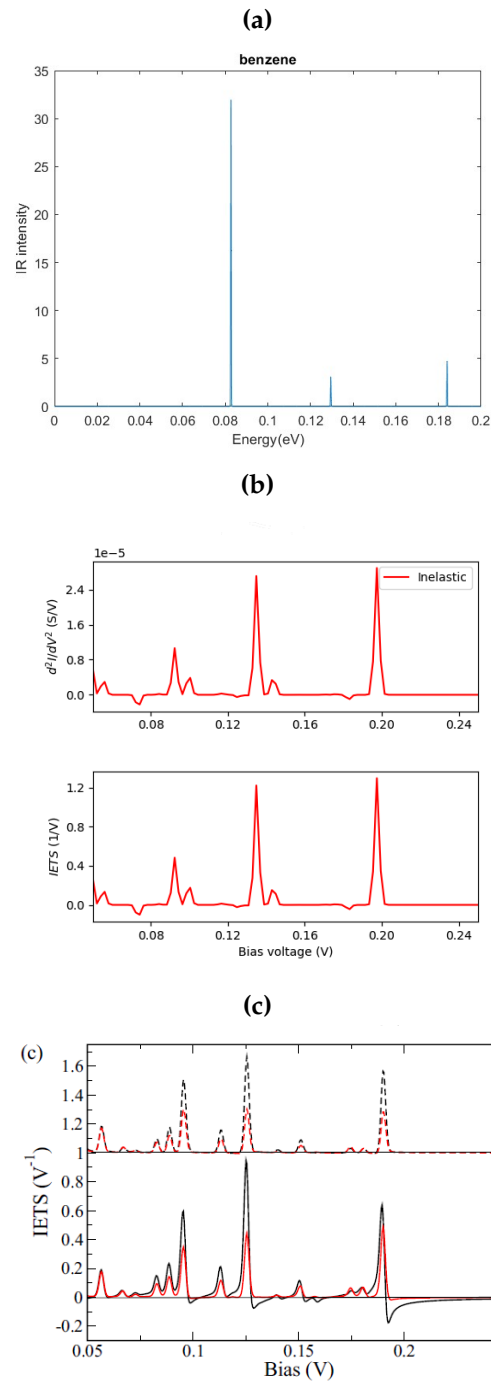


Figure 7.3: a) the IR spectrum of benzene b) the calculated IETS of benzene c) the reference IETS of benzene [128]. The position of the peaks matches between the inelastic tunneling spectrum and the IR spectrum

After obtaining the IETS of the sensor molecule ben-ant242, HCl was inserted into the system, and we calculated the IETS of this mixture. HCl was selected because it has the most IR active stretching mode, as previously mentioned.

There are three positions where HCl can be inserted: near the benzene, near the bridge, and near the anthracene. We calculated the IETS of the mixture with HCl in different positions. To our surprise, none of them has an obvious peak belonging to HCl, in sharp contrast to what we observed in the IR spectrum.

This observation is not consistent with the findings in the paper [96]. Sahoo utilized the molecular RTD proposed by Perrin [96] and claimed to successfully identify hydrogen cyanide through IETS. The geometries of the molecular junction, where the odorant is bonded to the sensor molecule covalently and non-covalently, are shown in Figure 7.5.

From Figure 7.5 we see that the characteristic peaks belonging to HCN are observed clearly, whether HCN is covalently or non-covalently bonded. It should be noted that the bonding method affects the peak positions in the inelastic tunneling spectrum. This is why two distinct peaks are observed, featuring covalently and non-covalently bonded HCN. The vibrational frequency of a bond is primarily influenced by bond strength, and how it is bonded to the sensor molecule also affects the strength of the H-CN bond, altering its vibrational frequency. What this difference exhibits in the IETS is two slightly different peak positions for the same odourant.

However, we found that HCN is too close to the sensor molecule, regardless of how it is bonded. The problem with these geometries is that we do not know whether the positions of HCN are energetically favorable. As shown in the geometry, the HCN seems too perfectly localized between the two benzenes, making us doubt the geometry is optimized.

Since the coordinates of the reference junction cannot be obtained, we cannot determine if the geometry is optimized. To find evidence supporting our suspicion about the reference geometry, we calculated the inelastic tunneling

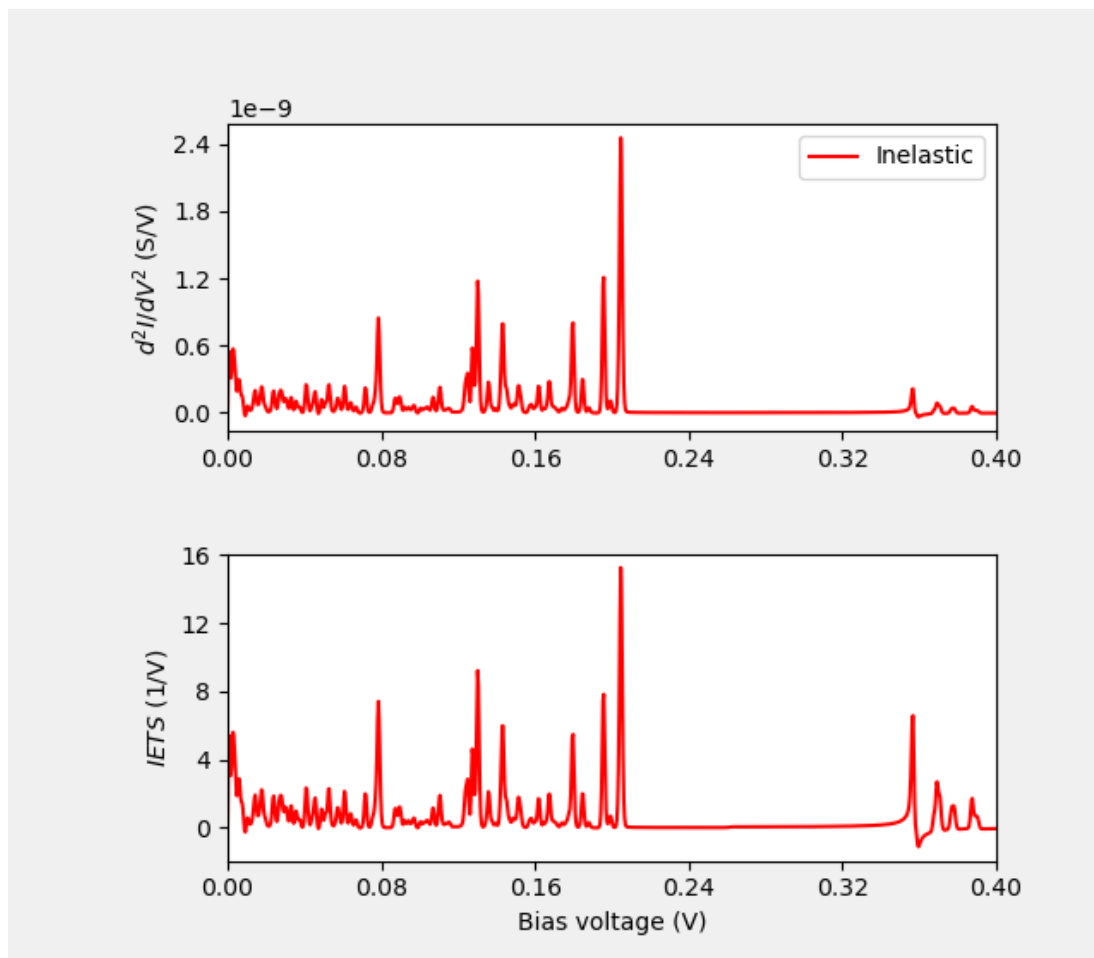


Figure 7.4: The inelastic tunneling spectrum of ben-ant242. The peak positions of the IR spectrum and IETS match despite differences in peak strength.

spectrum of our molecule junction, ben-ant242 with HCl, for both optimized and initial geometries, as shown in Figure 7.6. For the initial geometry, the HCl is placed in the middle position between the two H atoms on the benzene, simulating the non-covalently bonded geometry in Figure 7.5b.

As expected, while the inelastic tunneling spectrum of the optimized geometry shows no difference to that of the isolated ben-ant242 as aforementioned, the corresponding spectrum of the initial geometry does exhibit a strong peak at 0.4 eV belonging to the stretching mode of HCl, as shown in Figure 7.7.

However, the observation of the peaks of HCl does not demonstrate that the sensor can detect the existence of an external odorant. The initial geometry is not optimized, and the position is not energetically favorable for HCl. Instead,

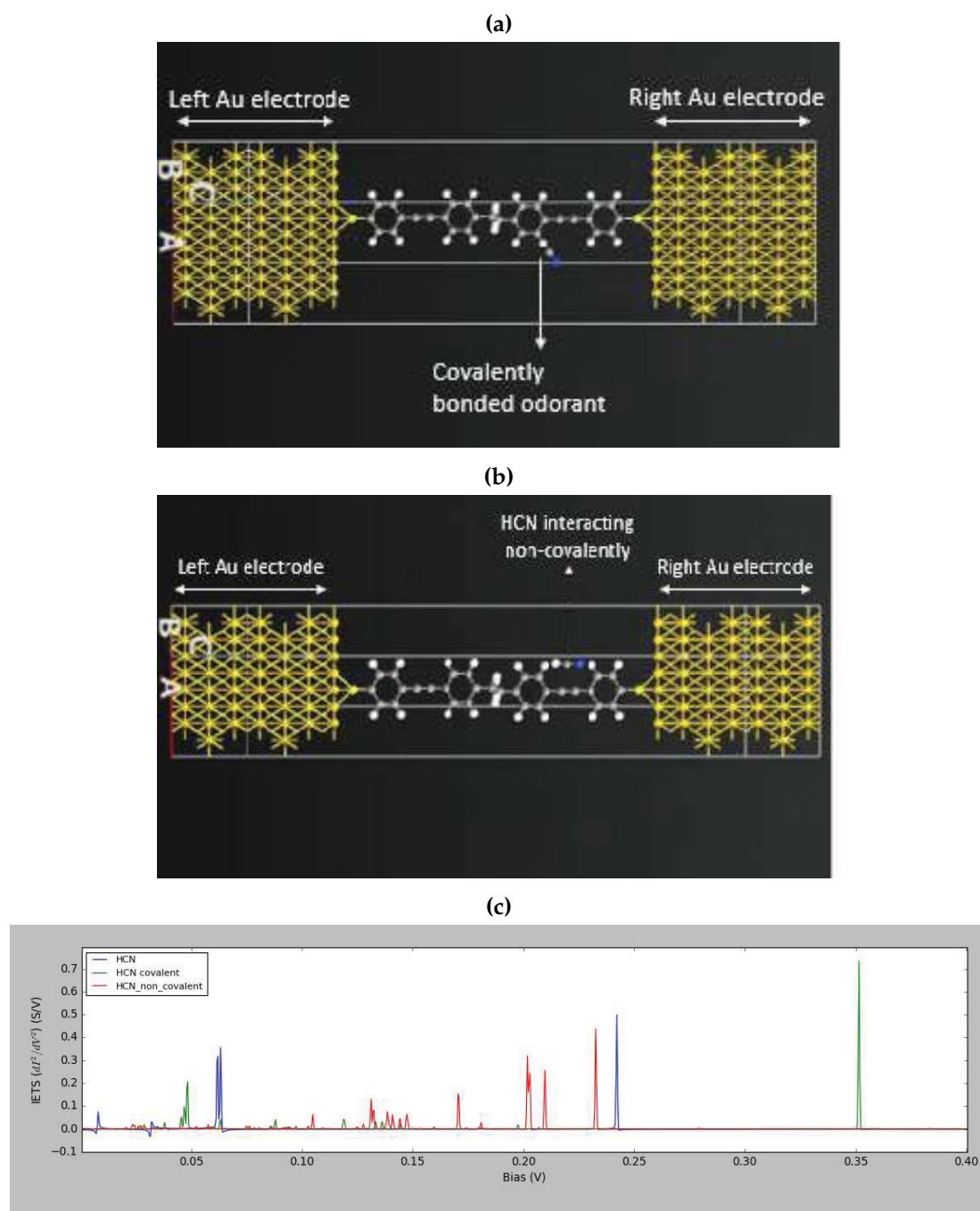


Figure 7.5: The geometries of the mixture in the reference [96] claiming to identify HCN successfully a) HCN is bonded to the substrate covalently b) HCN interacting with the substrate non-covalently c) the corresponding IETS of these two geometries

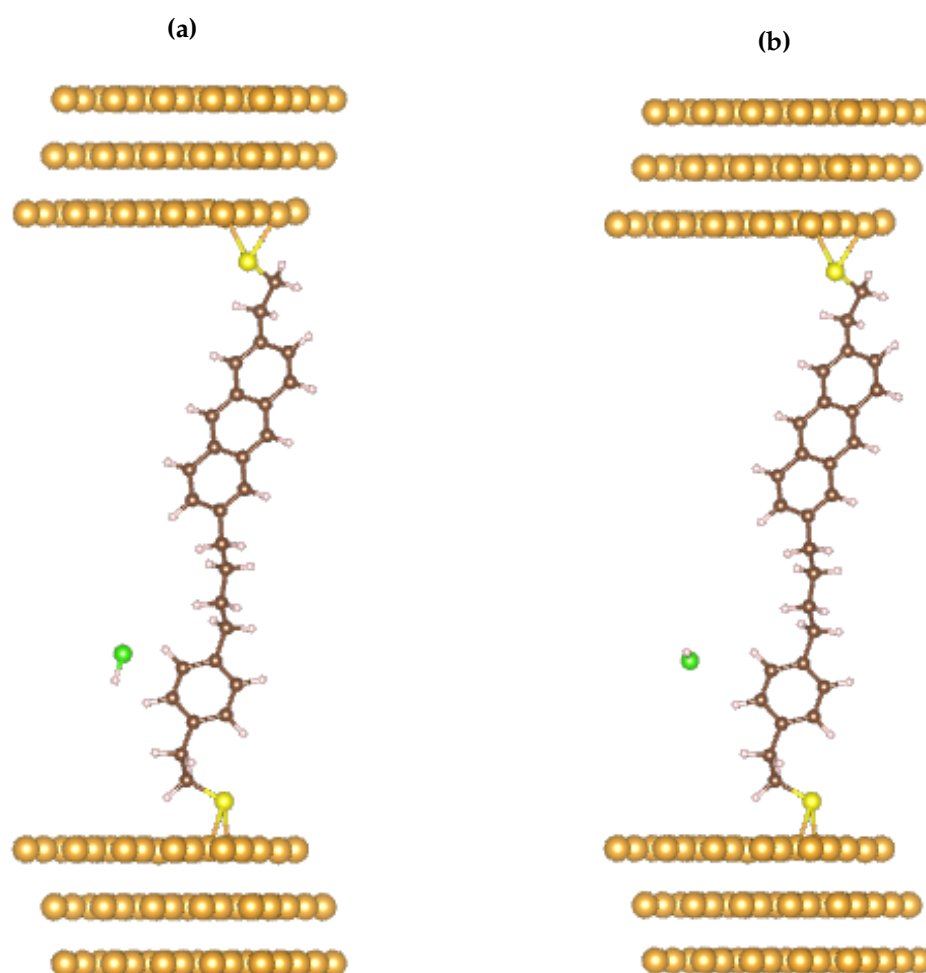


Figure 7.6: The geometries of ben-ant242 with HCl a) initial geometries b) optimized geometries. For the initial geometry, the HCl is placed in the middle position between the two H atoms on the benzene, simulating the non-covalently bonded geometry in Figure 7.5b

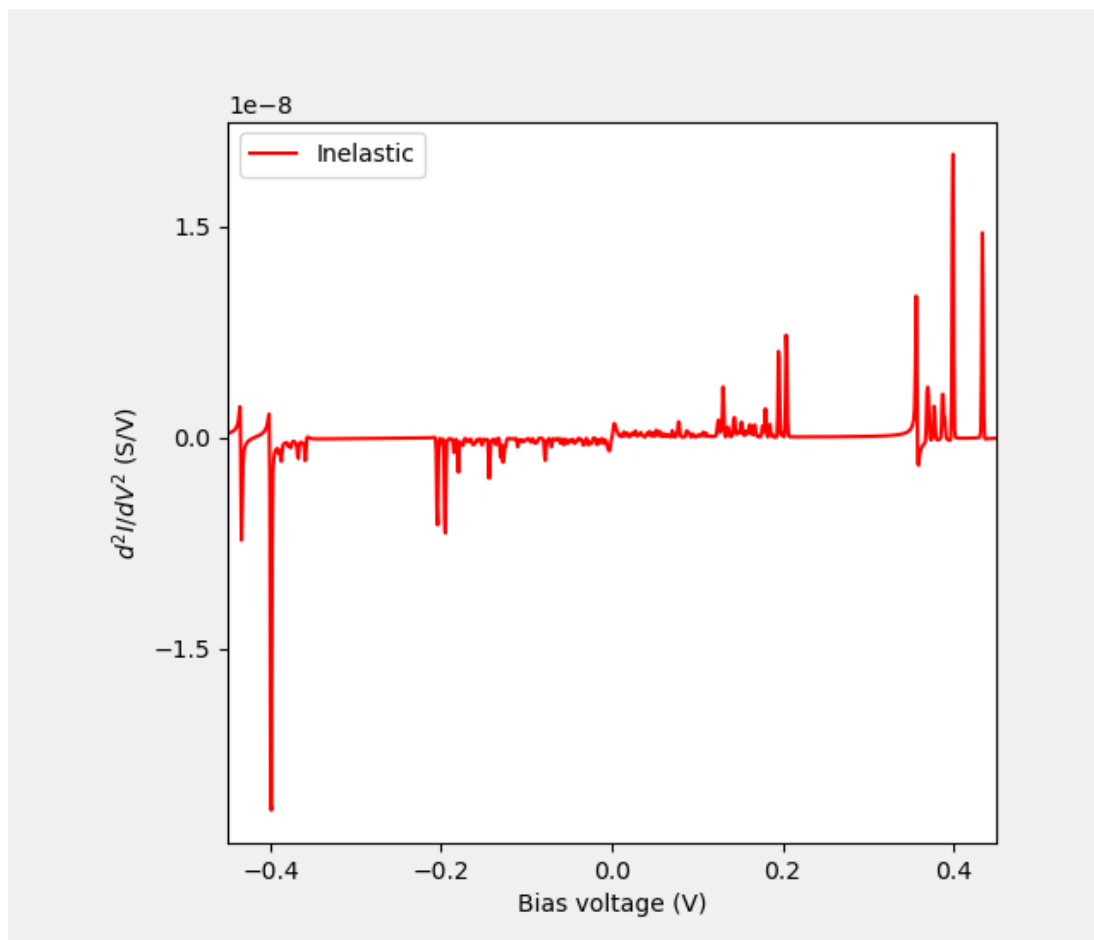


Figure 7.7: The IETS of ben-ant242 with HCl which is not optimized. The peaks at 0.4 eV belong to HCl. The observation of the peaks of HCl does not demonstrate that the sensor can detect the existence of an external odorant as the structure is not relaxed.

HCl probably tends to move within the region and finally settle at a position with lower energy. This means HCl will not stay in the initial position but escape from the sensor molecule. Even though HCl can be detected in the inelastic tunneling spectrum if it stays in the initial position, it cannot be guaranteed to remain there long enough for the sensor to recognize it. This is why the observation of the peaks, both in our results and those in the reference, is encouraging but not significantly meaningful.

The atomistic understanding of why we can observe the peaks of HCl in the initial geometry but not in the optimized geometry remains unclear. The key difference between the two geometries is the position of HCl, which also determines the distance from HCl to the sensor molecule. We speculate that

the closer the HCl is, the stronger the coupling between HCl and the sensor molecule. The stronger coupling enables the stretching mode of HCl to affect the electron transport through the sensor molecule to a large extent.

The odorant, HCl, functions as the side group in our geometries. The stretching mode of HCl is localized on the odorant itself, not extending to the main electron transport pathway if HCl is far from the sensor molecule. Therefore, the mode does not affect the electron tunneling, being inactive in IETS, according to Alessandro Troisi's work [144]. Alessandro Troisi has derived propensity rules for inelastic electron tunneling spectroscopy of molecular wire junctions using a perturbative approach to simple model systems. The author examines how IETS can follow well-defined propensity rules influenced by molecular symmetry and topology within the junction.

The main conclusion which can be insightful to our research is that modes that do not alter the coupling between electrodes along the primary tunneling paths are less influential in inelastic electron tunneling spectroscopy (IETS). As an illustration, vibrational motions predominantly involving side groups of a molecular wire exhibit reduced activity in IETS measurements. Furthermore, vibrations localized on atoms that do not contribute significantly to the crucial tunneling pathways also tend to be less active spectroscopically in IETS.

7.2.3 Inelastic Tunneling Spectrum without bridging areas

The bridging area is intended to connect the donor and the acceptor but now acts as a barrier, preventing the HCl from integrating into the electron pathway and affecting electron transport. The presence of the CH₂ groups provides an alternate channel for the electrons, significantly reducing the likelihood of electrons hopping into the odorant before hopping back to the sensor molecule.

Inspired by Alessandro Troisi's work, to exhibit the peaks of the odourant in the IETS the vibrational mode of HCl must affect the main electron transport pathway. As the bridging CH₂ groups create a barrier, the straightforward

way to incorporate the odourant into the main electron transport pathway is to remove the CH₂ groups and substitute HCl directly between the donor and the acceptor.

The new geometry is shown in Figure 7.8. To increase the connection between the odorant and the remaining donor and acceptor, OH functional groups are inserted at the tails, and the odorant HCl is replaced by HF, which has a stronger polar bond due to the greater electronegativity of fluorine. The negative charges on the oxygen atoms attract the hydrogen in HF, and the strong electrostatic interaction forms a hydrogen bond, causing HF to remain in the middle part between the sensor molecules.

The Inelastic Tunneling Spectrum (IETS) of the optimized new geometry is shown in Figure 7.9. A peak corresponding to the odourant at 0.38 eV is finally observed. With this optimized geometry and energy-favorable position for the odourant, we are confident that our sensor is capable of detecting the odourant through the inelastic tunneling spectrum.

In the high energy range, above 0.2 eV, the peaks are well-separated and it is convenient to determine their corresponding vibrational modes, typically stretching modes. In contrast, the peaks at the low bias range overlap with each other. These low bias peaks are analogous to the peaks in the fingerprint region of an IR spectrum, characterized by a unique, complex pattern of absorption peaks arising from various bending and twisting vibrations of molecular bonds. Similarly, the peaks at the low bias range in IETS correspond to the deformation modes of the molecules.

Stretching modes involve changes in bond lengths, while deformation (bending) modes involve changes in bond angles. Typically, deformation modes require lower energy because they involve altering the angles between bonds rather than changing the bond lengths. The force constants for bending motions are lower than those for stretching motions, resulting in lower energy requirements for bending vibrations.

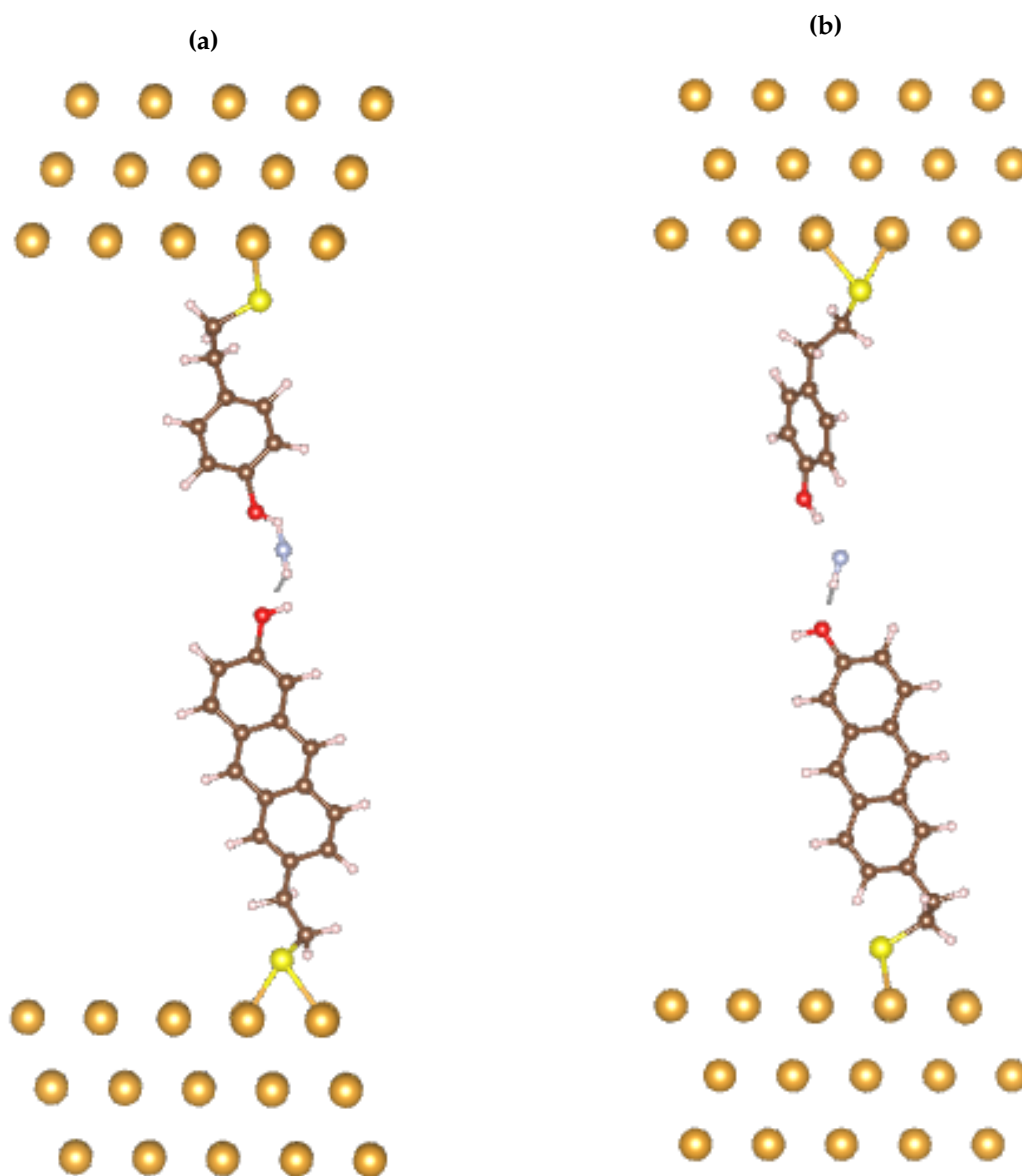


Figure 7.8: The new geometry replacing the CH_2 groups with the odourant. a) Initial geometry. b) Optimized geometry. To increase the connection between the odourant and the remaining donor and acceptor, OH functional groups are inserted at the tails, and the odourant HCl is replaced by HF

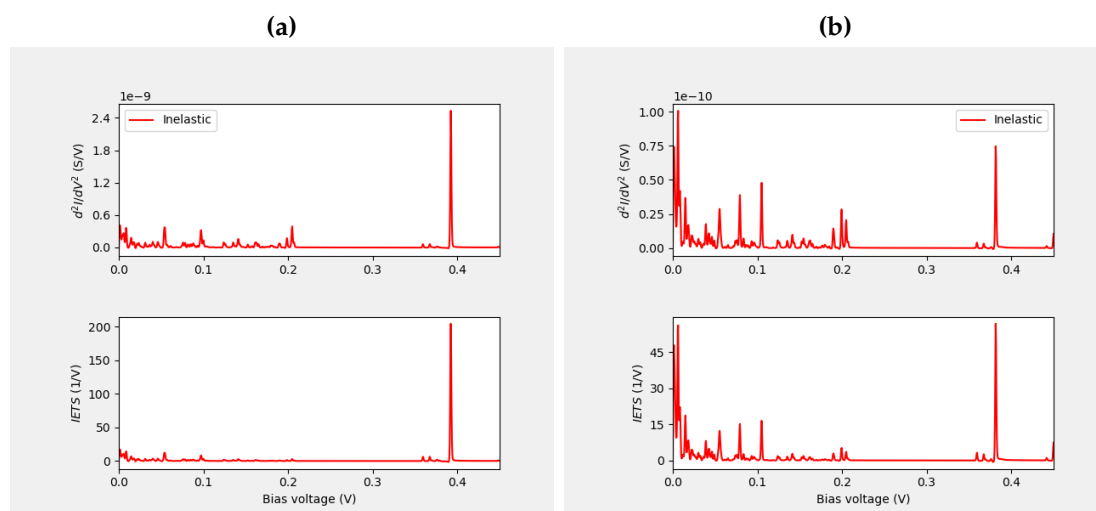


Figure 7.9: The IETS of the new geometry replacing the CH_2 groups with the odorant. a) Initial geometry. b) Optimized geometry. A peak at 0.38 eV corresponding to the odorant in the optimized geometry is observed. The HF peak in the initial geometry is significantly higher than the same peak in the optimized geometry.

The peaks at low bias ranges, as shown in Figure 7.9 b), are activated by the deformation modes of the molecules. The bending of the molecules typically involves most of the atoms, which contribute significantly to electron transport. Consequently, the intensity of the peaks near 0 V is strong. However, these strong peaks near 0 V are not useful for characterizing the molecule, as it requires only a small amount of energy to bend, and most molecules exhibit strong peaks near 0 V corresponding to deformation modes.

We also calculated the IETS of the initial, non-optimized geometry. The highest peak, corresponding to the stretching mode of HF, is a bit higher than the same peak in the optimized geometry. This makes sense, as in the initial geometry, as shown in Figure 7.8 a), HF is so close to the OH group that the hydrogen bond between them is comparable to the H-F bond. The close interaction between the odorant and the sensor molecule enables the stretching mode of the odorant to affect electron tunneling along the main pathway.

Similarly to our approach in testing the IR activity of our sensor molecules, small odourants were inserted into the system to form mixtures. We calculated

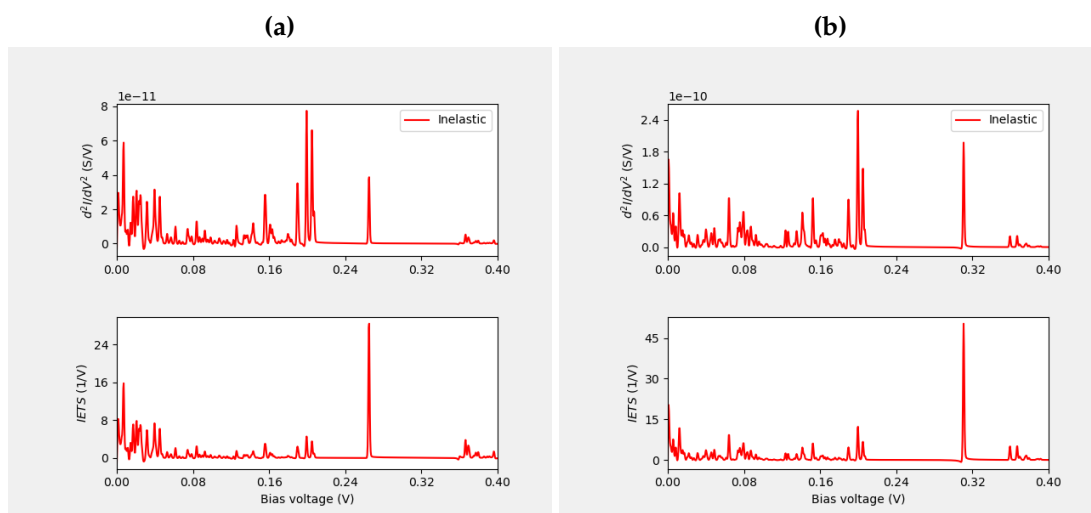


Figure 7.10: The IETS of the mixture of updated system a) HCN b) HCl

the IETS of these mixtures to observe the response of our sensor molecules to small odourants including HCl, and HCN, as shown in Figure 7.10.

7.2.4 The inelastic current of the corresponding model

The elastic and inelastic currents of our updated sensor system with HF inserted are shown in Figure 7.11. The overall currents, both elastic and inelastic, are small, reaching values less than 10^{-9} A. Compared to the current of ben-ant242s, the characteristic NDR peak is not observed in the elastic $I(V)$ figure of our new system. This is reasonable since the structure of our sensor molecule has been modified, resulting in a different molecule. We have deleted the four CH_2 groups that served as the bridging area and added OH groups at the tails of both fragments to trap the odorant.

To our surprise, an unexpected peak occurred around 0.4 V. The inelastic current was significantly larger than the elastic current, turning extremely negative and suddenly becoming positive. The origin of this negative peak remains unclear. We also calculated the inelastic current of our previous model, ben-ant242, with HF, which could not detect the existence of the odourant from IETS. As expected, the presence of the external odourant did not affect electron transport, and what

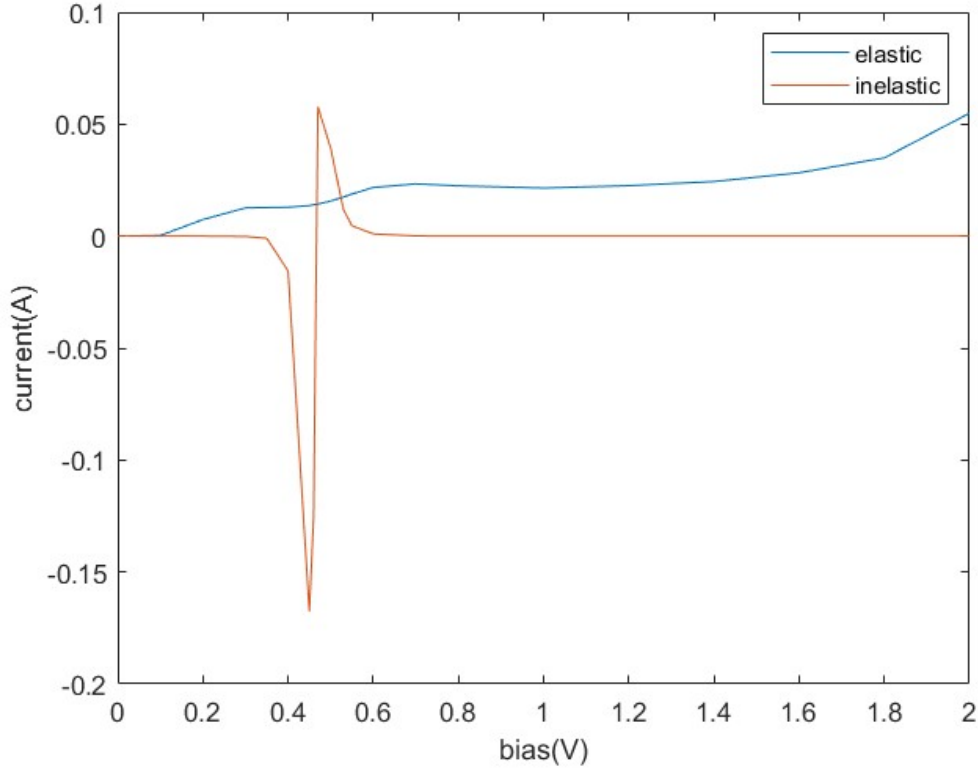


Figure 7.11: The elastic and the inelastic current of the updated sensor system. The overall currents, both elastic and inelastic, are small, reaching values less than 10^{-9} A. An unexpected peak in the inelastic current occurred around 0.4 V.

is shown in $I(V)$ Figure 7.12 is that the inelastic current is negligible compared to the elastic current.

In principle, the total current, including both elastic and inelastic components, should exhibit three peaks if the tunneling behavior of the electrons follows Fermi's Golden Rule, as shown in Figure 7.13. Fermi's Golden Rule is a formula in quantum mechanics that calculates the transition rate between two energy states, and is given by:

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \delta(E_f - E_i) \quad (7.1)$$

where:

- i is the initial state

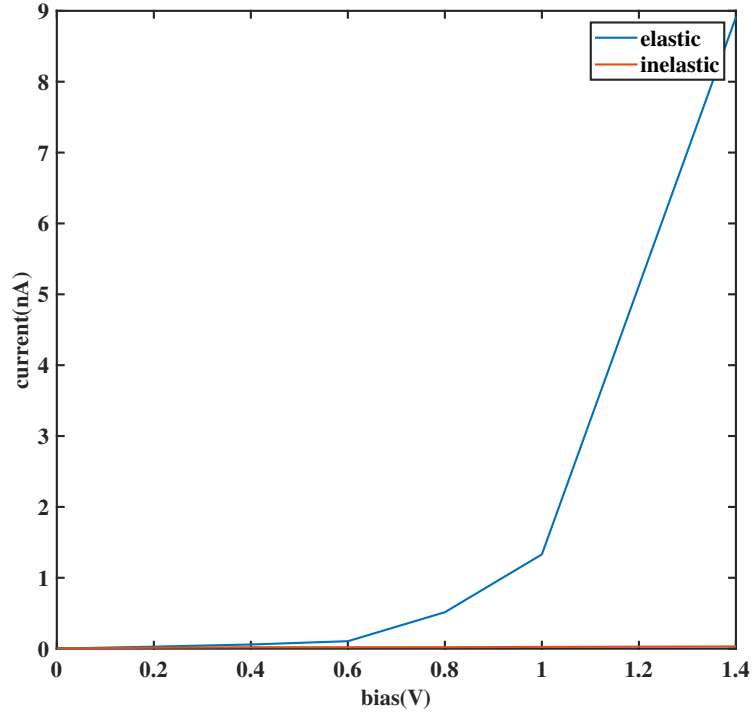


Figure 7.12: The elastic and the inelastic current of our previous sensor system. The inelastic current is negligible compared to the elastic current.

- f is the final state
- $\Gamma_{i \rightarrow f}$ is the transition rate from the initial state $|i\rangle$ to the final state $|f\rangle$.
- $\hbar$ is the reduced Planck constant.

Once the energy difference $E_f - E_i$ matches the vibrational energy of the odorant, the electron transitions from the initial state to the final state, releasing or absorbing energy to the odorant. Two inelastic current peaks would be observed alongside the main elastic peak.

7.2.5 The structure of capacitors

Apart from the previous linear structures, we are also exploring other potentially stable configurations that provide space for an odorant to reside.

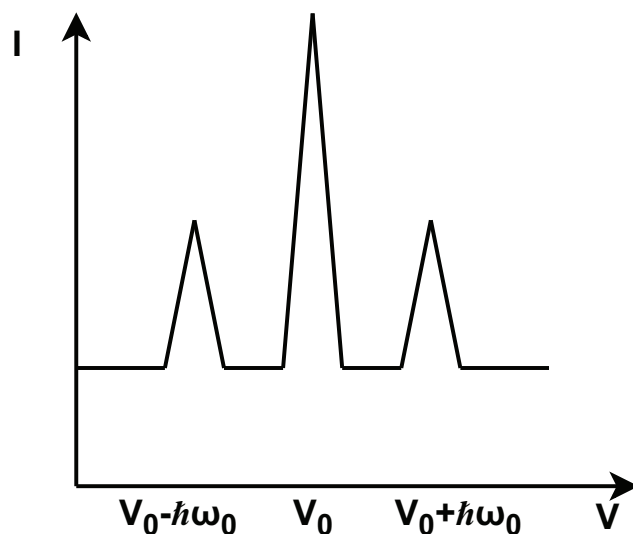


Figure 7.13: The ideal $I(V)$ figure if the inelastic electron tunneling follows Fermi's golden rule. Apart from the main highest peak, two smaller peaks originate from the inelastic interaction.

Porphyrins are a group of organic compounds characterized by their large heterocyclic ring structure, consisting of four interconnected pyrrole subunits forming a macrocycle. This macrocycle has the ability to coordinate metal ions at its center, giving rise to a variety of biologically significant molecules.

As depicted in Figure 7.14, porphyrins feature large aromatic rings conjugated throughout the molecules. By utilizing two porphyrins as the donor and acceptor respectively, we aim to utilize π - π stacking interactions to pair these molecules like capacitors. Similar to two parallel plates of a capacitor, the space between them accommodates the odourant, which can influence electron transport between the capacitors.

The optimized geometry inserted between electrodes is shown in Figure 7.15. Mg atoms were placed in the center, and the interaction between Mg and N on the other porphyrin molecule stabilizes the geometry, forming a dimer. The

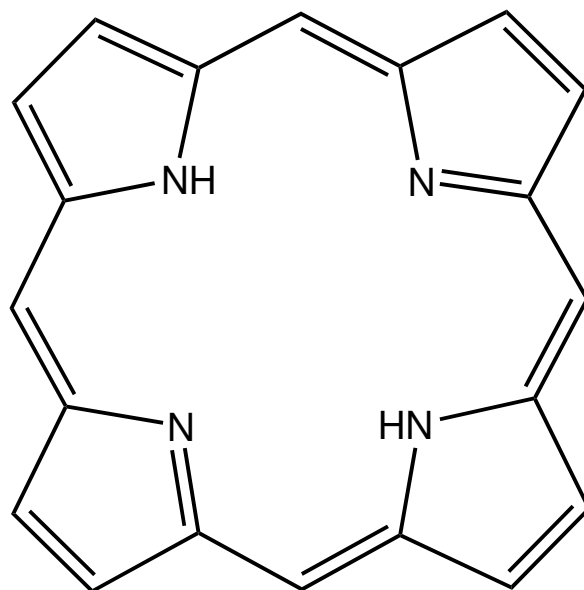


Figure 7.14: A porphyrin features large aromatic rings conjugated throughout the molecules.

reason why Mg is selected is that the calculation containing Mg does not involve spin calculations, which is less demanding for computational resources.

However, the stable geometry does generate a serious issue: the insertion of the odorant between the two porphyrins breaks the symmetry and makes the overall system unstable. We calculated the absorption energy of HCl as the odorant according to the following equation:

$$E_{\text{absorption}} = E_{\text{total}} - E_{\text{HCl}} - E_{\text{porphyrins}} \quad (7.2)$$

The absorption energy of HCl into the system is 0.278254 eV. The positive value indicates that it is energetically unfavorable for HCl to reside between the two capacitor-like porphyrins.

The more energetically favorable geometry is for the odourant to adhere to the Mg atoms on either side of the dimer, rather than between the two porphyrins, as shown in Figure 7.15 b). This geometry is rationalized by maintaining the symmetry of the dimer while ensuring HCl retains a strong connection to the sensor molecule. However, the odourant is not located in the main electron

pathway; instead, it functions as a side group of the sensor molecule. Its presence does not affect electron transport to the extent where a characteristic peak can be observed in the IETS

7.3 Strengths, Weaknesses, and Experimental Relevance

This chapter explores the impact of phonon interactions and inelastic tunneling on the transport properties of molecular junctions. As a complement to the previous chapter, the integration of vibrational effects into the electronic transport framework provides a comprehensive understanding of the electron transport behaviour in the molecular junctions. By employing inelastic electron tunneling spectroscopy (IETS) simulations, the study connects the configurations of molecular mixtures and the corresponding transport properties, offering valuable insights into the factors of electron phonon interaction. These findings contribute to the broader understanding of molecular electronics, particularly where vibrational modes play a critical role, such as chemical sensing.

The obvious limitation of the results in the chapter is the peculiar shapes of the elastic and inelastic current of the updated molecular sensor. There are several factors that could lead to the observed inelastic current which departs from what we expect from Fermi's Golden Rule. We calculated the dynamical matrix and the Hamiltonian derivative using only the Γ point to sample the Brillouin zone. Although this approximation is considered reasonable and widely used in transport calculations, we are uncertain about the potential impact of conducting k-point calculations, which are computationally expensive and currently beyond our resources. Adopting a higher k-point scheme would likely improve accuracy.

Additionally, we computed the dynamical matrix and the Hamiltonian derivative assuming zero bias, and reused these during finite bias calculations. Again, we employed this approximation to save computational time, but we are unsure about the accuracy compared to recalculating the dynamical matrix and Hamiltonian derivative for each applied bias voltage. Large biases can

potentially affect device geometry and even the atomic vibrations involved in vibrational modes.

Lastly, errors may stem from the lowest order approximation itself. The LOE approximation is applicable in systems with weak electron-phonon coupling and a slowly varying density of states (DOS) with energy. However, our sensor system violates these prerequisites. The NDR peak is sharpened due to the weak coupling between the molecule and the electrodes, as well as within the molecules themselves. Consequently, the density of states becomes exceptionally sharp. The interaction at the peaks of the density of states, which is crucial for generating the characteristic NDR peak, is neglected in the lowest order expansion because these peaks in the DOS fluctuate intensely. Thus, our sensor system directly contradicts the requirement of a slowly varying density of states (DOS) assumed in the lowest order expansion.

The experimental relevance of this chapter lies in its potential to provide general guidance for the design and testing of molecular sensors that rely on vibrational modes for selectivity. While the vibrational calculations may not fully account for experimental complexities and are oversimplified under some circumstances, they offer valuable general pointers for understanding how molecular structures influence inelastic contributions to current flow. Our effective modification of the original model suggests strategies for optimizing molecular structures to enhance sensitivity to specific vibrational modes.

Self-assembled monolayers (SAM) provide a practical approach to realizing the updated molecular model composed of two separated fragments discussed in this chapter. SAMs are widely used for organizing molecules on surfaces, making them suitable for creating the necessary molecular junctions for testing inelastic electron tunneling spectroscopy (IETS) and related transport phenomena. For instance, Wang et al. investigated the IETS of an alkanedithiol SAM using a nanometer-scale device, revealing distinct vibrational signatures of the molecules within the junction [145].

While the original model seems to fail to distinguish the inelastic vibrational contributions of external molecules in computational calculations, it remains valuable to test these aspects experimentally. Unlike the controlled setup in calculations, where one odorant corresponds to a single sensor molecule, experiments are likely to involve a significantly higher ratio of odorants to sensor molecules. This proliferated concentration of odorants could amplify inelastic contributions to the sensor, potentially deviating from the calculated predictions and introducing inelastic signals into the IETS measurements.

7.4 Conclusion

In this chapter, inelastic tunneling of electrons, which primarily involves electron-phonon interaction, has been included in the calculations to evaluate the performance of our sensor molecule, complementing the elastic study in the previous chapter. It turns out that our previous model, ben-ant242, with 4 CH₂ groups connecting benzene and anthracene, is not capable of detecting the existence of an external odorant in either the inelastic tunneling spectrum or the I(V) curve when the lowest order expansion approximation is applied.

The reason for this is that the presence of the 4 CH₂ groups as the bridging area facilitates easy elastic transport of electrons, rendering the odorant equivalent to a side group of the entire sensor molecule. Vibrational modes involving only a side group do not significantly affect electron transport in the primary pathway.

To detect the odorant in IETS, the sensor model was modified by removing the bridging area and inserting the odorant between the remaining fragments. In this case, electrons must travel through the odorant and are affected by its vibrational modes. With this modification, a series of molecules have been successfully detected in IETS. However, the modification did not affect the I(V) curve effectively, and unusual current peaks were observed, which require further investigation.

7.5 Methodology

In this chapter, all calculations were conducted using QuantumATK V-2023.12 [130]. We employed Trouiller–Martins type pseudopotentials [146] and Double Zeta Polarized basis sets, except for the gold atoms, where a single zeta polarized basis set sufficed.

The electrodes in our system consist of a 5×5 atom slab of gold, for which the use of a single zeta basis was adequate. The cutoff energy for the density mesh was set to 225 Ry, and a $1 \times 1 \times 100$ k-point mesh was utilized. NEGF calculations for transport properties were conducted using the Non-Equilibrium Green’s Function (NEGF) Method in QuantumATK V-2023.12 [119].

To obtain the inelastic tunneling spectrum of the system, we first calculated the Dynamical Matrix and the Hamiltonian Derivatives. Since our interest lies in the vibrational modes of the odourant and the sensor molecules, the gold atoms in the device region and electrodes were kept fixed during these calculations. Moreover, these quantities were sampled only at the Γ point to conserve computational resources. This approximation is justified as the device and electrodes in our system are sufficiently large to describe transport behavior at the Γ point.

Once the Dynamical Matrix and Hamiltonian Derivatives were obtained, they were used to compute the inelastic current and subsequently the inelastic tunneling spectrum, which is the second derivative of the current. Although these quantities were computed at 0 V bias, they were also applied in finite bias calculations to optimize computational efficiency and avoid redundant calculations.



Figure 7.15: The geometry of the porphyrin capacitors. Mg atoms were placed in the center, and the interaction between Mg and N on the other porphyrin molecule stabilizes the geometry, forming a dimer.

CHAPTER 8

CONCLUSION AND FUTURE PLAN

Look on every exit as being an entrance
somewhere else

—Tom Stoppard

8.1 Overview

This thesis details the development of a single molecular sensor designed to detect odourants based on the vibrational theory of olfaction. Beginning with a theoretical 1D tight-binding model, we established a foundational understanding of the relationship between current profiles and coupling strengths — both intramolecular and extramolecular. By manipulating onsite energies α_i and hopping integrals b_i , we simulated metal chains and molecular junctions featuring donor-acceptor pairs.

Expanding upon the basic 1D model, we substituted five constituent sites with actual molecules: a bottom anchoring group, a bottom moiety, a bridge, a top moiety, and a top anchoring group. Our investigation focused on achieving sharp Negative Differential Resistance (NDR) peaks essential for molecular sensor functionality. We systematically adjusted the lengths of bridges and

anchoring groups, analyzing their impact on the intensity and shape of the I-V curve, influenced by coupling strengths between donor-acceptor pairs and electrodes. These rules facilitated the design of a molecular resonant tunneling diode capable of exhibiting sharp NDR peaks, thereby enhancing sensor selectivity. Notably, our calculations omitted momentum relaxation and electron-phonon interactions within the DFT-NEGF framework, which is a limitation.

However, after including the inelastic tunneling interaction in our calculations using QuantumATK, our earlier model known as ben-ant242, which consists of benzene and anthracene linked by four CH₂ groups, has been found inadequate for detecting the presence of an external odorant. This inadequacy is apparent in both the inelastic tunneling spectrum and the current-voltage (I-V) characteristics when employing the lowest order expansion approximation.

To overcome these limitations, we redesigned the sensor model by removing the bridging region and positioning the odourant directly between the remaining molecular fragments. This modification forced electrons to pass through the odourant, thereby interacting with its vibrational modes. Subsequently, we successfully demonstrated the detection of various molecules using inelastic electron tunneling spectroscopy (IETS). However, this adaptation did not lead to improvements in the current-voltage (I-V) characteristics.

8.2 Concluding remarks and future outlook

Our findings provide insights into molecular engineering and could support a new type of electronic nose capable of recognizing odors. While purely theoretical-computational, our innovative approach offers insightful design rules for molecular sensors using the NEGF-DFT methodology. The design rules are as follows:

- Weak coupling between the molecular donor and molecular acceptor.
- Weak coupling between the molecules and the electrodes.
- Proximity of the highest occupied molecular orbital (HOMO) of the acceptor to the Fermi energy of the electrodes.

If we consider the inelastic tunneling behavior of electrons, our findings support Alessandro Trois's claims [144] that vibrational modes which do not significantly affect the coupling between electrodes along the main tunneling paths have a diminished impact on inelastic electron tunneling spectroscopy (IETS). For instance, vibrational motion primarily involving side groups of a molecular wire exhibit reduced activity in IETS measurements. Similarly, vibrations localized on atoms that do not contribute significantly to the main tunneling pathways tend to be less active in IETS.

The total current should exhibit two distinct peaks corresponding to the vibrational modes if the tunneling behavior of the electrons adheres to the Fermi Golden Rule. Further investigation could focus on improving the selectivity in the $I(V)$ figure. With additional computational resources, we could potentially obtain more accurate results without being restricted by the limitations of current approximations. Moreover, more complex structures, such as biological compounds, could be considered as candidates, potentially forming cages to trap odourants.

We believe that our findings advance theoretical modeling in single-molecule devices, nanoelectronics, and molecular electronics, contributing fundamental knowledge crucial for developing key components of molecular sensors.

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APPENDIX A



THE PYTHON CODE OF THE TIGHT-BINDING MODEL TO GENERATE THE FIGURES IN CHAPTER 5

```
class molecule_junction:
    def __init__(self, bias, M):
        self.aL = -bias / 2
        self.aR = bias / 2
        self.bL = -5
        self.bR = -5
        self.M = M
        self.left_leads = 2
        self.bias = bias
        self.N = self.M + 4
        # number of atoms in the device region
        self.a=[self.aL] * self.left_leads +[ 0 - self.
            bias/2 , 0 + self.bias/2 ] + [self.aR] *2
        # assign value to a0, a1 ...a of size M+2
        self.b=[self.bL] * self.left_leads + [-0.1]+
```

```

[-0.1]+ [-0.1] + [self.bR] *2
# assign value to b0, b1 ... of size M + 3

```

```

def get_AB(self, from_right = False):
    eta = 0.000001
    low_bound_E = max([self.aL - 2*abs(self.bL), self
        .aR - 2*abs(self.bR)]) + eta
    upper_bound_E = min([self.aL + 2*abs(self.bL),
        self.aR + 2*abs(self.bR)]) - eta
    E = np.linspace(low_bound_E, upper_bound_E,
        50000)
    k = np.arccos((E - self.aL)/(2 * self.bL))
    q = np.arccos((E - self.aR)/(2 * self.bR))
    if from_right:
        a = self.a[::-1]
        b = self.b[::-1]
        k, q = q, k
    else:
        a = self.a
        b = self.b

    A=[] for i in range(len(a))
    B=[] for i in range(len(a))
    A[0] = np.exp(-k*1j)
    B[0] = np.exp(k*1j)
    A[1], B[1] = 1, 1
    for i in range(2, self.N):
        A[i] = ((E - a[i-1]) * A[i-1] - b[i-1] * A[i
            -2]) / b[i]

```

```

        B[i] = ((E - a[i-1]) * B[i-1] - b[i-1] * B[i
            -2]) / b[i]
    return A, B, E, k, q

```

```

def get_trans(self, from_right = False):
    '''get the transmission of a simple model'''
    A, B, E, k, q = self.get_AB(from_right)
    T = (B[self.M+ self.left_leads +1] * A[self.M +
        self.left_leads] - B[self.M + self.left_leads]
        * A[self.M + self.left_leads +1]) / (B[self.M
        +self.left_leads+1] - B[self.M+self.left_leads
        ] * np.exp(q*1j))
    R = - ( A[self.M + self.left_leads +1] - A[self.M
        + self.left_leads] * np.exp(q*1j)) / (B[self.
        M + self.left_leads +1] - B[self.M + self.
        left_leads] * np.exp(q*1j))
    # take the square of the norm of T
    T= np.abs(T) **2 * self.bR * np.sin(q) / (self.bL
        * np.sin(k))
    return E, T ,R

```

```

def get_current(self):
    '''get the current '''
    E, T, R = self.get_trans()
    kb = 8.617343e-5 # eV/K
    Tem = 300 # K
    h = 4.135667662e-15 # eV/s
    e = -1.602e-19 # C
    delta_E = E[1] - E[0]
    fL = 1 / (1 + np.exp((E - self.aL) / (kb * Tem) ))

```

```

fR = 1 / (1 + np.exp((E - self.aR) / (kb * Tem) )
        )
I = 2 * e / h * (fL - fR) * T * delta_E
I = np.sum(I) #integral
return abs(fL - fR), I

```

```

def get_dos(self):
    A_l, B_l, E, k, q = self.get_AB()
    A_r, B_r, E, k, q = self.get_AB(from_right = True
        )
    E, T_l, R_l = self.get_trans()
    E, T_r, R_r = self.get_trans(from_right = True)
    c_l = np.zeros((E.shape[0], self.N ), dtype=
        complex)
    c_r = np.zeros((E.shape[0], self.N ), dtype=
        complex)
    for i in range(self.N):
        c_l[:, i] = R_l * B_l[i] + A_l[i]
        c_r[:, i] = A_r[self.N -1-i] + R_r * B_r[self.
            N -1-i] #+ R_r * B_r[self.N -1-i]
    dos = np.abs(c_l) ** 2 + np.real(c_r * np.conj(
        c_r)) #np.real(c_l * np.conj(c_l)) np.abs(c_r)
        ** 2
    return E, dos

```