Development of a Digital Measurement System for Inelastic Tunneling Spectroscopy of Single Molecular Junctions

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“We live in a society exquisitely dependent on science and technology, in which hardly anyone knows anything about science and technology.”

Carl Sagan
Abstract

The miniaturization of the silicon-based transistor is drawing ever closer to the physical limits set by quantum tunneling. In molecular electronics, quantum tunneling is the working principle of single molecular devices. Molecular electronics is thus one of the possible solutions for moving beyond the limits of the current technology. In order to realize single molecular electronics in devices, a complete understanding of the characteristics of a molecular junction is necessary.

A challenge in the field of molecular electronics is to determine if a target single molecule is measured as expected. To confirm the existence of a molecule in a junction, inelastic electron tunneling spectroscopy (IETS) is useful since it can resolve molecular vibrations. The activated vibrational modes by electron-phonon coupling open new conduction channels in the junction and thus change the charge transport characteristics. IETS can thus provide fruitful insight in the characteristics of single molecular junctions.

This research has focused on developing and applying a fully digital low-noise method for measuring IETS in a mechanically controllable break junction. The measurement system was developed using LabVIEW to realize a digital lock-in amplifier for IETS measurement. Running the signal through solid-state circuits adds pink noise (1/f), impacting the signal-to-noise ratio. Hence, the constructed system has an inherent advantage to conventional methods using commercially available lock-in amplifiers since there is no need to connect an external adder circuit. Taking advantage of the freedom of signal design, a carrier wave (CW) sweep type was developed. Using the CW sweep type allows for an order of magnitude higher IV curve resolution during the IETS measurement.

A fully automated IETS measurement setup was developed with sophisticated automatic amplifier gain and automatic control of the break junction process. The automated system allows for probing IETS in different single molecular conformations and also for investigating the effect of stretching a molecule. Several molecules were investigated, with focus on an oligothiophene molecule (5T).

The developed measurement system can effectively measure IETS in single molecular junctions at a low noise level. During stretching of the 5T molecule, a Au-S peak blue shift was observed indicating stretching of the bond. New vibrational modes were also observed near molecular detachment due to stretching, indicating charge transfer through the entire molecule.
Abstract


En utmaning i molekylärelektroniken är att bestämma om en specifik singelmolekylövergång är möjlig som förväntat. För att bestämma om en molekyl finns i en övergång är inelastic electron tunneling spectroscopy (IETS) användbart eftersom man analyserar molekylära vibrationer. Aktiverade vibrationer genom elektron-phononkoppling öppnar nya konduktionskanaler i övergången och kan således ändra laddningstransportskarakteristiken. IETS kan således ge användbar insikt i singelmolekylövergångars egenskaper.

Detta arbete är fokuserat på att utveckla och tillämpa en digital låg-brus metod för mätning av singelmolekylövergångar i en mechanically controllable break junction. En digital lock-in amplifier för mätning av IETS är utvecklad i programmeringsspråket LabVIEW. Om man leder en signal genom elektroniska kretsar adderas skärt brus (1/f) till signalen vilket påverkar signal-brusförhållandet. Därmed har systemet utvecklat i detta arbete en fördel jämfört med konventionella metoder som använder kommersiellt tillgängliga lock-in amplifiers eftersom det inte finns behov för att koppla in en extern adderare. En bärvägsmetod för IETS är även utvecklad i detta arbete. Användande av bärvägsmetoden tillåter en storleksordning högre upplösning i ström-spännings mätning under IETS jämfört med konventionella metoder.

En helautomatisk mätningssystem för IETS utvecklades med sofistikerad automatisk förstärkning och automatisk kontroll av mechanically controllable break junction enheten. Det automatiserade systemet möjliggör IETS för olika elektrod-molekyl konformationer och undersökning av sträckning av molekyler. Ett flertal molekyler undersöcktes med fokus på en oligotiofenmolekyl (5T).

Det utvecklade mätningssystemet kan effektivt mäta IETS i singel-molekylövergångar vid låg brusnivå. Under sträckning av 5T molekylen observerades en blåförskjutning av Au-S vibrationen, vilket indikerar sträckning av bindningen. Nya vibrationer uppstod även vid sträckning av molekylen vilket indikerar laddningstransport genom hela molekylen.
I would like to thank Professor Hirokazu Tada for having me at his laboratory. Without him, this project would have been an impossible task from the beginning. With this being the second time writing a thesis in his laboratory, I am much grateful for his hospitality.

I would like to thank my project advisor Associate Professor Ryo Yamada for providing invaluable guidance and mentoring throughout the process. I cannot help but feel that he has made me grow both as a person and as a scientist. I would further like to thank Dr. Tatsuhiko Ohto for fruitful discussions on the theoretical aspects of the field. I would also like to thank him for performing the calculations for Raman and IR spectroscopy of the 5T molecule, greatly helping with interpretation of the results.

I would like to thank my examiner Associate Professor Gunnar Malm for having an open mind and letting me perform research on the topic of my own interest. I would finally like to thank Takashi Shimomise for helping me through the junction manufacturing process, for performing measurements and for constructing a marvelous low temperature equipment.
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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>5T</td>
<td>5-Thiophene-di-SCN</td>
</tr>
<tr>
<td>8T</td>
<td>8-Thiophene-di-SCN</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AD</td>
<td>Analog-Digital</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BDT</td>
<td>Benzene-[1,4]-dithiol</td>
</tr>
<tr>
<td>DA</td>
<td>Digital-Analog</td>
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<td>DC</td>
<td>Direct Current</td>
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<tr>
<td>DFT</td>
<td>Discrete Fourier Transform</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HDD</td>
<td>Hard Disk Drive</td>
</tr>
<tr>
<td>IDFT</td>
<td>Inverse Discrete Fourier Transform</td>
</tr>
<tr>
<td>IETS</td>
<td>Inelastic Electron Tunneling Spectroscopy</td>
</tr>
<tr>
<td>IFFT</td>
<td>Inverse Fast Fourier Transform</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>IV</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>MCBJ</td>
<td>Mechanically Controllable Break Junction</td>
</tr>
<tr>
<td>NEGF</td>
<td>Non-Equilibrium Green’s Function</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>SAM</td>
<td>Self Assembled Monolayer</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-Noise Ratio</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscope</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
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Physical Constants

<table>
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<th>Constant</th>
<th>Value</th>
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<td>Euler’s number</td>
<td>$e = 2.71828$</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>$k_B = 1.38065 \times 10^{-23} \text{ J/K}$</td>
</tr>
<tr>
<td>Elementary charge</td>
<td>$q = 1.60218 \times 10^{-19} \text{ C}$</td>
</tr>
<tr>
<td>Reduced Planck’s constant</td>
<td>$h = 1.05457 \times 10^{-34} \text{ Js}$</td>
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Chapter 1

Introduction

This chapter begins with a brief introduction of the current state in nano-scale electronics. It then continues with a short overview of the field of molecular electronics. Inelastic electron tunneling spectroscopy is introduced as a possible method for researching some known issues in molecular electronics. Finally, the focus of this work is detailed.

1.1 Background

During the last fifty years, there has been a steady development of faster, more economic and efficient integrated circuits summarized by Gordon Moore in what is known as Moore’s law. Although described in different forms, the essence of Moore’s law is an exponential development of integrated circuits with a doubling of performance, or transistor density, roughly every two years. There is still demand for faster and better products, but the current way of improving the manufacturing process will soon run headfirst into the physical limits of small devices.

The top-down method of creating transistors by using photolithography to create patterns for integrated circuits has so far been the focus of development in the industry. To put it simply: develop a better lithographical unit and hence the circuit design can be made smaller and faster. There are of course a number of other challenges to take into account, but the main technological feature defining the industrial progress has been the resolution of the photolithographical unit. Moving toward the 10 nm scale requires the development of techniques such as extreme UV [1], which is economically expensive but still physically possible. Given a few more technological nodes, the problem is no longer of economic nature, but physical; namely quantum tunneling. The leakage current through the channel of the transistor will be too large in the off-state and there will
Chapter 1. Introduction

no longer be any use in making the transistor any smaller. Hence, there is a need to move beyond the era defined by photolithographical improvement to what is commonly known as more-than-Moore.

1.2 Molecular Electronics

Molecular electronics is a field involved in researching the properties of single or several molecules for creating possible future molecular devices. The birth of molecular electronics was in the early 1970’s with Mann and Kuhn’s paper on charge transport through fatty acid salt monolayers [2]. The idea of single molecular electronics was soon conceived in the theoretical paper by Aviram and Ratner in 1974, describing charge transport through a single molecule and single molecular rectification [3]. However, it was not until the 1980’s, when the scanning tunneling microscope (STM) and the atomic force microscope (AFM) were invented that the field really could start moving forward [4]. Since then, simple but effective methods for measuring single molecular junctions such as the mechanically controllable break junction (MCBJ) have been conceived; providing more tools for researchers to investigate the molecular junction characteristics. The advantage of the MCBJ technique, except for being simpler than the STM, is that it can maintain more stable junctions due to very low inter-electrode drift.

The inherent advantage of using single molecules as functional devices is the incredibly small volume occupied by a molecule. If for example a single molecule can be used as a functional element of an integrated circuit, the resulting component size can be drastically reduced and technological improvement might be able to move beyond Moore’s law.

There are, however, some issues with using single molecules for practical applications in the near future.

- Single molecular junctions are generally not stable at room temperature.
- Accurate positioning of molecules is difficult and there is still not good reproducibility for single molecular junctions [5].
- The characteristics of single molecular junctions are still not thoroughly understood.

In order for the field to move forward, the fundamental characteristics of molecules first need to be researched in order to provide a basis for developing practical devices. If there
is a thorough understanding and an experimental database of the features of molecular junctions, solutions for the issues mentioned above might become clear.

1.3 Inelastic Electron Tunneling Spectroscopy

Examining charge carrier transport through a single molecular junction is important for the realization of devices; but when measuring current–voltage (IV) response in single molecular junctions, it is difficult to determine if the target molecule exists in the junction. Even the most basic conductance measurement of single molecular junctions is problematic due to variations between measurements [4]. There is thus a need to use another technique in addition to the IV measurement to elucidate the nature of the probed junction. Inelastic electron tunneling spectroscopy (IETS) provides a way for analyzing the contents of a molecular junction by the inelastic contribution to the current passing through it [6]. The vibrational modes of the molecule in the junction may be excited by electron–phonon interaction, which shows up as peaks or dips in the second derivative of the current–voltage curve [7]. Peak location thus provides information on the nature of a molecular junction and is a valuable tool for analyzing single molecular junction characteristics.

When having molecules of different species adsorbed to a surface, it is of interest to be able to tell them apart. For molecules that are similar in chemical composition and structure, this might be very difficult; however, IETS can provide a solution for investigating such scenarios on the single molecular level. It was shown by Sainoo et al. that due to the selective activation of the $\nu$(C–H) mode between trans–2–butene and butadiene, IETS mapping by the STM could successfully distinguish closely spaced molecules of the two species apart [8]. This is an example of the power of the IETS technique.

Kim et al. showed a frequency shift of molecular vibrations for both Au–S and Pt–S configuration junctions by using IETS [9]. It is commonly known that the molecular anchor S–Au bond formed is strong. When the electrodes of a junction are retracted, the chemical bonds in a molecule attached to both electrodes will be stretched. The vibrational modes involving the stretched bonds thus change in frequency, in a sense as a guitar string changes in frequency as it is stretched. It was found that the soft nature of the gold electrodes made the Au–S vibrational mode shift less compared to when using the stiffer Pt electrodes. Arroyo et al. reasoned that the shifting of molecular peaks due to stretching unambiguously determines that the molecular junction probed only contains a single molecule [10]. Hence, IETS can be used as a tool for determining
if the junction consists of a single molecule and also for revealing the effect of mechanical stress on the single molecular scale.

Since the inelastic tunneling observed in molecular junctions is an unavoidable phenomenon, understanding it and its implications is important for designing molecular devices. For an alkanethiol single assembled monolayer (SAM) probed by an STM it has been determined by deuteration in combination with IETS that the entire molecule contributes to the IETS signal. According to Okabayashi et al., this connects to a deeper understanding of the inelastic processes in molecular junctions that might be of importance in understanding processes such as Joule heating and device breakdown [11].

It is also of interest to gain an understanding of how molecules behave when a current is passed through them. For nanoscale junctions, phenomena such as two-level switching have been observed by Ruitenbeek et al. in an MCBJ setup [12]. The two-level switching would occur as the bias voltage is increased above a certain level. They discussed that the reason for such behavior would either be motion of the atoms closest to the junction in the electrodes induced by the current, or excitation of charge-traps changing the surface density of states. A similar phenomenon was observed by Stipe et al. for acetylene (C$_2$H$_2$) on a Cu(100) surface in an STM setup [13]. In order to research the reason for the observed switching, they deuterated one side of the molecule, creating C$_2$HD, and used IETS to determine the characteristics of the deuterated acetylene compared to the pristine acetylene. Combining the conductance measurement with IETS mapping made it clear that the switching in their scenario was due to molecular rotation on the surface. This is an excellent example of how IETS can provide information otherwise very difficult to obtain.

1.4 The Focus of This Work

There are a few problems with measuring IETS. One is that in order to effectively probe a molecule many trials must be made before conclusive results can be attained. Another is that the time taken to measure the signal at a high enough resolution takes a long time, usually on the order of a few minutes. If the experimenter needs to be present during measurements to control the equipment, it will consume valuable time. Another is that it may be difficult to understand which configuration gives rise to a certain IETS spectrum. A third is that noise during measurements can disturb the measurement. In order to address these issues, it is desirable to develop an automated low-noise IETS technique that can be applied when performing MCBJ measurement. If IETS analysis can be performed at intervals while elongating a molecular junction it might be possible
to evaluate what is measured from two perspectives, providing a better insight on the molecular junction characteristics.

This work has focused on developing and applying a new setup for measuring the IETS of molecular junctions. Construction of a lock-in amplifier in the programming language LabVIEW enabled IETS measurement without adding any extra equipment to a standard low-temperature conductance setup. Sweeping voltage levels twice allowed for checking junction stability during the lock-in measurement. A more highly resolved IV curve during the IETS measurement could be obtained by constructing a carrier wave type sweep. The lock-in measurement platform was compared to a conventional set-up and the obtained results were found to show the same characteristics. An automated junction elongation program for the MCBJ setup was developed to be used in conjunction with the IETS measurement technique. The constructed lock-in amplifier was then used for measuring Au–benzenedithiol–Au and Au–oligothiophene–Au molecular junctions at liquid Helium temperatures.
Chapter 2

Principles and Methods

This chapter gives an overview of IETS alongside the methods required to perform the measurement. The IETS characteristics are discussed, where after the mathematics behind the lock-in amplifier measurement are derived in detail. Finally, experimental details such as peak broadening and the signal to noise ratio are discussed; concluding with some discussion on digital signal manipulation.

2.1 Experimental Methods for Conductance Measurement of Molecular Junctions

In order to prepare a molecular junction it is necessary to contact the molecule to two electrodes. Since the molecules of interest are small, on the order of a few nanometers or less, it is necessary to prepare a setup that is stable to not affect the measurement. There are a few common strategies for creating stable molecular junctions, where the most common is perhaps by using a STM or an AFM. Other than the STM, popular techniques include using the an electromigrated junction and also the MCBJ [5]. I previously used the MCBJ technique for analyzing the IV characteristics of molecular junctions at room temperature [14]. In this work a MCBJ in a cryostat was used for low noise measurement at liquid helium temperatures for increased stability.

Each technique for making molecular junctions has its respective pros and cons. The electromigrated junction can be prepared on top of a gate insulator in order to provide a gating effect, but the distance between the electrodes cannot be changed once manufactured so it is difficult to probe different junction geometries [5]. Making a junction by a STM and a MCBJ is equivalent in the sense that it is possible to vary the junction length using both techniques. On one hand, the STM and AFM can readily form thousands of
junctions for measuring statistical conductance data [15]. On the other hand, a MCBJ can provide a very stable junction [16].

A MCBJ makes use of a pushing rod combined with counter supports in order to bend a substrate. When the substrate is bent, a nano-junction on top of the substrate is slowly pulled apart. An illustration of the MCBJ set up is shown in Figure 2.1.

![Illustration of the MCBJ set up](image)

**Figure 2.1:** An illustration of the experimental set up used in a mechanically controllable break junction.

The pushing rod is controlled by a piezoelectric element in order to realize a small vertical movement. Pushing the rod translates to pulling apart the electrodes horizontally. The length difference $dl$ between the electrodes by changing the height $z$ of the pushing rod can be calculated by using Equation 2.1 [17].

$$dl = \frac{6tu}{L^2} dz$$

(2.1)

Here, $t$ is the thickness of the substrate, $u$ is the distance between the photolithographically defined electrodes before electrodeposition and $L$ is the distance between the counter supports. In this work, the substrate is a 0.1 mm thick copper plate with a roughly 2 – 4 $\mu$m thick spin coated heat treated polyimide insulation layer. Other than these details, the junction fabrication method is similar to that in my previous work [14]. Inserting $t \approx 0.1$ mm, $u \approx 2$ µm, $L \approx 1.5$ cm and a smallest possible $dz \approx 1$ $\mu$m into Equation 2.1 gives $dl \approx 5.33$ pm. The distance control is hence on the order of 0.05 Å, which is much smaller than the size of the measured molecules; indicating that the instrument is able to resolve a molecular junction. Ruitenbeek et al. showed that a
similar set up had an interelectrode drift of no more than 0.2 pm/h and suggested that the technique could allow measuring IETS of single molecular junctions [12].

2.2 Inelastic Tunneling Spectroscopy

2.2.1 Principles

2.2.1.1 IETS in Molecular Junctions

A molecule containing $N$ atoms will have $3N$ different vibrational modes. The vibrational modes each correspond to a frequency $\omega_{\text{vib}}$, usually in the THz region, with a corresponding energy $E = \hbar \omega_{\text{vib}}$. The molecular vibrations can be excited by different methods such as illumination or by driving a current through the molecule. Different molecules have vibrational modes apparent at different energies, leading to a molecular fingerprint accessible by measuring the vibrational spectrum.

Techniques used to study the vibrational states of molecules include infra red (IR) absorption spectroscopy, Raman spectroscopy and IETS [18]. IETS has been of interest in studying metal–insulator–metal junctions for nearly fifty years [6, 19]. Only more recently has IETS been used to study single molecular junctions [20, 21]. The IETS measurement, explained in detail in this chapter, is performed by measuring the second derivative of a current–voltage curve, $d^2I/dV^2$, where the peaks in the spectrum corresponds to vibrational modes of the contents of the junction [22]. IETS can thus provide information about the contents of the junction, which is an otherwise difficultly addressed problem in single molecular electronics [5, 18, 22].

Figure 2.2 shows an energy diagram of a metal-tunneling-metal junction with the application of a bias voltage $V_A$. When charge carriers tunnel elastically through the junction, physical parameters such as momentum and energy are conserved from one electrode to the other. However, in the case for a tunneling charge carrier that activates a vibrational mode in the junction, some energy of the charge carrier is lost to excite the vibration. Since the charge carrier loses energy during the tunneling, it is an inelastic tunneling process. The energy loss of the charge carrier during inelastic tunneling is equal to the energy of the vibrational mode, $\hbar \omega$. 
The inelastic tunneling process can only take place if the applied bias voltage to the junction is larger or equal to the energy of the vibrational mode, $qV_A \geq \hbar \omega$. When enough bias voltage is applied, the inelastic tunneling channel will open and there will be an increase in the conductance due to the extra pathway through the junction [23]. The sudden, albeit small, increase in current will lead to an upward shift in the conductance $(dI/dV)$ as shown in the red line in Figure 2.3. If the second derivative of the current with respect to the voltage $(d^2I/dV^2)$ is studied, the step-like increase in the conductance will show up as a peak. The peak locations in the second derivative measured at a voltage $V_A$ will thus provide information on the vibrational mode frequencies of the molecule in the junction. The second derivative is therefore the experimental quantity that is measured in IETS. Molecular vibrations of interest are in the linear IV range, on the order of $10\text{–}350 \text{ mV}$, meaning that effects due to resonant tunneling through molecular orbitals, usually occurring for higher bias, should not affect the second derivative signal.
Chapter 2. Principles and Methods

2.2.1.2 Selection Rules and Peak Characteristics

The selection rules for which states are excited are determined for both IR and Raman spectroscopy but not for IETS [22]. The reason why IETS does not show selection rules is that IETS is not an effect of field–dipole moment interaction, but rather a vibronic modification of the electronic levels in the junction [22]. So in effect, all the modes excitable by Raman or infra-red spectroscopy can be excited in IETS measurement [24]. It is thus possible to compare the vibronic modes of the molecule predicted by IR or Raman calculations and experiments with obtained IETS peak locations in order to extract information on what modes are excited.

Since IETS originates from electron–phonon coupling, it is possible to obtain information on the current pathway through a molecule. It is known that only the vibrational modes of the molecule along the charge carrier tunneling path will be excited as only these modes can modulate the current [25]. Solomon et al. further explains that the peaks of highest intensity are those of vibrational modes that disturb the low bias conduction channel electron density [26]; thus providing something close to a selection rule for IETS.

The IET process can both result in an increase and a decrease in conductance. A decrease in conductance would be observed as a dip in the IET spectrum. Lauhon and Ho reasoned that certain vibrational states can interfere with the elastic tunneling channel. The largest effect of the added inelastic tunneling channel contribution and the decreased elastic tunneling will thus decide if a vibrational state leads to peak or a dip in the IET spectrum [23]. Ratner et al. modeled IETS by using the non-equilibrium Green’s function (NEGF) formalism and found that the peak versus dip behavior is due
to the coupling strength and the frontier conducting molecular orbital energy level \[7\]. Gawronski et al. further considered that a dip in the IET spectrum is due to many-body effects \[27\]. Dips in the IET spectrum have for example been observed by Hahn et al. for O\(_2\) on a silver surface \[28\].

For reference, a peak followed by a dip behavior or vice versa occurs for charge-trapping or charge-trap assisted conduction in gate dielectrics \[29, 30\]. The peak–dip behavior was also calculated possible for certain molecular junction parameters \[7, 31\]. Thus, the effects of the vibrational modes in a molecular junction are on some level similar to those of traps in a metal oxide semiconductor structure.

### 2.2.1.3 Asymmetry and Bijective Odd-Even Splitting

A certain vibrational mode in a molecule should be activated in both the forward and reverse bias directions. However, as explained by Galperin et al. by using the NEGF framework, the excitation may be asymmetric in the sense that the amplitude of a certain excitation might be different for the positive and negative bias directions \[32\]. They found that the different energy dependencies of the retarded self-energy for the molecule–electrode coupling is a possible factor causing the asymmetric peak intensity in IET spectra. In essence, if the vibrational mode is asymmetric in the junction, the IETS peak intensity might also be asymmetric.

Although the IETS result may be asymmetric, the peak locations do not change in energy. Thus, in order to assign peak locations, bijective odd/even splitting can be used to extract peaks that are common between both bias polarities, as performed by Koslowski et al. \[33\]. The odd even splitting is performed as shown in Equations 2.2 and 2.3.

\[
f_{\text{odd}} = \frac{f(V) - f(-V)}{2} \tag{2.2}
\]

\[
f_{\text{even}} = \frac{f(V) + f(-V)}{2} \tag{2.3}
\]

The odd data indicate peak locations that are symmetric, i.e. they show up as peaks for both the positive and negative voltage bias. Thus, the peak locations obtained using odd splitting indicates the vibrational modes activated in the junction. Since the IETS signal is mainly odd, the odd/even splitting is just a mathematical method for minimizing the amount of displayed data \[33\].
2.2.1.4 Peak Broadening

A peak observed in the results will inevitably be broadened due to three factors. The first factor is the intrinsic linewidth $W_{\text{intrinsic}}$. This is due to a diversity of factors such as inhomogeneous broadening or vibronic coupling of the molecule to the continuum of electron hole pairs in the metal electrodes [7, 31]. In the case of a junction containing a few thousand C8 dithiol molecules the intrinsic linewidth was found to be $3.73 \pm 0.98 \text{meV}$ [21], which might act as a guideline for the single molecular case.

The second factor of linewidth broadening is the modulation voltage amplitude, $W_{\text{modulation}}$. This is due to the experimental dynamic lock-in technique applying a finite modulation voltage to the junction. This in turn leads to a convolution of the experimental quantity and an instrumental function, calculated as $1.22 V_{\text{mod}}$ by Sangster et al. [6]. In the case for root mean square notation of the alternating current (AC) modulation voltage amplitude, the line broadening due to the modulation is given by $W_{\text{modulation}} = \sqrt{2} \times 1.22 V_{\text{mod \ RMS}} \approx 1.73V_{\text{mod \ RMS}}$.

The third factor is the thermal broadening $W_{\text{thermal}}$. For the case of normal metallic electrodes, this has been calculated to be $W_{\text{thermal}} = 5.7k_BT$ by Jaklevic and Lambe [19]. The reason for the thermal broadening is the smearing of the electron energy distribution in the electrodes, randomly enabling or disabling the electrons with an energy close to the molecular vibration energy $E = \hbar \omega$ to excite a vibration.

The peak width is measured at full width at half maximum (FWHM), with the shape being fitted using a Gaussian curve by Reed et al. and the three peak broadening factors add as the squares of the individual contributions, shown in Equation 2.4 [21]. Equation 2.5 shows the theoretical linewidth with the expected contribution factors due to thermal and modulation amplitude broadening inserted into Equation 2.4.

$$W_{\text{theoretical}} = \sqrt{W_{\text{intrinsic}}^2 + W_{\text{thermal}}^2 + W_{\text{modulation}}^2}$$ (2.4)

$$= \sqrt{W_{\text{intrinsic}}^2 + (5.7k_BT)^2 + (1.73 V_{\text{mod \ RMS}})^2}$$ (2.5)

The expected contribution factors were confirmed by Lauhon and Ho, who found an estimated intrinsic width of 6 meV, a thermal contribution factor of 5.5 compared to the expected 5.7 and a voltage contribution factor of 1.75 compared to the expected 1.73 [23].

To conclude the discussion on peak broadening, a low-temperature environment is necessary for measuring IETS since the measured peaks will broaden and become indistinguishable from each other at higher temperatures. It is also necessary to use as low modulation voltage as possible in order to decrease the effects of peak broadening.
2.2.2 Detection Method

2.2.2.1 Use of the Lock-in Amplifier

In order to measure IETS, it is necessary to obtain the second derivative of the current with respect to the bias voltage. In the case for strong signals, there is nothing hindering an experimenter to perform numerical derivation of a IV curve in order to obtain the IETS signal. However, since the IETS signals of interest occur in the low-bias near-linear region, the signal to noise ratio (SNR) is low and numerical differentiation cannot produce satisfactory results. There is thus a need to find a method for measuring the second derivative that is less sensitive to noise than numerical differentiation.

The lock-in amplifier can be used for finding the second derivative of the current with respect to the voltage, hence it can be used for measuring IETS. The lock-in amplifier analyzes the response of an added sine modulation signal at different direct current (DC) bias voltages in order to find the corresponding second derivative amplitudes. The value of the second harmonic of the applied modulation frequency $f_{\text{mod}}$, in other words the amplitude of the signal at $2f_{\text{mod}}$, is proportional to the amplitude of the second derivative of the IV curve. In essence, the lock-in technique makes use of the orthogonality of sinusoidal functions of different frequency in order to create a less noise-sensitive measurement. The details of the lock-in function are described in the following sections.

2.2.2.2 Mathematical Derivation of Higher Harmonics

The applied signal to the molecular junction contains an added sine modulation signal at a frequency of $f_{\text{mod}} = \omega_{\text{mod}} / 2\pi$. A mathematical description of the applied signal is thus a function of the DC component and the added modulation, shown in Equation 2.6.

$$V_{\text{appl}} = V_{\text{DC}} + V_{\text{mod}} \sin(\omega_{\text{mod}} t) \quad (2.6)$$

Here, $V_{\text{mod}}$ denotes the amplitude of the sine wave and $V_{\text{DC}}$ is the signal onto which the modulation is added. In order to find the result of adding modulation to the DC signal when measuring a nonlinear system, it is necessary to analyze Equation 2.6 by performing a Taylor-series expansion on the response shown in Equation 2.7.

$$V_{\text{resp}}(t) = f(V_{\text{appl}}) = f(V_{\text{DC}} + V_{\text{mod}} \sin(\omega_{\text{mod}} t)) \quad (2.7)$$
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The definition of the Taylor-series expansion is shown in Equation 2.8.

\[ f(x) = f(a) + \frac{f'(a)(x-a)}{1!} + \frac{f''(a)(x-a)^2}{2!} + \ldots + \frac{f^n(a)(x-a)^n}{n!} \]  

(2.8)

Given that the modulation amplitude is selected to be sufficiently small, it is possible to expand Equation 2.7 around the DC bias voltage \( V_{DC} \) using Equation 2.8, shown in Equation 2.9. The variables \( x \) and \( a \) in Equation 2.8 corresponds to the applied voltage \( V_{appl} \) and the point around which the expansion is carried out, \( V_{DC} \).

\[ V_{resp}(t) \approx V_{DC} + \frac{dV_{resp}(t)}{dV_{appl}} \bigg|_{V_{DC}} V_{mod} \sin(\omega_{mod} t) + \frac{d^2V_{resp}(t)}{dV_{appl}^2} \bigg|_{V_{DC}} \frac{V_{mod}^2}{2} \sin^2(\omega_{mod} t) \]

\[ + O(V_{mod}^3) \]  

(2.9)

If the system is non-linear there will be a non-zero response in higher harmonics, seen in the higher orders of the expansion. In the case of a purely ohmic junction, higher order derivatives are equal to zero and the higher harmonics cannot be detected. It is convenient to simplify the second harmonic in Equation 2.9 to eliminate the second order sine function by using trigonometric identities, shown in Equations 2.10 through 2.11.

\[ \sin^2(\omega_{mod} t) = \frac{1 - \cos(2\omega_{mod} t)}{2} \]  

(2.10)

\[ = \left[ \cos(2\omega_{mod} t) = \sin(\frac{\pi}{2} - 2\omega_{mod} t) = -\sin(2\omega_{mod} t - \frac{\pi}{2}) \right] \]

\[ = \frac{1 + \sin(2\omega_{mod} t - \frac{\pi}{2})}{2} \]  

(2.11)

Inserting the resulting Equation 2.11 into Equation 2.9 gives Equation 2.12.

\[ V_{resp}(t) \approx V_{DC} + \frac{dV_{resp}(t)}{dV_{appl}} \bigg|_{V_{DC}} V_{mod} \sin(\omega_{mod} t) \]

\[ + \frac{d^2V_{resp}(t)}{dV_{appl}^2} \bigg|_{V_{DC}} \frac{V_{mod}^2}{4} \left(1 + \sin(2\omega_{mod} t - \frac{\pi}{2}) \right) + O(V_{mod}^3) \]  

(2.12)

The information contained in Equation 2.12 is the reason why the lock-in amplifier is useful for IETS measurement. One of the coefficients of the \( \sin(2\omega_{mod} t) \) term is the second derivative evaluated at the DC bias level applied when measuring. Since the applied modulation voltage amplitude \( V_{mod} \) is constant during a measurement, the only variable is the second derivative. Thus; upon measuring the amplitude of the second harmonic of the modulation, it is possible to extract the relative amplitude of the second derivative. An illustration of the expected signal in the frequency domain is shown in Figure 2.4.
Since peak locations is the quantity of interest in IETS analysis, the lock-in method of measuring the second derivative is utmost fitting. An important parameter in Equation 2.12 is the phase shift introduced between the first and second harmonics, which plays a part in the lock-in amplifier design.

### 2.2.2.3 Mechanism of the Lock-in Function

The lock-in amplifier utilizes the orthogonality of sine and cosine in order to pick out a signal many times smaller in amplitude than ambient noise. Upon recording the sinusoidally modulated signal, a sine and cosine of the same frequency and phase is multiplied to the signal in order to obtain the lock-in function. The overall principle in this section is similar to that presented by Li et al. [34].

As shown earlier in Section 2.2.2.2, the amplitude of the signal at a frequency of $2\omega$ compared to the applied modulation at frequency $\omega$ is proportional to the second derivative; shown in Equation 2.13. Here, the notation of the second derivative is given in current per voltage; this is just a convenience as the recorded voltage in the system is actually the current response through the junction passed through a current–voltage amplifier.

$$A_{2\omega} \propto \frac{d^2I}{dV^2} \quad (2.13)$$

The signal at the second harmonic frequency is generally very small, often much smaller than noise at surrounding frequencies. It is thus difficult to directly measure the amplitude $A_{2\omega}$. First, in order to decrease the impact of noise and other signals in the entire
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spectrum, the signal is bandpass filtered around $2\omega$. Rewriting Equation 2.12 taking into account the bandpass filter only leaves the $2\omega$ term, shown in Equation 2.14.

$$V_{BP}(t) \approx A_{2\omega} \sin(2\omega_{mod}t - \frac{\pi}{2} + \phi) + N(t) \quad (2.14)$$

Here, $V_{BP}(t)$ denotes the bandpass filtered signal and $\phi$ indicates the phase shift due to capacitance, inductance or delay in the circuit and $N(t)$ indicates the random noise in the signal. A rough sketch of the amplitude of the signal in Equation 2.14 is shown in Figure 2.5.

![Figure 2.5: A sketch of the frequency domain of the bandpass filtered signal in Equation 2.14.](image)

Now, the signal can be multiplied by the respective sine and cosines in order to perform phase-sensitive detection. One might believe that upon multiplication, the noise factor also would show up at a frequency $2\omega$; however, since the noise is approximately random, the frequency component is completely distorted and only becomes a part of the overall noise function. This can easily be verified by comparing the Fourier transform of a random signal and the same random signal multiplied by a sine function. The result after multiplying both sides of Equation 2.14 by the the sine signal at frequency $2\omega$ is shown in Equation 2.15.

$$V_{BP}(t) \sin(2\omega_{mod}t - \frac{\pi}{2}) = A_{2\omega} \sin(2\omega_{mod}t - \frac{\pi}{2} + \phi) \sin(2\omega_{mod}t - \frac{\pi}{2}) + N_2(t) \quad (2.15)$$

For the sake of clarity, two substitutions are performed: $V_{\sin} = V_{BP}(t) \sin(2\omega_{mod}t - \frac{\pi}{2})$ and $u = 2\omega_{mod}t - \frac{\pi}{2}$. Equation 2.15 with substituted parameters and omitted noise is shown in Equation 2.16. Using the sum–difference formula gives Equation 2.17. Expanding the brackets and using the double angle formula gives Equation 2.18. Next, utilizing the power–reducing formula gives Equation 2.19. Extracting the fraction, expanding brackets and rearranging gives Equation 2.20. Finally, the terms in the square
brackets can be simplified by the sum–difference formula, shown in Equation 2.21.

\[ V_{\sin}(t) = A_{2\omega} \sin(u + \phi) \sin(u) \]  
\[ = A_{2\omega} [\sin(u) \cos(\phi) + \cos(u) \sin(\phi)] \sin(u) \]  
\[ = A_{2\omega} \left( \sin^2(u) \cos(\phi) + \frac{\sin(2u) \sin(\phi)}{2} \right) \]  
\[ = A_{2\omega} \left( \frac{(1 - \cos(2u)) \cos(\phi)}{2} + \frac{\sin(2u) \sin(\phi)}{2} \right) \]  
\[ = \frac{A_{2\omega}}{2} (\cos(\phi) - [\cos(2u) \cos(\phi) - \sin(2u) \sin(\phi)]) \]  
\[ = \frac{A_{2\omega}}{2} (\cos(\phi) - \cos(2u + \phi)) \]  
\[ = A_{2\omega} \left( \frac{\sin(\phi) + [\sin(2u) \cos(\phi) + \cos(2u) \sin(\phi)]}{2} \right) \]  
\[ = A_{2\omega} \left( \frac{\sin(\phi) + \sin(2u + \phi)}{2} \right) \]  

Equation 2.21 is an important result. Multiplying the signal by the corresponding sine function gives rise to a signal with two components: the cosine of the phase delay angle and a cosine term at two times the frequency of the second harmonic. If the second harmonic term is suppressed using a low-pass filter, only the phase and amplitude terms remain.

It is necessary to make use of the orthogonality of the sine and the cosine functions in order to achieve phase-sensitive detection by also multiplying the signal by the cosine of the modulation signal, shown in Equations 2.22 through 2.23. Here, the substitution \( V_{\cos}(t) = V_{BP}(t) \cos(2\omega_{mod}t - \frac{\pi}{2}) \) is performed.

\[ V_{\cos}(t) = A_{2\omega} \sin(u + \phi) \cos(u) \]  
\[ = A_{2\omega} [\sin(u) \cos(\phi) + \cos(u) \sin(\phi)] \cos(u) \]  
\[ = A_{2\omega} \left( \sin(2u) \cos(\phi) + \cos^2(u) \sin(\phi) \right) \]  
\[ = A_{2\omega} \left( \frac{\sin(2u) \cos(\phi)}{2} + \frac{(1 + \cos(2u)) \sin(\phi)}{2} \right) \]  
\[ = \frac{A_{2\omega}}{2} (\sin(\phi) + [\sin(2u) \cos(\phi) + \cos(2u) \sin(\phi)]) \]  
\[ = \frac{A_{2\omega}}{2} (\sin(\phi) + \sin(2u + \phi)) \]  

The result in Equation 2.23 is remarkably similar to Equation 2.21. The significant difference here is that when multiplying by the cosine, the sine of the phase shift appears as a term instead of the cosine of the phase shift. Figure 2.6 shows a rough sketch of the signal after multiplying by either sinusoid.
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2.2.2.4 Time Constant

A conventional lock-in setup works by measuring the signal during a set time, usually referred to as the time constant, at each DC bias. The result is that the signal is averaged.
and the random noise in the frequency spectrum will be suppressed compared to the modulation signal at a constant frequency. The averaging is shown mathematically in Equation 2.29.

\[ V_{\text{sin,cos avg}}(t, T_c) = \frac{1}{T_c} \int_{t-T_c}^{t} V_{\text{sin,cos}}(\tau) d\tau \] (2.29)

Here, \( T_c \) denotes the time constant and the operation is performed both for the sine and cosine multiplied signals, indicated by \( V_{\text{sin,cos}}(t) \). Noise at frequencies not equal to the second harmonic goes toward zero in the above operation due to the orthogonality of sinusoidal functions. It is usually necessary to have a time constant much longer than one period of the modulation in order to adequately attenuate the noise.

### 2.2.2.5 S/N Ratio

The signal to noise ratio is of great importance in the lock-in measurement. If the noise level is much greater than the signal, it will be too distorted to give any valuable information; in this case, the equipment has failed and the parameters of the lock-in measurement has to be reconfigured or the ambient noise level due to poor shielding and electronic noise from amplifiers has to be decreased. The SNR can be described as shown in Equation 2.30 [35].

\[ \text{SNR} = \frac{A \times G}{\text{input noise} \times G \times \sqrt{BW}} = \frac{A}{\text{input noise} \times \sqrt{BW}} \] (2.30)

\[ = \frac{A \times \sqrt{2\pi T_c}}{\text{input noise}} \] (2.31)

Here, \( A \) is the amplitude of the signal, \( G \) is the gain of the amplifier, \( BW \) is the bandwidth of the signal and \( T_c \) is the time constant of the lock-in amplifier. From the Taylor expanded response signal due to the added modulation in Equation 2.12, it is clear that the signal magnitude depends on the square of the modulation voltage amplitude, \( A \propto V_{\text{mod}}^2 \). Thus, changing the modulation voltage amplitude by a factor of 2 makes for a factor of 4 change in the SNR. As discussed in Section 2.2.1.4, it is preferable to use as low modulation voltage amplitude as possible in order to increase the resolution of the measurement; however, decreasing the modulation voltage rapidly decreases the SNR. A corresponding decrease in the modulation voltage amplitude \( V_{\text{mod}} \rightarrow V_{\text{mod}}/\eta \) must be corrected by a measurement time increase by a factor of \( T_c \rightarrow T_c \times \eta^4 \) in order to keep the SNR at the same ratio [35].
2.3 Digital Signal Manipulation

2.3.1 Signal Windowing

The constructed lock-in system in this work makes use of the Fourier transform in order to realize digital filtering, explained in detail in Chapter 3. The Fourier transform assumes that a signal is infinitely periodic. If the signal should happen to not be of infinite duration, as is the case for all physical signals, there will be artifacts in the frequency spectrum for signal components that are not exactly periodic in the signal; this is due to the discontinuities at the borders of observation and the effect on the frequency spectrum is called spectral leakage [36]. Spectral leakage is an unwanted effect that will cause ripples in the time domain of a signal if for example filtering is applied. The main idea of windowing is to manipulate the signal such that the discontinuity of the signal at the borders of observation is less and hence attenuate the spectral leakage [36]. There are many different types of windows depending on the application, where perhaps the most commonly used windows are Hann and Hamming.

2.3.2 Filtering

2.3.2.1 General Considerations, Impulse Response and Causality

When a signal is transformed into the frequency domain, it is possible to modify the signal to the criteria required by the application. Filtering the signal in the frequency domain is equivalent to performing a convolution operation of the signal and the impulse response of the filter in the time domain; \( V_{\text{filt}}[n] = V[n] * h[n] \). If, for example, the filter design would be to set all frequencies to zero outside the passband, the operation is equal to multiplying the frequency signal by a rectangular function. The impulse response of a rectangular function is a sinus cardinalis function, sinc(\( \pi x \)) = \frac{\sin(\pi x)}{\pi x}. Thus, there will be considerable ripples in the filtered signal, which is unwanted. It is therefore a good idea to make a more careful filter design in order to produce as few filtering artifacts as possible.

The impulse response \( h[n] \) is the result of sending a signal consisting of a 1 followed by zeros through the filter. The ripples in the impulse response are known as Gibbs phenomenon, and can be suppressed by changing the filter design [36]. For example, using an exponentially decreasing function as the edge(s) of the passband will substantially decrease the ripples compared to using straight edges.

Causality is an important factor to take into account when deciding which type of filter is needed. If a filter is non-causal, filter effects at a certain point in a time signal depends
on future data in the signal. In a real-time application a non-causal filter is impossible to implement as it has to contain data from the future. However, it is still applicable if a delay is inserted into the filter; thus delaying the output signal, allowing for the future data to be collected. Filtering the signal by performing a Fourier transform to access the frequency domain implies that any filtering is non-causal, since the Fourier transform requires the signal in its entirety. In this work the entire signal is available, which means that the non-causal filtering by using the Fourier transform is possible and is also used.

2.3.2.2 Filter Types

There are many different filter types that can be used depending on the type of transform, if the filtering is causal or non-causal and the desired specifications. The lock-in amplifier in this work makes use of prerecorded data, thus allowing for non-casual filtering and the use of the fast Fourier transform (FFT) to implement the filters. Two types of filters are used in order to realize the lock-in function, a low-pass filter and a band-pass filter.

A low-pass filter essentially works by letting low frequency signals pass untouched through the filter and suppressing high frequency components. The cutoff frequency is defined as the frequency at which the filter has suppressed the signal to $1/\sqrt{2}$ of its original value, or $-3$ dB, shown in Figure 2.7. This filter type is typically used for removing noise from a DC signal.

A band-pass filter is a combination of a low-pass filter and a high-pass filter, consequently only letting signals of a frequency in between two cutoff frequencies pass undisturbed;
shown in Figure 2.8. This filter type is useful for extracting information contained at a certain frequency while decreasing the amount of noise in the result.

![Diagram of frequency response of a band-pass filter](image)

**Figure 2.8:** An example of the frequency response of a band-pass filter.

Using the Fourier transform for filtering instead of using analog or causal filters has the advantage that there is no phase delay in the passband of the filter. This is quite important, especially for phase sensitive measurement such as in the case for the lock-in amplifier.

### 2.3.2.3 Anti-alias Filtering

In order to record a signal in a digital system, it is necessary to sample the signal. An artifact that can occur due to sampling is similar to an effect most of us might have noticed while riding a motor vehicle on a highway. When observing the revolutions of the wheels of a vehicle perhaps passing you as you ride along, an interesting effect occurs as you might see the spokes of the passing vehicle suddenly seem to start rotating backwards in comparison to the direction of vehicle movement. This effect is known as aliasing and is due to the limited amount of frames per second the human optical recognition system can process. Due to the Nyquist–Shannon sampling theorem, if a certain signal occurs at a higher frequency than half the sampling frequency of the observing system, the higher frequency will effectively be mirrored down on the observable spectrum, as shown in Figure 2.9 and Equation 2.32, where \( N \) is an integer such that \( f_{\text{apparent}} < f_s/2 \).
In effect, signals in between the sampling frequency and the Nyquist frequency will seem to ‘fold down’ below the Nyquist frequency due to the negative frequency of the signal being appreciated as positive. The folding effect is shown in Figure 2.10.

\[ f_{\text{apparent}} = |f_{\text{signal}} - Nf_s| \]  

(2.32)

The aliasing effect is unwanted when measuring signals, especially when the frequency spectrum is of interest. For example, in a lock-in application, radio signals in the kHz to MHz range picked up by the wires might be aliased onto the spectrum close to or even at the modulation frequency. In order to avoid aliasing in digital measurement systems, it is necessary to implement what is known as anti-alias filtering. Anti-alias filtering is performed by low-pass filtering the signal with a cutoff frequency at the Nyquist frequency before performing sampling. Anti-alias filters are implemented in most analog to digital (AD) devices.
Chapter 3

Construction of a Measurement System for IETS

This chapter provides the details of the designed lock-in amplifier characteristics along-side an overview of the measurement process. A motivation for the carrier wave type sweep is given and the effects of applying the designed windowing function is shown. The advantages to using the designed system compared to a conventional setup are also discussed.

3.1 Design of Lock-in Detection System

3.1.1 How to Measure IETS

To measure IETS, the second derivative of the current with respect to the voltage is probed using the lock-in amplifier as specified in Chapter 2. The response of the AC modulation voltage needs to be measured at different DC bias voltages in order to obtain the IET spectrum. There are a few possible ways of delivering the AC modulation at different DC bias. One example is a stepped type DC bias used in the Nanonis SPM measurement system, shown in Figure 3.1.
A similar method to the step type measurement of IETS is by ramping the bias voltage between the minimum and maximum amplitudes in very small steps, while continuously reading the lock-in parameters. The ramping method for measuring IETS was for example used by Petit and Salace to construct a lock-in device for characterizing metal-oxide-semiconductor junctions [35].

The 12-bit DA device used by Petit and Salace led to an output voltage resolution of 244\(\mu\)V. In this work, taking advantage of the 24-bit DA device output resolution of about 1.2\(\mu\)V, it is possible to use a third technique for measuring IETS. Sweeping the voltage smoothly in a slowly changing triangular or sinusoidal wave and using the DA device for digitally adding a modulation signal to the output allows for a new type of lock-in technique. I will refer to this measurement technique as a carrier wave technique for measuring IETS and it is explained in detail in this chapter.

3.1.2 IETS Measurement System Overview

A method for performing lock-in measurement on single molecular junctions was developed using the graphical programming language LabVIEW [37]. In a conventional set up, a commercial lock-in amplifier would usually be applied in conjunction with an analog–digital/digital–analog (AD/DA) device and an adder circuit. In this work, a lock-in amplifier was developed with only the use of an AD/DA device by carrying out the lock-in calculations on a computer in order to avoid the electronic noise from the otherwise added equipment. A carrier wave type sweep was also developed in order to obtain a more highly resolved IV curve during the IETS measurement.

The following describes a quick overview of the measurement system process. The first step is to add a sinusoidal modulation wave to a slowly varying sinusoidal or triangular carrier wave of 1.2 periods. The second step is to perform Tukey windowing on the
edges (0.2 periods) of the modulated carrier wave signal. The synthesized windowed modulated carrier wave signal is then applied to the molecular junction, amplified by a current–voltage amplifier and recorded using an AD device. The result is then band-pass filtered by using the FFT to transform the signal to the frequency domain. The frequency amplitudes outside the passband are then attenuated using a home made digital filter design, where after the signal is transferred back to the time domain using the inverse FFT (IFFT). The band-passed signal is then manipulated by using the lock-in algorithm in order to find the phase and amplitude of the signal, shown in Equations 3.23 through 3.26. The signal is finally trimmed in order to remove the regions where the amplitude of the signal is affected by the Tukey window.

3.1.3 Motivation for Developing a Carrier Wave Lock-in Technique

I decided to develop a method where a continuous sine modulation wave of relatively high frequency is added to a triangle or sine wave of one period. I will refer to the triangle or sine wave that determines the DC component of the signal as a carrier wave. A carrier wave type measurement allows a step type measurement to be consolidated to a single data gathering section, followed by data processing. Using the fact that the carrier wave changes slowly in time compared to the added modulation signal makes it possible to perform a continuous lock-in measurement over the desired bias region by filtering the signal. Since a full period of a triangle and sine curve is used for the carrier wave, it is possible to verify the stability of the junction during the lock-in measurement by comparing the positive and negative sweep directions.

The resolution for a certain SNR of the carrier wave method is the same as for the step-type method. However, the main advantage of performing the carrier wave type sweep is the availability of a more highly resolved IV curve obtained during the lock-in measurement. An IV curve obtained during the step type measurement is inevitably limited to single data points spaced by the stepping interval. For the carrier wave sweep type on the other hand, it is possible to obtain the IV curve with no modulation by low-pass filtering with a cutoff appropriately below the modulation frequency. An IV curve measured with the carrier wave will be on the order of ~ 10 times more highly resolved than the IV curve obtained during the step type measurement. Both the step and the carrier wave type measurements were developed for comparison, but the carrier wave type was most frequently used during measurements.
3.1.4 Triangular Carrier Wave Definition

The main reason to use a triangular type carrier wave is that it has a constant IETS resolution as is explained in detail in Section 3.2. Another reason to use a triangle sweep type lies in the fact that the capacitance in the wiring of the experimental equipment will create a current contribution during measurement. The capacitive addition to the current is shown in Equation 3.1.

\[
I_C = C \frac{dV}{dt}
\]  

(3.1)

Here, \(C\) is the equipment capacitance, \(V\) is the voltage applied to the junction and \(t\) is time. Using a triangle sweep type leads to the amplitude of the derivative being constant over the sweep, changing sign at the maximum and minimum points in the triangle curve. The triangle sweep type thus makes it easy to remove the current contribution due to the experimental equipment.

The downside with using a triangle wave as a carrier wave is that the Fourier transform of a triangle wave is not contained at a specific frequency; rather, it spreads over the entire spectrum. In order to describe this mathematically, let us prepare the triangle function as a convolution between a set of box functions. The box function can be defined as Equation 3.2.

\[
\Pi(t) = \begin{cases} 
1 & \text{if } 0 \leq t \leq T \\
0 & \text{otherwise}
\end{cases}
\]  

(3.2)

Now, let us define the appropriate set of box functions that by a convolution with the box function will generate a triangle wave of period \(4T\). For a quick reminder of the convolution operation, please refer to Appendix A.3. An illustration of the proper convolution is shown in Figure 3.2.

![Figure 3.2: Box functions (blue) that convolved with another box function \(\Pi(t)\) creates a triangular wave (green).](image-url)
The function in Figure 3.2 can be described mathematically as shown in Equation 3.3, where $A$ is the amplitude of the triangular wave.

$$\Pi_{\text{boxes}}(t) = A\Pi(t) - A\Pi(t - 2T) \quad (3.3)$$

The triangle signal can now be prepared using the distributivity and the associativity with scalar multiplication of the convolution operation, shown in Equations 3.4 and 3.5.

$$\Lambda(t) = \Pi(t) * \Pi_{\text{boxes}}(t) \quad (3.4)$$

$$= A(\Pi(t) * \Pi(t) - \Pi(t) * \Pi(t - 2T)) \quad (3.5)$$

The most straightforward way to realize the effect the triangle function has on the frequency spectrum is to first perform a Fourier transform of the box function, shown in Equations 3.6 through 3.7.

$$\mathcal{F}\{\Pi(t)\} = \int_{-\infty}^{\infty} \Pi(t)e^{-i2\pi ft}dt \quad (3.6)$$

$$= \int_{0}^{T} e^{-i2\pi ft}dt$$

$$= \frac{1}{-i2\pi f} \left[ e^{-i2\pi ft}\right]_{0}^{T}$$

$$= \frac{e^{-i\pi fT}}{\pi f} \left( e^{i\pi fT} - e^{-i\pi fT}\right)$$

$$= \frac{T e^{-i\pi fT}}{\pi f} \sin \pi fT$$

$$= Te^{-i\pi fT} \sin fT \quad (3.7)$$

The resulting frequency spectrum of the box function is thus a phase shifted sinc function, spanning all frequencies. It is now easy to find the Fourier transform of the triangular function using the result in Equation 3.7 and the convolution theorem. It should also be noted that the Fourier transform of the time shifted box in Equation 3.3 is

$$\mathcal{F}\{\Pi(t - 2T)\} = Te^{-5i\pi fT} \sin fT$$

following the same steps as in Equations 3.6 through 3.7. The Fourier transform of the triangular function of period $4T$ in Figure 3.2 is hence shown in Equations 3.8 through 3.9.

$$\mathcal{F}\{\Lambda(t)\} = \mathcal{F}\{A[\Pi(t) * \Pi(t) - \Pi(t) * \Pi(t - 2T)]\} \quad (3.8)$$

$$= A\mathcal{F}\{\Pi(t) * \Pi(t) - \Pi(t) * \Pi(t - 2T)\}$$

$$= A(\mathcal{F}\{\Pi(t)\} \mathcal{F}\{\Pi(t)\} - \mathcal{F}\{\Pi(t)\} \mathcal{F}\{\Pi(t - 2T)\})$$

$$= AT^2 \left( e^{-i\pi fT} \sin^2(fT) - e^{-6i\pi fT} \sin^2(fT) \right) \quad (3.9)$$
The frequency response thus consists of two squared sinc functions of different phase shift. When performing the filtering in order to realize the lock-in amplifier, the frequency components of the carrier wave will inevitably interfere with the time domain signal as the sinc functions cover the entire frequency spectrum. When the amplitudes in the frequency spectrum are modulated by filtering, the frequency response of the triangular carrier wave will also be modulated and will result in ripples in the time domain signal. Since two of the high frequency component contributions are located in the middle of the sweep, the high frequency components cannot be adequately suppressed by windowing using a Tukey window, detailed in Section 3.1.6. To conclude, the triangular carrier wave thus has the advantage of providing a constant DC current as an effect to the capacitance in the equipment, but the disadvantage of introducing high frequency components not suppressible by windowing.

3.1.5 Sinusoidal Carrier Wave Definition

The main reason for using a sinusoidal carrier wave is the low impact it has on the frequency spectrum. The edge effects from starting the sine curve at zero bias and ending at zero instead of continuing the wave for an infinite time will be the same as for the triangular wave. However, the sharp features at maximum voltage amplitude in the triangular carrier wave are not present for the sinusoid.

The frequency spectrum can be realized by investigating the Fourier transform of the sine curve, which is a rather simple calculation when using the Euler formula for the sine function, shown in Equations 3.10 through 3.11.

$$\mathcal{F}\{\sin(2\pi Ft)\} = \int_{-\infty}^{\infty} \sin(2\pi Ft) e^{-i2\pi ft} dt$$ (3.10)

$$= \int_{-\infty}^{\infty} \frac{e^{i2\pi Ft} - e^{-i2\pi Ft}}{2i} e^{-i2\pi ft} dt$$

$$= \frac{1}{2i} \int_{-\infty}^{\infty} \left( e^{-i2\pi(f-F)t} - e^{-i2\pi(f+F)t} \right) dt$$

$$= \frac{1}{2i} [\delta(f - F) - \delta(f + F)]$$ (3.11)

The end result is just a delta function at the frequency of the applied carrier wave frequency, in this case $F$. Since the frequency of the carrier wave is much smaller than the modulation frequency, it will be effectively removed in the filtering. However, if only one period of the sine wave is used with the signal being zero elsewhere, the result is the same as multiplying one cycle of the sine function with amplitude $A$ by the rectangular
box function in Equation 3.2, shown in Equation 3.12.

\[ \Omega(t) = A \Pi(t) \sin 2\pi Ft \quad (3.12) \]

Here, \( A \) is the amplitude of the sine carrier wave. It is now of interest to research the frequency domain of the carrier wave in Equation 3.12. It should be noted that the frequency of the sine wave is related to the time of the box function as \( F = \frac{1}{T} \).

We can now use the modulation property of the Fourier transform in order to find the Fourier transform of Equation 3.12; the result is a convolution of the individual Fourier transforms of the box function and the sine function in the frequency domain, shown in Equations 3.13 through 3.14.

\[
\mathcal{F}\{\Omega(t)\} = A \mathcal{F}\{\Pi(t)\} \ast \mathcal{F}\{\sin 2\pi Ft\} \\
= \frac{AT}{2i} \int_{-\infty}^{\infty} \left[ e^{-i\pi f T} \text{sinc} (f - F)T \delta(f - F) - e^{-i\pi f (F+1) T} \text{sinc} (f + F)T \delta(f + F) \right] df
\]

We can now see that the resulting frequency spectrum is two shifted \( \text{sinc} \) functions, offset by \( 2F \) and one subtracted by the other. The \( \text{sinc} \) function contributions are due to the abrupt start and end of the sine curve requiring high frequency components to be resolved. In order to decrease these effects, it is possible to introduce a windowing function, as shall be explained in Section 3.1.6.

A drawback to using the sinusoidal function as a carrier wave is the changing current contribution due to the capacitance, shown in Equation 3.1. A quick calculation gives \( I_C = C2\pi F \cos 2\pi Ft \). Since the capacitive current addition is even over the sweep, it is still possible to do an averaging of positive and negative slopes in order to remove the capacitive current contribution as in the case for the triangular carrier wave. A second drawback in using a sinusoidal carrier wave is a changing resolution over time, which is explained in detail in Section 3.2.
Overall, the frequency domain of the sine carrier wave function is more well-behaved than that of the triangle function in the sense that high frequency components of the carrier wave is only due to the start and end of the time domain function. The two high frequency components due to suddenly switching between positive and negative slope sweeps in the triangle curve can effectively be removed by using the sine wave. The current contribution due to capacitance can also be removed in a similar manner to the triangle wave due to the symmetry of the cosine function. Without removing the capacitance, the IV results may be slightly skewed; however, the capacitive current has been found to be on the order of less than a few pA for 1 s sweeps and should not be a problem. From a signal processing perspective, it is best to use a sinusoidal carrier wave type as the only high frequency components can be reduced by windowing.

3.1.6 Tukey Window Definition

In a normal scenario, windowing would be a part of the signal processing. However, in this application, it is beneficial to perform windowing during signal synthesis rather than processing. Performing the windowing during synthesis means that the windowing operation only needs to be performed once, rather than for every measurement. Only performing the calculation once decreases the overall data analysis time, leading to a smoother user experience.

Since the amplitude of the modulation signal is of interest, it is not possible to use windows such as Hann or Hamming windows since they modulate the amplitude of all data points. Hence, it is necessary to use a window that does not affect the amplitude of the signal in some part. Such a window function is realized by the Tukey window, or otherwise known as the cosine-tapered window, shown in Figure 3.3 [36]. In this work, in order to not affect the amplitude of the signal when using this window, the output signal was prolonged by the duration of the cosine parts of the Tukey window. The parameter $\alpha \in [0, 0.5]$ decides the steepness of the cosine edges of the window. A parameter $\alpha = 1/12$ is used in order to obtain a good balance between ripple suppression and measurement speed.

It is now of interest to perform the calculations to obtain the frequency spectrum of the Tukey window. Let the Tukey window have a length $T$. The Tukey window is a convolution of a truncated sine function in the range of $[0, \pi]$ with period $2\alpha T$ and a box function of length $T(1 - \alpha)$. Since a convolution in the time domain is just a multiplication in the frequency domain, we can now easily transform the window function using earlier results.
First we need to correctly express the frequency spectrum of the truncated sinusoid. Equations 3.13 through 3.14 conveniently expresses the frequency spectrum of a truncated sine. In the case for the Tukey window, the periods of the sine and truncating box function are changed. The box function will have a period $\alpha T$ and the sine function will have a frequency $F = \frac{1}{2\alpha T}$; taking this into account we obtain Equation 3.15.

$$\mathcal{F}\{\Omega_{tr}(t, \alpha)\} = \frac{A\alpha T}{2} e^{-i\pi f_{\alpha T}} \left[ \text{sinc} \left( \alpha f T + \frac{1}{2} \right) + \text{sinc} \left( \alpha f T - \frac{1}{2} \right) \right]$$

(3.15)

Next, we need to express the box function of period $T(1 - \alpha)$ in the frequency domain. Conveniently, the Fourier transform of the box function is defined in Equations 3.6 through 3.7. The Fourier transform of the box function of correct length is shown in Equation 3.16.

$$\mathcal{F}\{\Pi_{tr}(t, \alpha)\} = T(1 - \alpha)e^{-i\pi fT(1-\alpha)}\text{sinc} fT(1-\alpha)$$

(3.16)
Now we can easily find the Fourier transform of the window function Υ(t, α) by using the convolution theorem, shown in Equations 3.17 through 3.18.

\[
\mathcal{F}\{Υ(t, α)\} = Υ(f, α) = \mathcal{F}\{Ω_tr(t, α)\} × \mathcal{F}\{Π_tr(t, α)\}
\]

\[
= \frac{AαT}{2}e^{-iαfT}\left[\text{sinc}(αfT + \frac{1}{2}) + \text{sinc}(αfT - \frac{1}{2})\right]
\times T(1-α)e^{-iαfT(1-α)}\text{sinc}fT(1-α)
\]

\[
= AT^2(α - α^2)e^{-iαfT}\left[\text{sinc}(αfT + \frac{1}{2}) + \text{sinc}(αfT - \frac{1}{2})\right]
\times \text{sinc}fT(1-α) \tag{3.18}
\]

The frequency response of the Tukey window found in Equation 3.18 is shown in Figure 3.4 for some values of α alongside the frequency response of a rectangular window.

**Figure 3.4:** Comparison of a Tukey window frequency response with a rectangular window and a Hann window (α = 0.5). The inset shows a close-up of the characteristics at lower frequencies. Parameters A = 1 V, T = 1 s were used. The amplitude was calculated as 20\log_{10}\left|\frac{Υ(f, α)}{Υ(0, α)}\right|.

From Figure 3.4, it is clear that the Hann window gives the best attenuation over the frequency spectrum. The worst window is by far the rectangular window. It is also clear that the Tukey window for a low α approximates the rectangular window and for a high
\( \alpha \) is close to the Hann window. \( \alpha = 1/12 \) gives a relatively good trade-off between an increase in measurement time and less ripples due to a finite signal. For comparison, the form of the frequency response of the Tukey window found in this work by using analytical methods is also similar to that found by Harris using the discrete Fourier transform (DFT) [36].

### 3.1.7 Band-pass Filter Definition

The band-pass filtering is performed by a simple but efficient filter designed in this work. A bandwidth and a filter order is decided by the user through the user interface. This is then used to determine the filter characteristics. The filter type is designed with exponentially decreasing edges in order to suppress the ripples otherwise obtained if all frequencies outside the band-pass would be set to zero. The use of an exponential window ensures that any signals outside the passband are strongly attenuated and will thus not have a noticeable effect on the measurement. The filter coefficient design is given in Equation 3.19.

\[
\text{coeff} = \begin{cases} 
10^{-\frac{N_{\text{mod}}(1-\beta)+N}{\text{order}}}, & N \in [0, \, N_{\text{mod}}(1-\beta)-1] \\
10^{-\frac{N_{\text{mod}}(1+\beta)-N}{\text{order}}}, & N \in [N_{\text{mod}}(1+\beta)+1, \, 2N_{\text{mod}}] \\
0, & N \in [2N_{\text{mod}}+1, \, N_{\text{pad}}/2-1] \\
1, & N \in \left\{ [N_{\text{mod}}(1-\beta), \, N_{\text{mod}}(1+\beta)], \right. \\
& \left. [N_{\text{pad}}/2, \, N_{\text{pad}}-1] \right\} \tag{3.19}
\end{cases}
\]

Here, \( N \) is the corresponding frequency vector sample index, \( N_{\text{pad}} \) is the length of the zero padded signal vector, \( N_{\text{mod}} = f_{\text{mod}}N_{\text{pad}}/f_s \) is the frequency vector number of the center of the passband signal and \( \beta \) is the filter bandwidth expressed as a fraction of \( f_{\text{mod}} \). The frequency spectrum of the signal at vector index \( N \) is multiplied by the corresponding calculated filter coefficient in 3.19. For the zero values in the filter design, the values in the frequency domain signal are simply set to 0 + 0i. The components can be set to zero because the filter coefficients are less than what is resolvable by the double data type. Values above \( N_{\text{pad}}/2 \) are kept constant as they are not taken into account in the inverse fast Fourier transform (IFFT) implementation in LabVIEW. A sketch of the filter design is shown in Figure 3.5.

The order parameter decides the aggressiveness of the exponential edges, where a low order specifies an aggressive edge and a high order means an unaggressive edge. An order near zero essentially means that the filter edges are close to being vertical lines. A filter order around 15 was found to give the best trade-off between ripples and noise in the filtered signal. The designed filter has the advantage of only performing multiplication
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Figure 3.5: A sketch of the band-pass filter design in the frequency domain. The exponentially decreasing filter edges are straight lines on a logarithmic scale.

operations for a relatively short part of the signal, while the many 0 coefficients is just a matter of reinitializing the values in memory and the 1 coefficients is just a matter of leaving the frequency spectrum untouched.

A test program was constructed in order to test the parameters of the designed lock-in amplifier band-pass filter. A white noise signal of constant amplitude was added to the output signal of the lock-in amplifier and then directly sent to the result band-pass filter section of the program without being applied to the junction. The resolution was kept constant by matching an increase in sweep time by a corresponding decrease in bandwidth. The band-pass filtered first harmonic signal was subtracted by the unfiltered signal and the mean of the absolute value of the result was used as an indication of noise amplitude in the filtered signal.

It is clearly shown in Figure 3.6 that there is a square root dependence between filter bandwidth and noise amplitude in the filtered signal, thus confirming that the constructed filter obeys Equation 2.30. The bandwidth of the signal corresponds to the filter design factor $\beta$ as $BW = \beta f_{\text{mod}}$. 10 trials were averaged for each bandwidth in order to reduce stochastic variation.
Figure 3.6: Noise amplitude for different bandwidths at constant resolution. The modulation frequency used for synthesizing the signal was 1 kHz. The noise amplitude was normalized such that the largest value was 1.

### 3.1.8 Signal Preparation

A sinusoidal modulation signal of a freely selectable frequency is first linearly added to a carrier wave signal of selectable duration. The carrier wave acts as a DC current to apply the modulation voltage at different bias voltages in order to realize the IETS measurement sweep. Technically, it is only necessary to sweep each DC bias voltage once; however, one full period of the carrier wave is used in order to provide information on the junction stability during the measurement. If the signal differs between the positive and negative slope sweep directions, the conformation of the molecular junction has changed during the measurement and the data can be regarded as invalid. By performing a full period, it is also possible to cancel out any effects due to wiring capacitance by averaging the positive and negative slope sweeps.

Instead of performing windowing of the signal by post processing, I decided to apply a window to the output signal itself as this decreases the calculation time for each measurement. An illustration of the prepared output signal synthesis for a sinusoidal carrier is shown in Figure 3.7. The process is analogous for a triangular carrier wave.
Next, it is of interest to find the effect of applying the Tukey window to the output signal in the frequency domain in comparison to a nonwindowed signal. I will use a sinusoidal carrier wave for this example. Let the modulation frequency be $f_{\text{mod}} = 1 \text{kHz}$, the period of the carrier wave be $T = 1 \text{s}$, the amplitude of the carrier wave be $A = 0.3 \text{V}$ and the amplitude of the modulation be $A_{\text{mod}} = 11 \text{mV}$. In the case for the nonwindowed signal, the Fourier transform of the signal is just an addition of the two frequency spectra due to linearity. The frequency spectrum of the modulation signal can be expressed conveniently using Equation 3.13 through 3.14. Now, the frequency $F = \frac{1000}{T} = 1000 \text{Hz}$. 
The frequency response is shown in Equation 3.20.

\[
\mathcal{F}\{\Omega_{\text{mod}}(t)\} = \frac{A_{\text{mod}}T}{2i} e^{-i\pi f T} e^{-i\pi 1000} [\text{sinc} (fT + 1000) - \text{sinc} (fT - 1000)]
\]

\[
= \frac{0.011}{2i} e^{-i\pi f} [\text{sinc} (f + 1000) - \text{sinc} (f - 1000)]
\]

(3.20)

We can now express the frequency spectrum of the entire nonmodulated signal with a sinusoidal carrier wave, shown in Equation 3.21.

\[
\mathcal{F}\{\Omega_{\text{sig}}(t)\} = \frac{0.011}{2i} e^{-i\pi f} [\text{sinc} (f + 1000) - \text{sinc} (f - 1000)]
\]

\[
+ \frac{0.3}{2i} e^{-i\pi f} [\text{sinc} (f + 1) - \text{sinc} (f - 1)]
\]

(3.21)

It is now of interest to plot Equation 3.21 alongside the frequency spectrum of the windowed signal using \(\alpha/12\) used in this work. In order to do this, we need to find the correct frequency domain representation of the windowed signal. In the case for the windowed signal in this example, the corresponding carrier wave period is the same as for the nonwindowed wave; however, the box function cutting off the signal at the edges has a period \(T \rightarrow 1.2T = 1.2\) s. There is also a phase shift in the sinusoidal carrier wave in the sense that it does not start at 0. This phase shift is \(-2\pi/12 = -\pi/6\) radians. Finally, since the signal is multiplied by the window in time domain, the frequency response is a convolution of the window and the modulation wave added to the carrier wave in the frequency domain. Equations 3.18 and 3.21 are first convolved with correct parameters and then, with some algebra for simplification, the frequency response of the Tukey windowed output signal is shown in Equation 3.22.

\[
\mathcal{F}\{\Omega_{\text{windowed}}(t)\} = \left\{ \frac{0.011 \times 1.2}{2i} e^{-1.2i\pi f} [\text{sinc} (1.2f + 1000) - \text{sinc} (1.2f - 1000)]
\]

\[
+ \frac{0.30 \times 1.2}{2i} e^{-1.2i\pi f - \pi/6} [\text{sinc} (1.2f + 1) - \text{sinc} (1.2f - 1)]
\}

\[
\times \left\{ \frac{1.2^2}{12 - (1/12)^2} e^{-1.2i\pi f} \right\}
\]

\[
\times \text{sinc} 1.2f \left( 1 - \frac{1}{12} \right)
\}

= \left\{ \frac{0.0066}{i} e^{-1.2i\pi f} [\text{sinc} (1.2f + 1000) - \text{sinc} (1.2f - 1000)]
\]

\[
+ \frac{0.18}{i} e^{-i\pi(1.2f + 1/6)} [\text{sinc} (1.2f + 1) - \text{sinc} (1.2f - 1)]
\}

\[
\times \left\{ 0.055 e^{-1.2i\pi f} \left[ \text{sinc} \left( 0.1f + \frac{1}{2} \right) + \text{sinc} \left( 0.1f - \frac{1}{2} \right) \right] \right\}
\times \text{sinc} 1.1f
\}

(3.22)

The convolution in Equation 3.22 is tedious to perform by hand, so it is evaluated
numerically using MATLAB and shown in Figure 3.8. The result is interesting. Using
the window, it is possible to significantly suppress the sidelobes of the signal. Suppressed
sidelobes essentially means that when the signal is filtered, there are less ripples in the
time domain of the filtered signal.

\[ \text{Figure 3.8: A numerical analysis of Equation 3.22, comparing the use of a rectangular}
\text{window and a Tukey window with } \alpha = \frac{1}{12}. \text{ The inset shows a magnification of the}
spectrum around the modulation frequency. The above figure essentially shows the}
frequency domain of the signal sketched in Figure 3.7 c) with a modulation frequency
of 1 kHz.} \]

3.1.9 Signal Processing Procedure

3.1.9.1 Anti-alias Filtering

The signal is recorded by an AD device, in this case it is a 24-bit 204.8 kS/s PXI-4461
board (National Instruments). The PXI-4461 has a built in analog anti-alias filter with
a cutoff frequency at 102.8 kHz and uses a digital filter to remove frequencies lower than
this in case lower sampling rates are used.

3.1.9.2 Finding the Phase Offset

The first step in the designed lock-in device is to find the phase offset at 0 V DC bias
in order to set the phase offset correctly. There will inevitably be some offset due to
capacitance in the wiring to the source and drain electrodes, providing a phase shift for
the whole signal. The phase offset is found before the carrier wave sweep by applying the
modulation frequency to the junction for a freely selectable time, where a value around
0.1 s is reasonable for finding a stable value. The built in method “Extract Single Tone
Information.vi” in LabVIEW is used to detect the phase of the signal at the modulation
frequency $f_{mod}$.

### 3.1.9.3 Band-pass Filtering

The next step after finding the 0 V phase shift and recording the signal is to separately
band-pass filter the signal for the first and second harmonic analysis with cutoff frequen-
cies above and below $f_{mod}$ and $2f_{mod}$ respectively. In order to translate the signal to
the frequency domain for the filtering, the FFT algorithm is utilized. A motivation for
using the FFT to transform the signal to the frequency spectrum for this application
can be found in Appendix A.2. Before the signal is transformed it is padded with zeros
in order to reach a length of $2^N$, where $N$ is an integer and $2^N$ is greater than or equal
to the length of the signal; this is performed for greater performance when using the
FFT algorithm at the cost of momentarily higher memory allocation. In the worst case
scenario, padding the signal will approximately double the memory allocation of the
filtering process.

### 3.1.9.4 Multiplying by In and Out of Phase Components

The next step after band-pass filtering the signal is to multiply it by a sine and cosine
of frequency $f_{mod}$ and the 0 V phase offset found earlier. In the case for the second
derivative analysis, there is a $-\pi/2$ radians phase offset compared to the applied modu-
lation signal as shown in Equation 2.12. Here, the sine and cosine also need to be of a
frequency $2f_{mod}$ in order to lock in to the second harmonic.

### 3.1.9.5 Low-pass Filtering

As shown in Equations 2.21 and 2.23, multiplying by the in and out of phase components
has transformed the signal to one part at double the frequency and one part close to
DC frequency. The valuable information for the lock-in measurement is located in the
near-DC frequency components. Let $f_{lh}$ indicate the low and high cutoff frequencies
of the band-pass filter, respectively. The near-DC frequency signal has a bandwidth
of $BW = (f_h - f_l)/2$. The signal can thus be safely low-pass filtered at a frequency
around $f_{mod}/2$ to remove the unwanted high frequency components without sacrificing
resolution. The low-pass filter edge design is the same as that for the upper band-pass filter edge.

### 3.1.9.6 Extracting Lock-in Phase and Amplitude

Now, the signal has been sufficiently prepared for lock-in parameter extraction. Rewriting Equations 2.24 and 2.25 for the carrier wave type measurement gives Equations 3.23 and 3.24.

\[
V_{\sin \text{LP}}(t) = \frac{A_{2\omega}(t)}{2} \cos \phi(t) \\
V_{\cos \text{LP}}(t) = \frac{A_{2\omega}(t)}{2} \sin \phi(t)
\] (3.23)

The amplitude \(A_{2\omega}(t)\) and phase \(\sin \phi(t), \cos \phi(t)\) components will now slowly vary in time with a bandwidth \(BW = (f_h - f_l)/2\). Performing scalar operations on these vectors, analogous to those in Section 2.2.2.3, gives the results in Equations 3.25 and 3.26.

\[
\phi(t) = \arctan \left( \frac{V_{\cos \text{LP}}(t)}{V_{\sin \text{LP}}(t)} \right) \\
A_{2\omega}(t) = \frac{2V_{\cos \text{LP}}(t)}{\sin \phi(t)}
\] (3.25)

\(A_{2\omega}(t)\) is the vector containing the IETS signal. This can now be compared to the originally added slowly changing carrier wave to find out to which voltage the second derivative amplitude corresponds. The case above is explained for the second derivative, but is analogous to that for the first derivative.

### 3.2 Resolution

It is now of interest to find the resolution of a measurement recorded by the lock-in amplifier. The resolution is a combination of the time duration of the sweep, the voltage span of the carrier wave, the carrier wave type and the bandwidth of the resulting amplitude signal \(BW = (f_h - f_l)/2\). Let us begin by analyzing the triangular carrier wave, as this is the simplest case.

During a period \(T\) of a triangular sweep, the slope is \(\left| \frac{dV}{df} \right| = \frac{4A}{T}\), where \(A\) is the amplitude of the carrier wave. The bandwidth of the signal essentially acts as a low-pass filter of the same frequency, making any resolution of time components faster than this frequency impossible. In time, the resolution is thus \(1/BW\). The time resolved lock-in measurement is applied over the entire triangular curve, which leads to the resolution
in V shown in Equation 3.27.

\[ R_{\text{tria}} = \left| \frac{dV}{dt} \right| \frac{1}{BW} = \frac{4A}{T \times BW} (V) \]  \hspace{1cm} (3.27)

Inserting some typical parameters for a 10 s sweep gives \( R_{\text{tria}} = \frac{4 \times 0.3 \, \text{V}}{10 \times 10 \, \text{Hz}} = 12 \, \text{mV} \). It is interesting to compare this to the peak broadening of the signal in Section 2.2.1.4, as the measured signal will not change faster than this. For a root mean square (RMS) voltage amplitude of 8 mV at 1.5 K and an intrinsic width of 4 meV, the FWHM is about 14 meV, which means that the resolution is more fine than the FWHM of the IETS signal. The parameters used are thus of reasonable value.

In order to increase the resolution of the IETS measurement, it is necessary to first decrease the FWHM of the peaks. Since the modulation voltage dominates the peak broadening, the modulation voltage should be decreased, say by a factor of \( \frac{1}{\eta} \). Decreasing the modulation voltage amplitude leads to a necessary factor of \( \eta^4 \) increase in sweep time and a factor \( \frac{1}{\eta^4} \) decrease in the bandwidth in order to keep the signal to noise ratio at a constant level for a constant time resolution as explained in Section 2.2.2.5. Since the factors \( \eta^4 \) and \( \frac{1}{\eta^4} \) cancel out in Equation 3.27, an additional measure is necessary to increase the resolution of the measurement to a value below the new FWHM obtained with \( V_{\text{mod}}/\eta \). This can be accomplished by further increasing the sweep time at a constant bandwidth.

For the sinusoidal carrier wave type, the slope of the carrier wave changes in time. To be precise, it is \( \frac{dV}{dt} = \frac{A2\pi}{T} \cos \frac{2\pi}{T} t \), where \( A \) is the amplitude of the carrier wave. The resolution in Equation 3.27 is thus modified in the case for the sinusoidal carrier wave type and is shown in Equation 3.28.

\[ R_{\text{sin}}(t) = \left| \frac{dV}{dt} \right| \frac{1}{BW} = \frac{A2\pi}{T \times BW} \left| \cos \frac{2\pi}{T} t \right| (V), \quad t \in [0, T] \]  \hspace{1cm} (3.28)

It is now of interest to compare the resolutions of the triangular and the sinusoidal carrier sweep types. In the worst case scenario the resolution is approximately \( 2\pi/4 \approx 1.57 \) times the resolution of the triangle wave, which occurs near 0 V in the carrier sweep. If signals near 0 V are of interest, it is thus a good idea to use the triangular sweep type from a resolution perspective. The sinusoidal sweep type is of better resolution than the triangular sweep type for \( \left| \cos \frac{2\pi}{T} t \right| < \frac{A}{2\pi} \). Performing the algebra for the lowest solution gives \( \frac{1}{T} \approx 0.14 \), which means that the resolution of the sinusoidal carrier wave is better than the triangular carrier wave when the value of the carrier sweep is higher than \( A \sin 2\pi 0.14 \approx 0.77A \).
The triangular carrier wave has a better resolution for about 64% of the sweep time; however, it must be noted in this discussion that there will be some ripple effects due to filtering near the amplitude $A$ in the triangular carrier sweep type that can introduce some unwanted artifacts. To summarize, from a resolution perspective, it is a good idea to use a triangular sweep type unless the experimenter is more interested in having a higher resolution at a higher bias voltage.

### 3.3 Comparison to Conventional Techniques

#### 3.3.1 Conventional Method for Lock-in IETS

The conventional method of IETS measurement is to use a commercial lock-in amplifier with an adder circuit in conjunction to a standard experimental setup for measuring IV characteristics. For example, Jafri et al. used two Stanford research systems Model SR830 DSP lock-in amplifiers in parallel to their DC source equipment in order to measure IETS of octane-di-thiol–Au nanoparticles [38]. Tsutsui et al. used a home-built voltage adder and the same type of lock-in amplifier as Jafri et al. to read the first harmonic and then numerically found the second derivative from this result [39]. Honciuc et al. also used a lock-in amplifier with a homemade adder circuit to add a separate modulation signal to the DC bias for measuring IETS [40]. The standard lock-in measurement has also previously been performed in conjunction with conductance measurement using a MCBJ setup by Taniguchi et al. [41]. They used a home-made voltage adder, a lock-in amplifier and a separate circuit for measuring the conductance of the junction.

The measurement is typically carried out by stepping the DC voltage in small increments, where a certain time constant would be used to let the lock-in amplifier find the second derivative for each point. For example, Rezaei et al. developed an STM capable of measuring single molecular IETS with the use of a lock-in amplifier [20]. They used a triangular DC voltage ramping curve and a RMS modulation voltage of 5 mV. The lock-in time constant used was 0.1 s. They waited for three time constants on each DC bias voltage before reading the lock-in harmonics and moving to the next DC bias in the range of 0–500 mV, leading to a total sweep time of approximately two minutes.

Another method commonly used is to average several sweeps in order to find the second derivative. For example, Lauhon and Ho used an STM setup to measure IETS spectra of acetylene on a Cu(001) surface [23]. A relatively short lock-in time of 50 ms was used and the DC bias was stepped up and then down in a specified range, using an interval of 2.5 mV. The final results they presented were averages of 15–25 sweeps. Okabayashi
et al. also presented IETS results as an average of several measurements [42]. 32 cycles were averaged to obtain a clear IET spectra of C₈ alkane thiol, where each cycle was about 7 minutes long in the range of -500–500 mV.

3.3.2 Advantages to the Designed IETS System

There are advantages to using the IETS system designed in this work compared to a conventional setup, that are presented below.

- The first advantage is that if a research group already has a cryostat, an AD/DA device and a preamplifier for conductance measurement, there is no need to purchase any extra equipment for measuring IETS. In the conventional case, one or two lock-in amplifiers and analog filters need to be purchased and an adder circuit needs to be constructed.

- The second—and perhaps most interesting—advantage is that there is no need to use an adder circuit to add modulation to the DC signal. Adding more electronic equipment to the noise sensitive leads will inevitably lead to an increase in the noise in the signal, lowering the SNR. Especially 1/f noise, or pink noise, due to passing a signal through semiconductors can be avoided.

- The third advantage is that there is no need to switch between two different circuits for measuring DC conductance and IETS.

- The fourth advantage is that the first and second harmonics can both be analyzed in parallel from the same measurement. This can be realized in a conventional set up by adding an extra lock-in amplifier or switching the harmonic reading on a single lock-in amplifier, but the latter will increase the time taken for a full measurement. Since LabVIEW is designed to make use of the multi-core central processing unit (CPU) architecture of modern computers, the signal processing time for two harmonics can be made in roughly the same time as for only one harmonic.

- The fifth advantage is that the raw data for a measurement is available in its entirety, so effectively, lock-in parameters can be changed at a later date if the SNR was too high or if the phase offset could not be found correctly. It is possible to change the zero volt DC phase offset and to tighten the filter, with the latter leading to a worse resolution but a higher SNR.

- The sixth advantage is that by using a carrier wave type measurement, a more highly resolved IV curve can be obtained during the measurement of IETS.
Chapter 3. Construction of a Measurement System for IETS

3.4 Instrument

The instruments used for the IETS measurement in this work are minimal. A 24-bit AD/DA device (PXI 4461, National Instruments) is used for applying the IETS measurement signal to the junction and recording the response. A V/A amplifier (DLPCA-200, Femto) is used as a preamplifier in order to make the signal less susceptible to noise and to provide better detection in the AD device. Some amplifier characteristics in the low noise setting are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Transimpedance (V/A)</th>
<th>Bandwidth (-3 dB) (kHz)</th>
<th>Equ. Input Noise (/√Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3$</td>
<td>500</td>
<td>20 pA</td>
</tr>
<tr>
<td>$10^4$</td>
<td>500</td>
<td>2.3 pA</td>
</tr>
<tr>
<td>$10^5$</td>
<td>400</td>
<td>450 fA</td>
</tr>
<tr>
<td>$10^6$</td>
<td>200</td>
<td>130 fA</td>
</tr>
<tr>
<td>$10^7$</td>
<td>50</td>
<td>43 fA</td>
</tr>
<tr>
<td>$10^8$</td>
<td>7</td>
<td>13 fA</td>
</tr>
<tr>
<td>$10^9$</td>
<td>1.1</td>
<td>4.3 fA</td>
</tr>
</tbody>
</table>

Table 3.1: DLPCA-200 amplifier characteristics.

Noteworthy is that the bandwidth at the $10^9$ gain setting actually attenuates the second harmonic signal for the commonly used modulation frequency of 1 kHz. If the signal is still large enough to be detectable by the 24-bit AD device, attenuating the second harmonic is not a big problem since noise in the narrow passband around the IETS modulation frequency will be attenuated to a similar degree. However, the signal should preferably not be attenuated for best detection. Another noteworthy amplifier characteristic is that the input noise decreases for a higher gain setting.

The amplifier is controlled by a PXI 6289 board (National Instruments). This board is not required in order to control the amplifier, but was already present when the measurement system was developed and is convenient to use. Any type of device capable of applying three DC signals in the range of 0–5 V may be used. An ANC300 Piezo Positioning Controller (attocube) is used to control the junction length in the MCBJ setup.

Oversampling a signal by using a higher sampling rate than two times the highest frequency of interest increases the signal to noise ratio, as detailed by Li et al. [34]. Since a high SNR is desirable, the highest sampling rate possible of the AD device is used in this work. However, oversampling at such a high rate puts requirements on the measurement program construction due to the extreme data amounts involved. The data saved on the hard disk drive (HDD) are usually downsampled after analysis to decrease the storage data amount. A non-downsampled data file of a 60 s sweep consists of 12 288 000
samples for each of the five data vectors of time, DC voltage, current, first derivative and second derivative. As the recorded values are not significant beyond the 6th digit, the single data type is used for saving the data in a binary file to reduce HDD space usage, leading to a 12,288,000 sample data file requiring 240 MB of storage. Usually, the data is downsampled via a control on the user interface of the measurement program to require about 4 MB space on the HDD.

The devices are controlled by a 64-bit LabVIEW 2014 application running on a 64-bit version of Windows 7. The program is developed for using the parallel processing power of modern CPUs to analyze both the first and second derivatives of the IV curve simultaneously. In order to increase the effectiveness of the FFT used in the digital filtering, the signals are padded with zeros to reach a length of $2^N$ where $N$ is an integer. For details on the FFT, refer to Appendix A.2. Due to the padding, oversampling of the signal and parallel processing structure of the program, it is rather important to use a 64-bit system. 60 s carrier wave type sweeps require the usage of about 7.6 GB of random access memory during data analysis for the highest data acquisition rate of 204.8 kS/s. In case there is no possibility to obtain a 64-bit setup, carrier wave sweeps of about 20 s can be performed at the highest sampling rate. It is also possible to switch to the step type measurement, allowing for virtually any sweep time.

A figure of the overall setup is shown in Figure 3.9. The blue cables indicating the source/drain leads have a separate shielding from the piezo positioning controller and the cryostat system in order to decrease the noise in the signal. Having a separate shielding for the signal wiring was found to be extremely important for creating a low-noise environment. Especially harmonics of the 60 Hz power supply frequency were found to contaminate the signal if a common shielding was used for the entire setup.
3.5 Automated IETS Measurement Control Program

3.5.1 Overview

The idea of using an automated measurement is to provide a consistent and convenient method for performing IETS without the need of constant overview. The user can control a set of parameters for deciding the characteristics of the automated IETS measurement program. After starting the automatic measurement, the program will continue controlling and measuring the junction until it has reached a set cycle parameter, the user stops the measurement or the hard disk space runs out.

3.5.2 Automatic Amplifier Gain

Molecular junction measurement requires switching the preamplifier gain in order to resolve both atomic contact and molecular conductance. The gold nanojunction conductance is on the order of 10–50 $G_0$, where $G_0 = \frac{2e^2}{h} \approx 7.748 \times 10^{-5}$ S is the quantum...
conductance of a single channel conductor. The molecular conductance spans $10^{-5} - 10^{-1} G_0$. The preamplifier DLPCA-200 (Femto) used in this work has an adjustable gain between $10^3 - 10^9$. Since higher gain allows for a lower noise in the amplified signal, the gain is controlled such that the DC level of the IETS spectrum is amplified at as high gain as possible without overloading the amplifier input. Normally, a gain of $10^3$ was used when resolving the atomic contact and $10^6 - 10^9$ was used for during IETS measurements.

The voltage output of the amplifier is monitored at the update rate of the program during DC measurement in-between IETS measurements. The update rate is equal to the amount of samples read per program cycle divided by the sampling rate, both selectable by the user, and is commonly at around 50-100 Hz. The voltage values output from the amplifier are averaged within each cycle to receive an indication of the amplifier status. The averaged amplifier output voltage value decides whether the program should switch the amplifier to a higher or lower gain, or if the program should continue measuring. The limits for amplifier overload and underload are user selectable, with typical values set as default. The amplifier can output a maximum value of 10 V. The NI PXI 6289 device is used to send a signal to the DLPCA-200 amplifier in Remote Control for deciding the gain. If the gain has been changed, the program automatically waits for 0.1 s before continuing to monitor the DC current in order to remove any transient signals due to the mechanical switching in the amplifier.

### 3.5.3 Breaking the Junction

The first step in the program is to break the gold junction until the conductance is less than a set value. The setpoint is usually selected somewhere between $0.1 - 0.3 G_0$. The junction is broken by controlling the ANC300 Piezo Positioning Controller in steps, in-between which the junction conductance is monitored. When the conductance reaches a value lower than the set-point, a 3 s delay is performed to let the junction stabilize. A second parameter is then used, enabling the measurement to start even if the conductance has risen a set percent above the conductance set-point.

### 3.5.4 IETS Sweep

The program then automatically sends instructions to the NI PXI 4461 device to perform an IETS measurement sweep detailed by the user. For example, a triangular or sinusoidal carrier might be used, of freely selectable modulation voltage amplitude and frequency, carrier wave amplitude and frequency and length of the signal. The program waits until the sweep has been carried out, analyzed and saved on the HDD before continuing.
In case the amplifier overloads during the IETS sweep, even though safety margins are incorporated in the selection of the amplifier gain switch limits, the program tries several IETS sweeps until a valid sweep is performed. When a valid sweep is saved, the program moves on to the next step.

3.5.5 Widening the Junction Gap

The next step is to send an instruction to the ANC300 Piezo Positioning Controller to break the junction by one step. The stepping voltage controls the equivalent junction distance increase of each step and is selectable by the user. After a step has been performed, the program waits for 0.3s in order to not measure the capacitive current induced by the positioning controller wiring before moving on to the next step in the program.

3.5.6 Parameter Check

One sweep has now been performed. The program checks the parameters set by the user and the conductance of the junction. At this point one of two things can happen:

- The conductance is still within the upper and lower limits set by the user. The program will then move on to measuring an IETS sweep again, widening the junction and then come back to this step. If the set amount of sweeps per cycle of breaking and reattaching the junction has been reached, the program moves on to reattach the electrodes to each other to a set-point usually around 5–15 \(G_0\).

- If the conductance is too low or too high, the program moves on to reattach the junction to the 5–15 \(G_0\) set-point.

When the junction is reattached, the measurement cycle parameter is increased by 1. The program then checks if the set amount of cycles has been reached. If not, the program starts breaking the junction again and so forth. If the set-point has been reached, the program stops measuring.

3.6 Instrument Performance Test

3.6.1 Noise in a Molecular Junction

The noise level of the instrument was analyzed by applying a constant DC voltage of 0.2 V to a molecular junction containing the 8T molecule during 100.66 s using a sampling
rate of 200 kHz, see Appendix B for further details of the 8T molecular structure. The result was analyzed by using the FFT in MATLAB. The 20,132,000 samples in the frequency domain were convoluted by a 100 samples long vector consisting of equal amplitudes in order to smooth the data, where 50 samples of each edge of the data were removed in order to remove the edge effects. Figure 3.10 shows the resulting frequency spectrum of the signal in the molecular junction.

It is clear that the transition between pink noise \((1/f, -20 \text{ dB/decade})\) and white noise (constant level for all frequencies) occurs around 1 kHz. There is also a presence of high frequency noise above 10 kHz. The lowest noise level is hence between 1–10 kHz, which makes it beneficial to perform lock-in measurement in the low kHz region. The switching events apparent in the time domain of the signal occur faster than is measurable by the AD device. The switching might be due to charge trapping, a small change in the electronic structure or a conformational change in the electrodes; however, more sophisticated equipment is necessary in order to research the reason for the observed stochastic switching.
3.6.2 Comparison to Numerical Differentiation

In order to show that the designed lock-in amplifier successfully can measure the first and second derivatives, numerical derivation was performed on the IV curve as well as the first harmonic reading for a junction containing the 8T molecule. The conditions for the measurement was 4.2 K, 7.8 mV RMS modulation amplitude and a 30 s sweep with an equivalent signal bandwidth of 3 Hz was used. The voltage range was -300–300 mV, with a full period of a sinusoidal type carrier wave leading to a resolution of at worst 21 mV near 0 V bias and an average of 13 mV resolution over the entire sweep. The results for the first harmonic compared to the differentiated IV curve is shown in Figure 3.11. The differentiation was performed by using the ‘diff’ method in MATLAB and the first value in the voltage vector was removed in order to match the vector sizes. The IV curve was strictly low-pass filtered using the FFT before differentiating in order to produce visible results.

The overall shape seems to match between the differentiated curve and the curve measured by using the designed lock-in amplifier. However, the noise in the curve measured
by the lock-in amplifier is of a much lower magnitude than for the differentiated curve, indicating the strength of the lock-in measurement. Next, it is of interest to see that the second harmonic measured by the lock-in amplifier is in agreement to the numerical derivative of the first harmonic, shown in Figure 3.12.

![Figure 3.12: Comparison between a second harmonic reading extracted by the designed lock-in method and the numerical differentiation of the first harmonic reading. The black curve shows the first harmonic signal proportional to \( \frac{dI}{dV} \) for reference. The differentiated curve is only plotted in the range -295–295 mV in order to remove divergent effects as the slope of the sinusoidal carrier wave is close to zero. The curves are normalized by dividing the entire sweeps by their maximum values, respectively.](image)

The peak locations are in excellent agreement between both methods. The second derivative measured is thus confirmed to provide a similar result as the numerical derivation of the first harmonic, as expected. The overall curve sign agreement shows that the phase sensitive detection of the constructed lock-in amplifier is indeed working correctly.

### 3.6.3 Comparison to Step Type Measurement

The carrier wave type measurement was compared to a step type measurement in order to confirm that the carrier wave type lock-in measurement gives the same result as the conventional method. The step type measurement was performed first, where after the carrier wave type measurement was carried out. The measurements were both performed
at 1.6 K and 7.8 mV RMS modulation amplitude on a stable benzene-di-thiol (BDT) junction. Figure 3.13 shows an example of the obtained results.

Figure 3.13: A comparison between the step type and carrier wave type lock-in measurement. The first and second harmonic readings are normalized to match the maximum value of the IV curve for visual comparison. CW indicates the carrier wave type measurement and Step indicates the step type measurement.

A Hann window was used on the data recorded on each step before filtering and the lock-in data was averaged for each entire step. A time constant of 0.3 s was used when performing the step type measurement in 2 mV increments for a total of 90.8 s sweep time. A period of 60 s was used for a triangular carrier wave type sweep with an equivalent bandwidth of 1.6 Hz. As is shown in Figure 3.13, there is an excellent agreement between the step type lock-in method and the carrier wave type lock-in measurement. There is thus no room for doubt that both methods provide an equally valid result. The IV curve from the carrier wave type measurement was used as it is more highly resolved.
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3.6.4 Comparison to a Conventional Lock-in Amplifier

In order to make sure that the results from the developed lock-in amplifier are precise, the designed setup has been compared to a conventional setup using a NF LI 5640 digital lock-in amplifier. A home-built adder circuit was used to add the reference oscillator signal from the lock-in amplifier to the output of the NI PXI 4461 DA device. When measuring, a RMS voltage of 35 mV was used in order to get a strong signal since there was considerable noise at 60 Hz harmonics due to the adder circuit. The molecule present during the testing was a porphyrin with hydrogen bonded to its center site and the anchor groups were thioacetate for forming the S–Au bonds to the electrodes. The molecular characteristics were overall unstable and difficult to lock in to due to observed 4-level switching; however, using the large RMS modulation voltage of 35 mV provided a few chances for comparison. Figure 3.14 shows the resulting $d^2I/dV^2$ of a relatively stable junction, where it was measured by the designed lock-in amplifier and then measured by the conventional setup by switching the cabling of the experimental setup.

![Figure 3.14: Second derivative of a H–Porphyrin junction measured at 35 mV comparing a conventional lock-in setup and the setup designed in this work. The time constant of the conventional lock-in amplifier was 100 ms and the step increment was 3 mV in the range of -300–300 mV swept once. The sign of the second derivative was obtained by multiplying each amplitude by the sign of the respective phase reading. The sweep time of the designed lock-in amplifier was 4 s with an effective signal bandwidth of 25 Hz. The inset shows the $dI/dV$ measured by switching the harmonic in the case for the conventional setup and found by parallel computing in case for the designed lock-in amplifier.](image)
Although it may look like the measurement performed using the designed lock-in system in Figure 3.14 is more noisy than the conventional setup, it is necessary to take into account the time taken for both the sweeps. The designed system swept each voltage level two times due to the triangular sweep type used with a period of 4 s. The total time spent making the conventional sweep waiting at each bias voltage for two times the time constant was 120 s. Both sweeps were normalized by dividing them by their respective maximum value. The overall shape of the IETS signal is in very good agreement between the conventional setup and the designed lock-in amplifier. The junction was observed to break down during measurement with the conventional lock-in amplifier around the 280 mV mark, explaining the sudden dip in this region. The measurements were performed at 1.5 K.

3.6.5 Peak Broadening Due to Modulation Amplitude

One method to confirm that the lock-in measurement works as expected is to measure the relative peak broadening due to increasing the modulation amplitude. A junction containing 8-thiophene–di-SCN (8T) was measured with a RMS modulation amplitude of, in order, 7.8, 15.6, 31.2, 62.4, 124.8, 62.4, 31.2, 15.6, and 7.8 mV in order to both confirm junction stability during the measurement and to check the effect of modulation amplitude on the peak width. The sweep type used was a carrier wave sweep of sinusoidal shape of period 10 s with an effective bandwidth of 10 Hz. The results are shown in Figure 3.15.

It is clearly shown that the peaks broaden upon applying a higher modulation voltage. In fact, the two peak regions near 0 V completely unite in the case of 124.8 mV modulation, showing the importance of using as low modulation voltage as possible. The junction was stable enough to support the sweeps and provided similar peak results when decreasing the amplitude, as shown by the similarity of the similar colored lines in Figure 3.15.

It is of interest to compare the peak widths obtained through measurement to the theoretically expected FWHM in Equation 2.5. The measurement temperature of 1.7 K and an intrinsic peak width of 4 meV is used when determining the theoretical peak widths in Table 3.2. The experimental FWHM were determined by plotting each second harmonic lock-in reading alongside the numerical differentiation of the first harmonic and performing an overall estimate of the value using the zoom tool in the MATLAB figures. There is an overall agreement with the theoretical values; however, a more rigorous method would be to test several lower modulation voltage amplitudes on a more stable molecule than 8T.
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Figure 3.15: A comparison between the peak widths and modulation amplitude. The sweeps of equal modulation amplitude have a similar RGB color value, where blue indicates a sweep of low modulation amplitude and red indicates a sweep of high modulation amplitude. The values presented are not normalized. The sweep positive and negative slope directions were averaged for each individual sweep in order to increase visibility.

<table>
<thead>
<tr>
<th>Modulation ampl. (mV)</th>
<th>Exp. FWHM (mV)</th>
<th>Theoretical FWHM (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>14</td>
<td>14.1</td>
</tr>
<tr>
<td>15.6</td>
<td>25</td>
<td>27.3</td>
</tr>
<tr>
<td>31.2</td>
<td>55</td>
<td>54.1</td>
</tr>
<tr>
<td>62.4</td>
<td>90*</td>
<td>108.0</td>
</tr>
<tr>
<td>124.8</td>
<td>160*</td>
<td>215.9</td>
</tr>
</tbody>
</table>

Table 3.2: Experimental versus theoretical line widths. * indicates that the values were incredibly difficult to determine and should not be trusted. The experimental values should be treated as an overall indicator rather than a rigorous result.
Chapter 4

IETS Results and Discussion

The first purpose of this chapter is to show IETS measurements for the widely studied benzene–di-thiol (BDT) molecule in order to test the function of the system. The second purpose is to use the designed IETS measurement system for analyzing the characteristics of a new molecular junction, di-SCN-oligothiophene (5T).

4.1 Experimental and Analytical Methods

4.1.1 Experimental Conditions

IETS was measured in between incremental piezo stepping in cryogenic temperatures allowing for IETS mapping during conformational changes of the junction. The modulation voltage most often used to measure IETS was 7.8 mV RMS amplitude. The cryostat was generally operated by letting in liquid helium into the sample chamber, closing the needle valve inlet and evacuating the helium gas in the chamber by using a vacuum pump; this allowed for operation at a temperature of 1.7 K.

4.1.2 Data Presentation

Figure 4.1 shows an example of data recorded using the automated IETS measurement program. a) shows the conductance transient recorded just before each IETS sweep as the electrodes are retracted in a stepwise manner. The y-axis shows the conductance in units of $G_0$ in logarithmic scale for increased visibility and the x-scale indicates the amount of piezo steps performed. For a vacuum tunneling junction, a linear slope is expected in the conductance versus electrode retraction graph. Plateaus or clear steps
in the conductance indicate that something else than a vacuum tunneling junction is measured.

![Figure 4.1: An IETS colormap of a stretching curve with a BDT molecule present.](image)

- **a)** shows the conductance transient in a logarithmic scale.
- **b)** shows a colormap of the IETS signal throughout the electrode retraction process. A red value indicates a strong peak while a purple value indicates a strong dip.
- **c)** shows the peaks found by the peak locator program.
- **d)** shows a histogram of the peak locations found in **c)**.

b) shows a colormap of all IET spectra recorded after each individual step. In order to display the IETS results in the same figure, it is necessary to normalize each IETS sweep to a maximum amplitude of 1 due to the large differences in amplitude between measurements. The y-axis in **b)** displays the DC voltage applied, which corresponds to the energy of the corresponding vibrational mode by the relation $E = qV = \hbar\omega$.

c) indicates the peak locations found by an automatic peak finding program developed by Assoc. Prof. Yamada. First, the signal was split into the odd spectrum in order to extract peaks found in both sweep polarities, as shown in Equation 2.2. Thus, the peak results are mapped onto the positive voltage spectrum. Second, the signal was filtered by a Savitzky-Golay filter with 10 side points and of second polynomial order to remove any noise effects. The peak locations were finally found by using the “Peak Detector.vi” peak detection program found in the signal processing library in LabVIEW, with a peak width of 15 points. An example of BDT IETS odd data with peaks found by the automatic peak finder is shown in Figure 4.2.
Chapter 4. *IETS Results and Discussion*

4.2 BDT

4.2.1 The BDT Molecule

BDT was selected for first trials since it is a widely studied molecule in molecular electronics [5, 43–45]. Since it is one of the simplest molecules with delocalized π-orbital, it serves as a good molecule for confirming the function of the IETS measurement. The molecular structure of BDT is shown in Figure 4.3.

![Molecular structure of BDT](image.png)

**Figure 4.3:** The molecular structure of BDT.
4.2.2 Peak Inversion in a BDT Colormap

Figure 4.4 shows an example of a stretching process of a BDT junction. It can be clearly seen that there are two distinct plateaus in the conductance transient, indicating two different Au–BDT–Au configurations. During the high-conductance plateau there is a dip at 10 mV that changes into a peak when the conductance decreases to the second plateau. The 10 mV is close to the vibrational energy of Au–Au calculated by Nakamura et al. [46]. It is expected that vibrational modes might switch signs as is observed in this measurement due to parameters such as coupling strength to the electrodes and frontier energy level [7].

Figure 4.4: An IETS colormap of a stretching curve of a BDT molecule. a) shows the conductance transient and b) shows a colormap of the IETS signal throughout the electrode retraction process. The area indicated by the red ellipse shows a peak sign inversion for the Au-Au vibration.
4.2.3 Histogram of BDT IETS

The IETS results measured during a multitude of break junctions were analyzed using the peak analysis software shown in Figure 4.1. A histogram of 355 data with an acceptable noise level out of the original 1114 data is shown in Figure 4.5. The noise level was analyzed by hand for each measurement to determine if the peaks were due to noise or due to vibrational modes. If sweeps in succession had randomly varying peak locations over the entire measured spectrum, the data was considered due to noise.

There are several distinct peaks clearly visible in the histogram. The peak result shown above can be used as an overall indicator of a molecular fingerprint for the BDT molecule. However, in order to research the vibrational modes that correspond to each frequency, the peak locations need to be compared to theoretical calculations. For reference, I will compare the peaks observed in this work with the peak locations calculated by Lin et al. [43]. The sharp peak near 130 mV and 175 mV is close to that of the $\nu(19a)$ BDT C–H in-plane bending modes. The 80 mV peak is near the $\nu(6b)$ C–C–C bending modes. The peaks near 50 mV are likely due to the $\nu(S–C)$ stretching mode and the peak near 30 mV is likely due to the S–Au stretching mode. The strong peak at around 10 mV coincides with the Au–Au vibrational mode present for gold atomic chains.
4.3 5T Oligothiophene

4.3.1 The 5T Molecule

The room temperature transport characteristics of oligothiophenes has been investigated in our group previously. It was shown that the oligothiophene molecules are good molecular wires, allowing for long range electrical conduction due to the low tunneling decay constant of \(0.1 \, \text{Å}^{-1}\) \[^{15}\]. The results were found by statistical measurements of oligothiophenes containing 5, 8 and 14 units, respectively. It was also confirmed through statistical STM break junctions of 5–23 thiophene units that the conduction mechanism through the oligothiophene molecules changes from tunneling to hopping between 11 and 14 thiophene units \[^{47}\]. However, the detailed current-voltage characteristics and molecular behavior in a stable junction have not yet been clarified. It was therefore decided that the 5T molecule should be investigated using the IETS measurement equipment developed in this work. An oligothiophene molecule containing 8 thiophene rings was also investigated, but the results were inconclusive and are therefore presented in Appendix B.

The molecular structure of the 5T molecule is shown in Figure 4.6. The imaginable ways in which the molecule binds to the gold electrodes is either directly by the SCN anchoring group, or by replacing the SCN bond on the anchor groups by a S–Au bond.

![Figure 4.6: The molecular structure of the 5T molecule. The S–H anchor groups were used for calculating the IR and Raman spectra, while SCN are the anchor groups for the probed molecule. Color map: Red = O, Yellow = S, Gray = C, White = H, Deep blue = N, Light blue = Si.](image)

The vibrational IR and Raman spectra were calculated by Dr. Ohto in our group using the Gaussian 09, B3LYP/6-31G(d,p) package for a free floating molecule not bound to electrodes and the results are shown in Figure 4.7. Any mode activated in IR or Raman
spectroscopy can be activated by IETS; however, peak intensities between IR/Raman and IETS have no relation. Upon closer inspection of the modes it can be seen that in general, lower energy modes around 80 meV are due to the entire molecule bending or twisting, while the higher energy modes are due to for example C–S–C ring breathing. For reference, animations of the 80 meV, 140 meV and 170 meV vibrational modes calculated are shown in Appendix D. Dr. Ohto further showed that the SCN–Au electrode bond is unlikely and that the only stable SCN–Au configuration was for a single Au atom not bound to a gold lattice. Modes pertaining to the SCN anchor were found around 263 meV for a free 1-thiophene–di-SCN molecule and modes around 283 meV were found for a Au–SCN–1-thiophene–SCN–Au configuration.

![Figure 4.7: Calculated IR and Raman modes for 5T. The peaks are slightly broadened using Gaussian broadening to improve visibility.](image)

### 4.3.2 New IETS Peaks after Elongation in a 5T Colormap

The conductance trace in Figure 4.8 a) show some clear steps and even increasing conductance upon stretching the junction, which would not be the case if there was just a vacuum tunneling barrier. It can thus be concluded that something else than a vacuum tunneling junction is measured, which is likely a 5T molecule. For this measurement, each IETS sweep was 5 seconds long.
Chapter 4. IETS Results and Discussion

Figure 4.8: An IETS colormap of a stretching curve of a 5T molecule. a) shows the conductance transient and b) shows a colormap of the IETS signal throughout the electrode retraction process. The red ellipse indicates two new peaks appearing toward the end of the electrode retraction process.

The mode visible around 30–40 mV is well known to be due to the Au–S vibration [9, 38, 42]. It is clear that the Au–Au and Au–S peaks are present during the entire stretching process of the molecule. Next, it is interesting to investigate the peaks around 140 meV and 170 meV. Comparing to the vibrational modes calculated by Dr. Ohto, the vibrational modes at around 140 meV mostly involve C–O–C side ring breathing. The vibrational modes around 170 meV involve vibrational modes where the center thiophene performs a breathing type vibration. These vibrational modes are strongly present
during the entire sweep, indicating that the current likely passes through the center and at least one of the sides of the molecule during the entire stretching process.

In the final conductance plateau of the stretching process, two new strong peaks appear near 70 meV and 90 meV. Vibrational modes in the low energy region below 100 meV mostly involve the entire molecule. Since modes along the current pathway are likely to be visible in the IETS measurement it might be concluded that the current likely passes through the entire molecule in the final plateau of the electrode retraction process.

4.3.3 Stepwise Plateau Conductance Transient

An interesting junction behavior is shown in Figure 4.9 a). There are clear steps as the electrodes are retracted, which indicates that the conduction channels decrease in a stepwise manner. This may be due to sliding of the molecule, conformational changes in the electrodes or a decrease in the amount of bridging molecules in the junction. Unfortunately, the SNR is too low to resolve clear peaks in the IETS for any other than the first plateau. Toward the end of the electrode retraction process, it is clear that the conductance decrease becomes linear on the log scale; this indicates that the molecule has detached from one of the electrodes, leading to a vacuum tunneling junction barrier behavior. During the last part of the sweep, the colormap of the IETS signal mostly shows no consistent peaks. The colormap presentation can thus be used to distinguish peak signals from noise in the molecular stretching IETS measurement.

Although the junction showed instability and a noisy IETS signal, there is still some vital information to be gained from the IETS spectrum. The first plateau is clearly the most stable, where several strong peaks are visible. The 70 mV peak indicates that a mode involving the entire molecule is activated, indicating a likely charge transfer throughout the molecule. Since the 70 mV peak seems to be present even after the first plateau, the likely explanation to the stepwise plateaus is either conformational change in the electrode–molecule–electrode junction or a decrease in the amount of molecules that bridge the junction. The center plateau around step 40 is smoothly decreasing in conductance, which supports the interpretation that there might be some conformational change in the junction as it is difficult to imagine that a molecule would be smoothly released from the junction over the course of minutes.
4.3.4 Au–S Peak Shift

As shown by Kim et al., peaks in the IETS signal may shift in frequency upon elongating a molecular junction [9]. The peak shift has also been observed using the present setup and is shown in Figure 4.10 for a 5T molecular junction. In the final part of the stretching of the junction, the likely Au–S peak shows a significant blue shift. A blue shift of the Au–S peak is in contradiction to the results published by Kim et al.. They investigated the Au–hexane–di-thiol–Au and Pt–hexane–di-thiol–Pt junctions and found that while the Pt–S peak shifted by a maximum of $\Delta E = 12\,\text{meV}$, the Au–S peak did not shift as much. They concluded that the gold atoms form chains and thus contributed the lack of shift of the Au–S stretching to the assumption that the Au–Au bonds were elongated rather than the Au–S bonds.
In Figure 4.10, it is clear that the Au–S peak shifts by $\Delta E \approx 20\text{ meV}$ between step 165 and step 192. The stretching characteristic is approximately linearly correlated to the stretching distance, which is the same result as found by Kim et al. for the Pt–S peak shift. As an explanation in light of the results presented by Kim et al., I would like to propose that the sulphur anchor groups of the 5T molecule in this junction is not bound to gold chains; rather, due to a different electrode geometry they are bound to gold atoms more tightly lodged in the electrodes. Another factor that needs to be taken into account is that the measurement temperature for the 5T molecule was 1.7 K compared to a likely measurement temperature of 4.2 K used by Kim et al.; however, the temperature should not greatly affect the ductility of gold due to its fcc structure.

Figure 4.10: Peak shift in an IETS signal. a) shows the conductance trace and b) shows the colormapped IETS. The red circle indicates Au–S peak blue shift.
4.3.5 Histogram of 5T IETS

1472 of the 3150 data measured had an acceptable noise level and were selected for the histogram. The results are shown in Figure 4.11. The most common peak locations are significantly different to that of BDT. There are peaks at 10 mV and 40 mV likely due to the Au–Au vibration mode and the Au–S vibration mode, respectively. The peaks are much wider than in the case of BDT, due to an increase in peak position variation. The strong peak near 170 mV is near vibrational modes involving the center thiophene ring in combination with the bulky protector group. The peak near 90 mV is in the region with vibrational modes involving the entire molecule.

![Figure 4.11: Peak histogram of 1472 IETS data for 5T. Only data that showed clear peaks were selected.](image-url)
4.4 Control Experiment

A blind trial was performed to see if peaks showed up for a clean junction. The data mostly just consisted of noise; however, for one of the trials a junction where IETS was measurable was formed. The reason for this is unclear, but it might be due to some contamination in the junction. A histogram of the peak locations for the stable junction for a clean substrate is shown in Figure 4.12.

![Image of histogram]

**Figure 4.12:** Peak histogram of 24 IETS data for a gold junction without any added molecule.

In order to elucidate the situation, it is convenient to analyze the colormap of the recorded vacuum junction IETS. Figure 4.13 shows the conductance transient and the IETS colormap for the only stable vacuum IETS measurement. It can clearly be seen that the conductance decreases exponentially as the electrodes are withdrawn, indicating that the junction does not contain a bridging molecule. It can thus be concluded that some contamination is likely attached to one of the electrodes and is excited by the tunneling current passing through the junction.
Figure 4.13: A colormap of the only stable IETS vacuum junction measured.
Chapter 5

Conclusion and Future Work

This chapter gives a brief overview of the results in this work alongside some details to keep in mind when constructing an IETS measurement system. Some details on possible future work for constructing an even better measurement system are also given.

5.1 Conclusion

In light of the necessity of creating a low-noise environment for measuring IETS of single molecular junction, every possible method at hand should be considered. Moving instruments from the analog realm to the digital realm is advantageous for the noise level in an experimental setup. Analog filter components involve resistors and capacitors, which introduce Johnson-Nyquist noise to the signal. If the filtering is instead performed digitally, it is possible to completely avoid this extra noise contribution. Since a digital implementation of the the lock-in amplifier and surrounding equipment was developed in this work, this provides a guideline for how IETS measurement setups can be constructed with a lower cost and higher SNR ratio.

The constructed digital implementation of the lock-in amplifier also opens up new possibilities such as designing a carrier wave type measurement for simultaneous lock-in and high resolution IV measurement. Some groups decide to wait for 2–3 time constants before reading the lock-in value of the lock-in amplifier. This is not necessary for the carrier wave type measurement and will in this case lead to a much faster sweep time. In order to decrease the ripples in the resulting carrier wave lock-in measurement to a near-zero level, Tukey windowing is employed with an increase in the signal sweep time of 20%. The slight extension in sweep time is an acceptable loss in comparison to the increase in preciseness of the result.
Constructing an automated measurement setup allows for data collection that otherwise would be very tedious work. Implementing automatic amplifier gain and piezo stepping control greatly simplifies the measurement process and allows for straightforward recording of IETS during a junction stretching process. The rich data amount of automated IETS during electrode retraction allows for creating a colormap of the IET spectrum in order to obtain a clear picture of the evolution of the junction. The colormap of the IETS gives a clear picture of the modes excited at the different stages of the electrode retraction, which led to an increased understanding of a 5T conductance transient. The colormap also helped with indicating the peaks that are due to noise and clearly showed features such as the Au–S peak shift observed for a 5T junction.

5.2 Future Work

In order to further decrease the time spent analyzing the carrier wave IETS, at the moment at about 17% of the sweep duration, it is possible to implement a fast IETS algorithm as reported by Li et al. [34]. This could perhaps save about 1–4 s per sweep for normal measurement times, further increasing the effectiveness of the setup. Employing their algorithm for calculating IETS would also lead to less random access memory allocation, allowing for even longer carrier wave IETS sweeps.

The DLCPA-200 preamplifier used in this system could also preferably be upgraded to an amplifier with a higher bandwidth at a factor $10^9$ gain. Since the lowest noise part of the frequency spectrum is around the range of 1–4 kHz in the setup, the modulation frequency used for measurement is 1 kHz to measure the second harmonic at 2 kHz. However, the preamplifier has a bandwidth of 1.1 kHz (−3 dB) for the highest gain setting, leading to an attenuation of the second harmonic and to potential detection problems in the AD converter. The second harmonic signal should preferably not be attenuated. An amplifier such as the Programmable Current Amplifier CA5350 (NF) with a 70 kHz bandwidth at $10^9$ gain could be employed for better low-conductance IETS measurement.

The final notes I would like to present for possible future work in upgrading the effectiveness of the measurement system is on the digital filter designs. One could develop a notch filter instead of using a low-pass filter in order to remove the modulation signal from the IV result. Using a notch filter would effectively lead to an even more highly resolved IV curve than with the use of a low-pass filter. Lastly, more care can be given to make the edges of the band-pass and low-pass filters smooth. At the moment, they are very roughly shaped using the exponential edge attenuation. If other shapes such as a cosine type edge are investigated, even better filtering might be possible.
Appendix A

Clarifications for the Interested

This Appendix serves as a container for explanations of some concepts that are relevant to this work. The most notable might be the FFT, the convolution operation and the Landauer model current–voltage characteristics.

A.1 The Discrete Fourier Transform

The function of the Fourier transform is to take a signal and analyse it to receive the frequency and phase components of the signal. It is possible to perform useful modifications on the signal in the frequency domain before synthesizing the signal back to time domain by using the inverse Fourier transform.

There are a number of transforms available such as the Laplace transform, z-transform, Fourier transform and so on for analysing signals. Which transform is appropriate is decided by the type of signal and the type of measurement system. For real-time applications for example, using the Laplace transform gives an easy description of the filter in the continuous time case and the z-transform does the same for discrete time case. In the lock-in application in this work, the entire analog signal response is sampled digitally at a frequency $f_s$ in a DA device in order to digitize the information. The sampling leads to a discretization of the signal. Since the signal is available in its entirety and it is discrete, the DFT is the best alternative for analysing the signal.

Sampling the signal gives rise to data in the form $x[n]$ in the time domain, where $n$ is the sample number. Given that the sampling interval is $T_s = 1/f_s$, the sampled signal can be written $x[n]/T_s = x(nT_s)$. By taking the DFT of the signal, the resulting frequency
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Domain signal $X[k]$ is determined, shown in Equations A.1 and A.2.

\[
X[k] = \frac{1}{NT_s} \sum_{n=0}^{N-1} x[n] e^{-j\frac{2\pi nk}{N}} 
= \frac{1}{N} \sum_{n=0}^{N-1} x(nT_s)e^{-j\frac{2\pi nk}{N}}, \quad (n,k) \in [0,1,...,N-1] 
\] (A.2)

Here, $k$ denotes the sample number in the complex frequency domain signal, $n$ is the sample number in the time domain signal and $N$ is the total amount of samples. Each $X[k]$ is a complex number containing information of the amplitude and phase shift of the sinusoidal signal contribution at a frequency $\frac{k}{N}f_s$. Care needs to be taken in choosing the sampling frequency, as the Nyquist criterion specifies that only frequencies $f \leq \frac{f_s}{2}$ can be resolved in the frequency domain; for samples where $k > \frac{N}{2}$, $X[k]$ is just a mirrored repetition of $X[k]$ for $k < \frac{N}{2}$. For the lock-in application, it is thus necessary to sample the signal at least at a rate $f_s > 4f_{\text{mod}}$ since the second harmonic is a sinusoid at frequency $2f_{\text{mod}}$.

After manipulating the signal in the frequency spectrum, it is necessary to return the signal to the time domain by performing the inverse DFT (IDFT), shown in Equation A.3.

\[
x[n] = \sum_{n=0}^{N-1} X[k]e^{j\frac{2\pi nk}{N}} 
\] (A.3)

A.2 The Fast Fourier Transform

Calculating $X[k]$ using Equation A.2 is a computationally expensive task, $O(N^2)$, as the sum has to be calculated $N$ times for each frequency sample number $k$. It is thus useful to make use of the FFT whenever calculating the DFT of a signal.

The most commonly used algorithm for calculating the FFT is the radix-2 Cooley–Tukey FFT proposed by Cooley and Tukey in 1965 [48]. The FFT algorithm is based on the principle of divide and conquer. If the sequence of data is divided into smaller parts and the DFT algorithm is performed on these smaller constituents, it is possible to reduce the number of calculations. In the extreme case, reducing the problem to $N/2$ parts leads to each part having a form shown in Equations A.4 and A.5.

\[
X_{\text{part}}[k] = \frac{1}{2} \sum_{n=0}^{1} x(nT_s)e^{-j\pi nk} 
= \frac{1}{2} \left( x(0) + x(T_s)e^{-j\pi k} \right) 
\] (A.5)
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The exponential term conveniently reduces to $\pm 1$ and the two values can thus be found by performing a simple addition and subtraction, respectively, shown in Equations A.6 and A.7. It is necessary to note that the two samples in Equation A.5 are not in order, but from different parts of the signal.

$$X_{\text{part}}[0] = \frac{1}{2} (x(0) + x(T_s))$$  \hspace{1cm} (A.6)

$$X_{\text{part}}[1] = \frac{1}{2} (x(0) - x(T_s))$$  \hspace{1cm} (A.7)

The size reduction first occurs by splitting the signal into two parts: even and odd numbered samples only. Then, the two parts are yet again separately split into even and odd numbered samples only. This continues until the parts are non-reducible. It is thus a smart option to pad the signal with zeros such that the length is $2^m$, where $m$ is an integer, such that the smallest parts are always of length 2. Padding the signal and using the above algorithm leads to a total reduction in the order of computations necessary from $O(N^2)$ to $O(N \log N)$.

### A.3 Convolution

The convolution operation is a vital tool for signal analysis and construction. A good overview of the convolution operation and the relation between the continuous and discrete operations was given by Cooley et al. [49]. This section is dedicated to a short presentation of the convolution operation for refreshing latent knowledge. For a deeper understanding, I would like to refer the reader to a text book such as “Schaum’s Outline of Signals and Systems” by Hsu [50].

In essence, the convolution is of sorts a mixing of two signals. Let $x(t)$ be a signal in the time domain and $y(t)$ be an impulse response in the time domain. The convolution of the two is given by $z(t)$ in Equation A.8.

$$z(t) = \int_{-\infty}^{\infty} x(t - \tau) y(\tau) d\tau$$  \hspace{1cm} (A.8)

The first thing to make note of is that the convolution operation makes use of an integrating dummy variable $\tau$. Consider both the signal and the impulse response as a function of $\tau$, $x(\tau)$ and $y(\tau)$. The first action in order to perform the convolution is to mirror the signal $x(\tau)$ around the y-axis to $x(-\tau)$. Next, an independent variable $t$ is introduced to the signal in order to enable sliding along the $\tau$ axis, $x(t - \tau)$. The mirroring and introduction of $t$ are shown in Figure A.1.
Let us now discuss a simple example. Let the impulse response be a delta function $y(\tau) = \delta(\tau)$, which is defined as $\infty$ for $\tau = 0$ and 0 elsewhere. Since $y(\tau) = 0$ for $\tau \neq 0$, the convolution operation will only give nonzero output when $\tau = 0$. In this very point, the function $x(t - \tau) = x(t)$ is multiplied by the area of the impulse response, 1, returning $z(t) = x(t)$. Thus, we can extend our reasoning such that the convolution integral only needs to be evaluated in the range where $y(\tau)$ is nonzero. Let $a$ and $b$ be two real numbers with $a < b$. If $y(\tau)$ is zero outside the range $a \leq \tau \leq b$, the convolution integral simplifies to Equation A.9.

$$z(t) = \int_{a}^{b} x(t - \tau)y(\tau)d\tau \quad \text{(A.9)}$$

As we have established the limits of the convolution integral, we can now discuss a more interesting example. Let the signal and the impulse response both be a box function in the range $0 \leq t \leq T$ as defined in Equation 3.2, $x(t) = y(t) = \Pi(t)$. Let us now follow the procedure of the convolution graphically in Figure A.2. a) shows the zero response in $z(t)$ when the signal and impulse response do not intersect. b) shows the rising $z(t)$ as the yellow intersecting area between $x(t - \tau)$ and $y(\tau)$ linearly increases. c) shows the maximum value of $z(t) = T^2$ when the functions completely overlap. d) shows how $z(t)$ has decreased to zero again as the signal and impulse response do not overlap beyond

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**Figure A.1:** Signal transformation during convolution. The example signal is a box function. The independent variable $t$ makes the signal able to slide along the $\tau$ axis.
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$t = 2T$.

It is now easy to understand that the convolution of two box functions provide a simple mathematical expression for a triangle function, such as that introduced in Chapter 3.

In addition to being useful for constructing signals, the convolution has a number of useful properties. In particular, there is one property connecting to the Fourier transform that can greatly simplify calculations; namely, the convolution theorem. It states that the Fourier transform of a convoluted pair of functions is equal to the individual Fourier transforms of the signals multiplied by each other, shown in Equation A.10.

\[
\mathcal{F}\{x(t) \ast y(t)\} = \mathcal{F}\{x(t)\}\mathcal{F}\{y(t)\} \tag{A.10}
\]

The convolution theorem is very useful in for example finding the Fourier transform of the triangular wave, since it ends up being a multiplication of the Fourier transforms of two box functions which are trivial to find.

A.4 Confirming the Frequency Domain of the Tukey Window

In order to check that the result for the Tukey window in the frequency domain is reasonable we can insert $\alpha = 0$. We expect that the Tukey window approaches a
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rectangular window for $\alpha = 0$. If the frequency response of Equation 3.15 is a delta function, the convolution of the delta function and the box function of period $T$ becomes another box function. We begin by rearranging Equation 3.15 to a more convenient form by expanding the sinc functions and using the Euler formula, shown in Equations A.11 through A.12.

$$\mathcal{F}\{\Omega_{tr}(t, \alpha)\} = \frac{A\alpha T}{2\pi} e^{-i\pi f_{\alpha}T} \left[ \frac{\sin(\pi \alpha f T + \frac{\pi}{2})}{\alpha f T + \frac{1}{2}} + \frac{\sin(\pi \alpha f T - \frac{\pi}{2})}{\alpha f T - \frac{1}{2}} \right]$$  \hspace{1cm} \text{(A.11)}$$

$$= [\sin(a \pm b) = \sin a \cos b \pm \cos a \sin b]$$

$$= \frac{A\alpha T}{2\pi} e^{-i\pi f_{\alpha}T} \left[ \cos(\pi \alpha f T) - \cos(\pi \alpha f T) \right]$$

$$= \frac{A\alpha T}{2\pi} e^{-i\pi f_{\alpha}T} e^{i\pi f_{\alpha}T} + e^{-i\pi f_{\alpha}T} \left[ \frac{1}{\alpha^2 f^2 T^2 - \frac{1}{4}} \right]$$

$$= \frac{AT}{2f^2 T^2} \left( 1 + e^{-i2\pi f_{\alpha}T} \right) \frac{1}{\pi} \left[ \frac{\alpha}{\alpha^2 + \left( \frac{i}{2fT} \right)^2} \right]$$  \hspace{1cm} \text{(A.12)}$$

An experienced eye can now see that Equation A.12 is on a convenient form for limit evaluation. Using the property $\lim_{x \to 0} \frac{1}{\pi} \frac{x}{x^2 + x^2} = \delta(x)$ gives Equation A.13.

$$\lim_{\alpha \to 0} \mathcal{F}\{\Omega_{tr}(t, \alpha)\} = \frac{AT}{f^2 T^2} \delta \left( \frac{i}{2fT} \right)$$  \hspace{1cm} \text{(A.13)}$$

Thus, the frequency response is as expected a delta function, although of peculiar nature. We have now shown that Equation 3.15 seems to hold for $\alpha = 0$.

A.5 Current–Voltage Characteristics – Landauer Model

In order to understand the nature of the single molecular junction, it is convenient to introduce the Landauer model for explaining the current transport. The current through a one-dimensional ballistic junction with a transmission function $T$ with an applied bias is shown in Equation A.14 [51].

$$I(E) = \frac{2q}{h} \int_{-\infty}^{\infty} T(E) \left[ f(E - \mu_1) - f(E - \mu_2) \right] dE$$  \hspace{1cm} \text{(A.14)}$$

Here, $q$ is the electron charge, $h$ is Planck’s constant, $f(E)$ is the Fermi-Dirac distribution function and $\mu_{1,2}$ are the potentials of electrodes 1 and 2, respectively. In the limit of absolute zero temperature, the Fermi-Dirac distributions become Heaviside step functions and the equation simplifies to an integral of the transmission function over the
bias window opened around the electrode Fermi level when applying a bias voltage $V$, shown in Equation A.15.

$$I(V) = \frac{2q}{\hbar} \int_{E_F-qV/2}^{E_F+qV/2} T(E) dE$$  \hspace{1cm} (A.15)

It is worth noting that this is a rather good approximation at cryogenic temperatures for purely ballistic transport. The unresolved part of Equation A.15 is the transmission function, which usually is modeled by Lorentzian functions at the molecular orbital levels. The transmission function quickly increases in complexity if more parameters are added for increased accuracy of the model.
Appendix B

IETS of 8T Oligothiophene

This Appendix serves as a container for the data recorded for the 8T molecule. Since the data is inconclusive, it is not included in the main body of this work.

B.1 The 8T Molecule

8T was selected for measurement to compare a molecule of similar chemical composition and structure to 5T in order to investigate the sensitivity of IETS. The structure of the 8T molecule is shown in Figure B.1.

\[\text{Figure B.1: The molecular structure of the 8T molecule.}\]

B.2 Histogram of 8T IETS

8T was significantly more difficult to measure than 5T due to frequently observed stochastic switching behavior during measurement. 248 of the 977 data measured had an acceptable noise level and were selected for histogram display. The result is shown in Figure B.2.
It is clear that the most common peak locations of 8T are not the same as for 5T. The dissimilar peak locations between the molecules can be due to an insufficient data collection amount, as similar molecules should show peaks in similar locations. If not enough data is collected for histograms, one stable measurement can skew the results to the peak locations of that certain measurement. Figure B.3 shows the measurement that is likely to have skewed the results in the histogram in Figure B.2. Most of the data points in Figure B.3 were used for constructing the total histogram, meaning that most of the data in the total peak histogram is actually only from one measurement.
Figure B.3: The reason behind the skewed results in Figure B.2.
Appendix C

System Implementation in LabVIEW

This Appendix contains five images of the lock-in program implementation in LabVIEW. Due to the complexity and size of the program, which consists of 79 VIs (LabVIEW program files), only the most important parts are shown here. The front panel is introduced, where after the main program structure (producer consumer) is shown. Finally, the details of the lock-in amplifier and the filter are displayed.
Figure C.1: Front panel of the developed LabVIEW program. The program is divided into sections to allow simultaneous monitoring and parameter control. The lower right panel named Magnet Control is developed for controlling the Oxford 3D vector magnet system in the cryostat.
Figure C.2: An example of the producer consumer structure of the designed program. The producer consumer state machine allows for input during runtime. The upper producer loop catches user input and enqueues a proper action to the lower consumer loop. The consumer (state machine) loop shows the state of outputting a carrier wave type IV sweep and checking for amplifier overload.
Figure C.3: The lock-in implementation in LabVIEW. The recorded signal from the carrier wave sweep is split into three parts to extract the IV curve, first and second derivatives. The ‘Phase at 0 mV’ variable is the phase offset found by modulating at 0 V DC bias.
Figure C.4: Sine/cosine multiplication for first and second derivative analysis before low-pass filtering the signal in Figure C.3. The sine and cosine signals are synthesized with an appropriate phase offset due to for example capacitance, found by modulating at 0 V DC bias during a short period before the sweep.
Figure C.5: The band-pass filter designed in LabVIEW. The signal is first padded with zeros before the FFT in order to realize a faster FFT implementation and then truncated after the IFFT. Both edges of the passband are attenuated in the same loop for a faster filter implementation.

The remaining values from $2N_{\text{mod}}$ to $N_{\text{pad}}/2$ are set to zero. Values above $N_{\text{pad}}/2$ are left untouched.
Appendix D

Animations of 5T Vibrations

It is necessary to use a PDF viewer capable of displaying Flash content such as Adobe Acrobat Reader DC to view the animations in this Appendix. For Adobe Acrobat Reader of version 11 and above, it is necessary to install the Flash Player plugin separately on your computer.
Bibliography


[37] National Instruments, Austin, TX 78759-3504.


