Semi-Empirical Computational Approach Towards Resonant Tunneling Through Inorganic Nanowires

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ABSTRACT: *In this research paper, our work focussed on investigating the impact of the variation of molecular length of on the electron transport properties of Cadmium telluride and Cadmium selenide inorganic nanowires stringed to semi-infinite gold electrodes using semi-empirical computational approach. We observed that as the length of the nanowire was increased, there was definite impact on the various parameters namely current, conductance, differential conductance, stress and transmission spectrum. We elucidated that as we varied the length of Cadmium telluride and Cadmium Selenide nanowire, a gradual decrease in the current and conductance, differential conductance was observed while stress increased. Most important phenomena observed was Kondo assisted resonant tunneling in both nanowires on account of lifting of coloumb blockade. Another important observation was less perturbation in the transmission spectra with increase in molecular length indicating fewer chances of electron transportation. The vital information collected through this simulation work can be significantly beneficial in molecular electronics applications especially as nanoscale switching device.*

KEYWORDS: Nanowire, Perturbation, Molecular Length, NDR, Kondo assisted Tunneling
PACS: 73.63.Nm Quantum wires
73.40.Gk Tunneling

1. INTRODUCTION

Since 70s, the miniaturization by obeying Moore's law has persistently lead to an exponential increase in the quantity of information that can be processed, stored, and transmitted per unit area of microprocessor, memory and fibreglass respectively. A modern integrated circuit contains one billion transistors, each smaller than 100 nm in size, i.e. a hundred times smaller than the diameter of a human hair. The crossing of this symbolic 100 nm threshold at the outset of the 21st century ushered in the era of nanotechnology [1]. As semiconductor device feature sizes continue to be reduced, ensuring reliable operation has become a growing challenge. Packaging of semiconductor electronic device is a challenge due to the progressive increase in the power level of operating devices which is associated with the increasing device performance. Alternative technologies are desired which will allow continued increase in the density of memory and logic into the terabit regime. At the same time, there is a realization that the architectures necessary at ultra-high densities may have to be quite different than those currently employed in for example microprocessor design, in order to accommodate new device concepts, and the increasing need of fault-tolerance as device to device fluctuations become larger at the ultimate limits of integration. It is in fact likely that conventional digital architectures will co-exist with special purpose applications using Nano scale devices which perform parallel analog processing at much greater speeds than digital ones based on algorithms such as those based on quantum computation, and biologically inspired cellular architectures. Hence, there is a strong motivation for understanding and designing new and functional device structures at the Nano scale [2].

Molecular junctions are promising candidates as future electronic devices because of their small size and self-assembly feature. Such junctions are usually composed of

two metallic electrodes (source and drain) joined by individual molecule (bridge). The charge is transferred under the bias voltage and current-voltage (I-V) characteristics are measured experimentally [3]. The past Fifteen years have seen the development of techniques to measure the conductance of small numbers of molecules between electrodes, bringing a renewed challenge to understand the details of molecular junction electron transport. Much of today's qualitative understanding comes from the earlier work on intra molecular electron transfer and the theories of Marcus, Sutin and Hush [4, 5]. The future of communication and information processing technologies depends on the use of Nano metric and sub micro meter integration as an essential tool [6].

Single molecule circuits represent a lower limit on the scalability of electronic devices and are hence an ultimate goal of nanotechnology. As circuits approach the Nano scale, transport variations overwhelm ensemble averages and play a more critical role. While important experimental and theoretical advances over the past decade have yielded some insight into electron transport in metal-molecule-metal junctions [7, 8].

Charge transport through molecular junctions depends on the intrinsic properties of the molecules, the contacts, metal leads, molecular length, conformation, the gap between HOMO and LUMO, the alignment of this gap to the metal Fermi level, and the metal-molecule coordination geometry. Other factors of influence comprise temperature, mechanical stress, environment (UHV, gas, or solution phase), and the applied potential. One-dimensional materials such as various kinds of nanowires and nanotubes have attracted considerable attention due to their potential application in electronic and energy conversion devices [9].

In this research work, we analysed the effect of variation of molecular length on the current, conductance values and transmission spectrum of Cadmium Telluride and cadmium selenide, important constituents of the zinc blende group. We observed the important phenomena of lifting of the coloumb blockade and resultant kondo assisted tunneling. Though the I-V curves were observed to be linear for small bias range and at constant room temperature, dI/dV curves exhibited huge variations with small interval changes during the entire bias value selected for our modelling.

2. MODELLING AND SIMULATION WORK

A nanowire consisting of a single Cadmium selenide/cadmium telluride molecule was placed between two semi-infinite gold electrodes as shown in figure1A, B and the bias voltage ranging -1 V to 1 V was applied with the step size of 0.5 V at room temperature. The Simulations were repeated for nanowire consisting of two and three molecules of Cadmium Selenide/Cadmium Telluride. Electron transport properties using Extended Huckle Theory (EHT) based semi-empirical model were evaluated. The proposed model for electron transport through nanowire (scattering region) forming hetero junctions with metallic electrodes (left & right regions) was simulated using commercial simulation package Atomistix Tool Kit (ATK 12.2.0) with its graphical user interface Virtual Nano Lab (VNL).

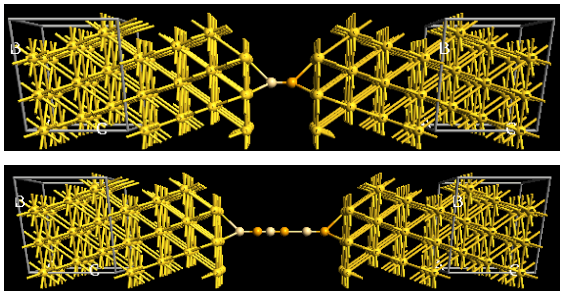


Figure1-A: A Nanowire of a) single CdSe molecule b) Three CdSe molecules stringed between the semi-infinite gold electrodes.

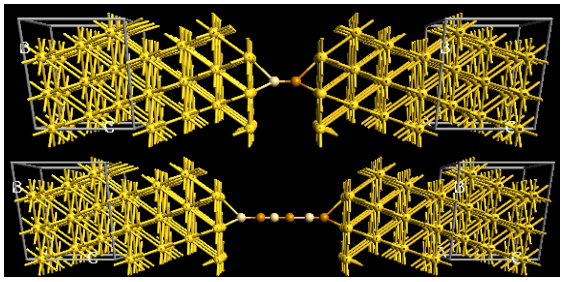


Figure1-B: A Nanowire of a) single CdTe molecule b) Three CdTe molecules stringed between the semi-infinite gold electrodes.

3. RESULTS AND DISCUSSIONS

To measure the impact of the change in length of these nanowires on the electron transport characteristics, we varied the length of the both CdSe and CdTe nanowires by adding more molecules. Our objective to extend the length nanowires sandwiched between gold electrodes was to elucidate the stress experienced during the elongation of the nanowire. The corresponding values of current, conductance and stress for different lengths of Cadmium Selenide and cadmium telluride nanowires under variegated applied voltage were reported in table1, 2 and 3 respectively.

CURRENT:

Variegated bias voltages ranging from -1 V to +1 V in discrete steps of 0.5 V were applied on the metallic electrodes and the electric current was calculated using the Landauer-Buttiker formula [10–12]. The current flowing through the device was obtained from the transmission function T through the integration procedure. The current through a single molecule connected to two metal electrodes can be calculated using the following expression:

$$I = \frac{2e}{h} \int_{\mu_R}^{\mu_L} T(E,V_b)[f_R(E,V_b) - f_L(E,V_b)]dE \quad .....(1)$$

where $f_L(E, V_b)$, and $f_R(E, V_b)$ are the Fermi-Dirac functions for the left and right electrodes at energy E under the bias voltage, V_b; $T(E, V_b)$ is the sum of the transmission probabilities of all channels available at energy E under bias V_b , μ_L and μ_R are the chemical potentials of the left and right electrodes; and $\mu_L (V_b)$, $\mu_R (V_b)$ is the energy region for the current referred as the bias energy window [13]. The bias energy window is given by $\mu_L = E_F - eV_b/2$ and $\mu_R = E_F + eV_b/2$, and E_F is the Fermi energy which is the average value of the chemical potential of the left and right electrodes, is usually set to zero [14].

Table1: I-V Values for different lengths of

a) Cadmium Selenide

APPLIED BIAS IN VOLTS(V)	CURRENT IN NANO AMPS OF NANOWIRE CONTAINING		
	1molecule of CdSe	2 molecules of CdSe	3 molecules of CdSe
-1	-38423.5	-20803.5	-2355.67
-0.5	-21258.1	-11586.0	-1328.15
0	0	0	0
0.5	23172.90	13034.967	1482.849
1	43457.06	25006.23	2884.294

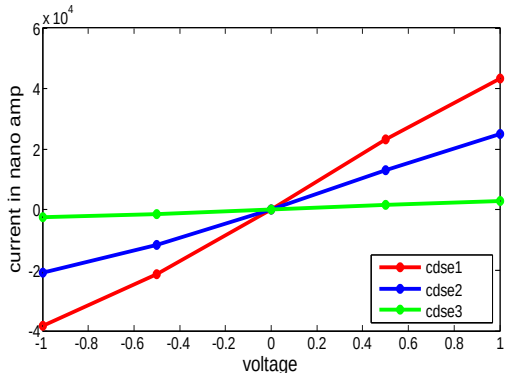
b) Cadmium Telluride nanowire.

APPLIED BIAS IN VOLTS(V)	CURRENT IN NANO AMP OF NANOWIRE CONTAINING		
	1molecule of CdTe	2molecules of CdTe	3molecules of CdTe
-1	-60424.7	-37834.91	-13293.72
-0.5	-32570.1	-20510.83	-7566.444
0	0	0	0
0.5	33890.97	21480.02	8539.78
1	62503.28	39996.86	16771.77

The respective values of current for different voltages at different lengths have been displayed in table 1 for cadmium selenide and telluride nanowires. With increase in the bias voltage the current increased for different lengths of cadmium selenide and cadmium telluride nanowires. With the elongation of nanowires the current decreased in all the samples as the resistance increased with the length of the nanowire as shown in figure 2. Red line in the graphs represents nanowire containing single molecule, blue line represents nanowire constituting two molecules and green line represents nanowire consisting three molecules. At 1 volt of applied bias current decreased from 43457.06 to 2884.294 Nano amps in case of cadmium selenide nanowire and decreased from 62503.28 to 16771.77 Nano amps for cadmium telluride

nanowire. Though the nature exhibited by the I-V curves is similar, but the values became more confined as length of the nanowire increased. This reduction in the value of current is because of the bonding becoming weaker with increase in molecular length. The conducting path was extended that caused the increase of the LUMO-HOMO gap energy of the molecule and that of contact resistance.

a)



b)

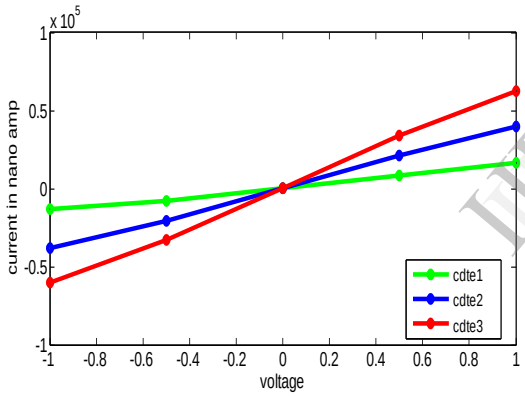


Figure 2: I-V curves for different lengths of a) Cadmium Selenide b) cadmium telluride nanowire.

CONDUCTANCE:

The quantized conductance of the molecule as suggested by Landauer can be given by the following relation

$$G_0 = N e^2 / h \ldots\ldots. (2)$$

Here e and h are electron charge and plank's constant respectively, while N depends upon the spin. Because in zero magnetic field, molecular device junction, has a spin degeneracy of 2, so the above relation at (2) takes the following form

$$G_0 = 2 e^2 / h \ldots\ldots. \quad (3)$$

The quantized conductance G_0 is the conductance at zero bias and this value works out to be 77.27 µS. The total transmission coefficient is also a function of conductance at any bias voltage and is given by

$$G = G_0 T (E_F) \quad \ldots\ldots\ldots (4)$$

Where $T(E_F)$ is the transmission coefficient at Fermi energy. The transmission function is typically computed from the Green's function of the central region in presence of the coupling with the electrodes and reflects the efficiency of the electron transmission from one contact to other [15].

Conductance for different molecular lengths of Cadmium Selenide and cadmium telluride nanowires were reported in table3 a) and b) respectively. We observed that conductance decremented with increment in molecular length of the nanowire as shown in figure 3. As the resistance offered by the nanowire is directly proportional to the length of the nanowire, increased resistance or in other words, reduced conductance as observed as we added more molecules of CdSe to lengthened the nanowire. The conductance of cadmium selenide nanowire consisting of single molecule, two molecules and three molecules was observed to be 47.9107µS, 27.886 µS and 3.31042 µS respectively at zero-bias. Similarly conductance of cadmium telluride nanowire consisting of single molecule, two molecules and three molecules was 68.32 µS, 44.3304 µS and 18.1955 µS respectively.

Table3: Conductance- voltage for different lengths of a) Cadmium Selenide nanowire.

APPLIED BIAS IN VOLTS	CONDUCTANCE (IN µS) OF NANOWIRE CONTAINING		
	1molecule of CdSe	2molecules of CdSe	3molecules of CdSe
-1	42.245	23.0291	2.6628
-0.5	43.134	23.572	2.710257
0	47.373	26.2052	3.01507
0.5	46.6216	26.25	3.0013
1	47.9107	27.886	3.31042

We observed that for all molecular lengths, CdTe nanowires were almost 150% more conducive than CdSe nanowires. We noticed that the contacts formed by CdTe with gold electrodes were more conducting than contacts formed by CdSe with gold electrodes, although both contacts were tunnel contacts in nature. As the conductance exhibited by all our samples, were reported less than quantum conductance, electron transport through these can happen because of tunneling only.

b) Cadmium Telluride nanowire.

VOLTAGE	CONDUCTANCE(IN µS) OF NANOWIRE CONTAINING		
	1molecule of CdTe	2molecules of CdTe	3molecules of CdTe
-1	65.7076	41.643	14.865
-0.5	65.9326	41.615	15.405
0	70.51643	44.7068	17.1741
0.5	68.15	43.286	17.2565
1	68.32	44.3304	18.9155

This decrease of conductance with increase in length is on account of the exponential dependence of the conductance with increasing molecular length and can be described as [16, 17]

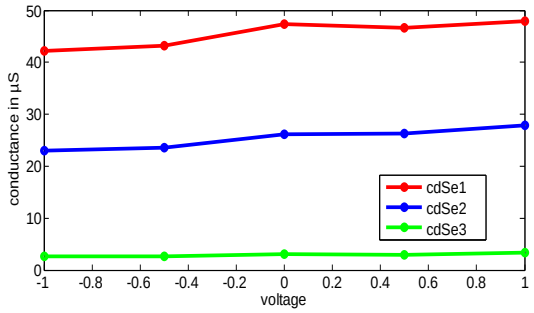
$$J \alpha e^{(-\beta d)} \quad \ldots\ldots\ldots (4)$$

Where J is the conductance of the molecule, β is the decay constant in A^0 and d is the length of molecule. β,

The decay constant, also named tunneling attenuation factor, in general, depends on the nature of bonding in the molecular backbone the exponential dependence of current density versus molecular length results from electrode/molecule/electrode direct transition, namely tunneling.

As molecular length increases, the positive β Value indicates the decreased conductance, if the Fermi level of the electrodes lies between the HOMO-LUMO of the molecules. The energy gaps of conjugated molecules are proportional to the inverse of molecular length. Reduction in the value of current was seen which is because of the bonding becoming weaker with increase in bond length. The conducting path was elongated that caused the increase of the LUMO-HOMO gap energy of the molecule and that of contact resistance.

a)



b)

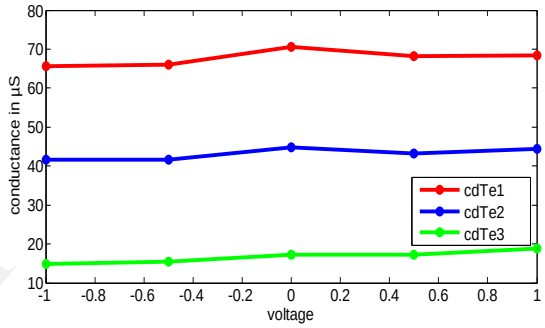


Figure3: voltage-conductance curves for different lengths of a) Cadmium Selenide b) cadmium telluride nanowire.

DIFFRENTIAL CONDUCTANCE:

The differential conductance curves for Cadmium selenide and Cadmium telluride nanowires different nanowire lengths are shown in figure 4 and 5 respectively. The differential conductance peaking at zero bias voltages exhibited condo assisted tunnelling and lifting of coulomb blockade in all the samples of the nanowires.

We observed that with increase in the length of nanowire, the value of differential conductance for cadmium selenide decreased from 47000 nS for nanowire with molecular length 1.51 $\mathbf{A^0}$ to 26000ns for nanowire with molecular length 3.78 A^0 and finally to 3015 nS with increasing nanowire molecular length to 7.18 A^0. Similarly the value of differential conductance decreased from 70000nS for nanowire with molecular length 1.62 $\mathbf{A^0}$ to 44000ns for nanowire with molecular length 4.05 A^0

and finally to17000 nS with increasing nanowire molecular length to 6.85 A^0. From the both figures 4 and 5, we observed that the values of the conductance remained quantized between -1 V to -0.6 V as well as from 0.6 V to 1 V. What really impressed us most, the huge change observed in the value of conductance between -0.6 V to 0.6 V. A perfect switching from "off" to "on" state was observed as the bias voltage varied from -0.6 V to 0 V and then from "on" to "off" state as the bias voltage changed from 0 V to 0.6 V. As the switching observed was on account of resonant tunneling, we think that these nanowires can be good substitute for resonant tunneling diodes (RTDs).

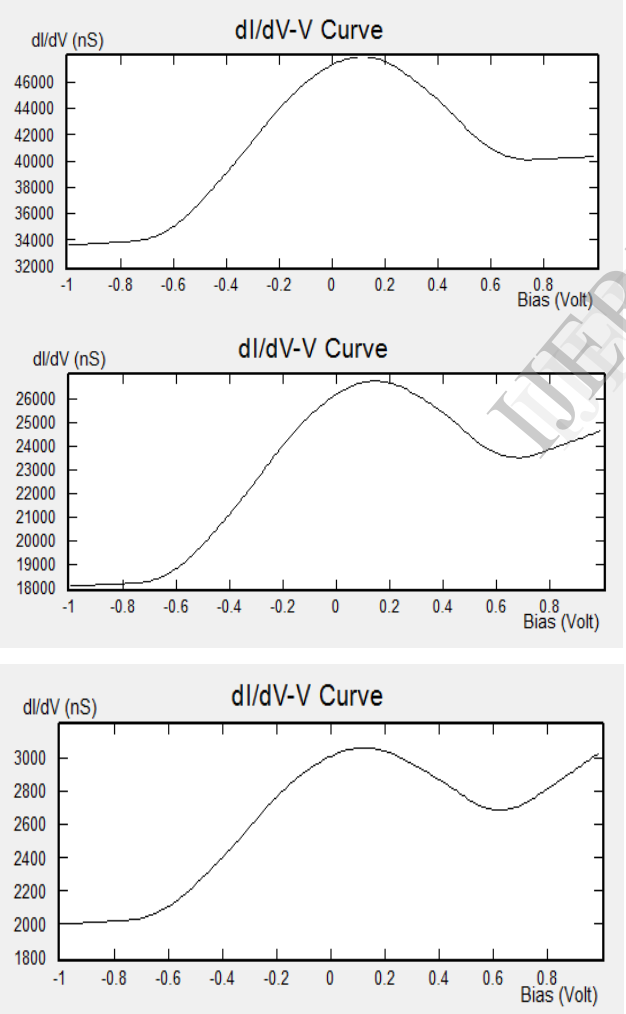


Figure 4: Differential conductance of nanowire containing a) Single CdSe molecule b) 2 CdSe molecules c) 3 CdSe molecules

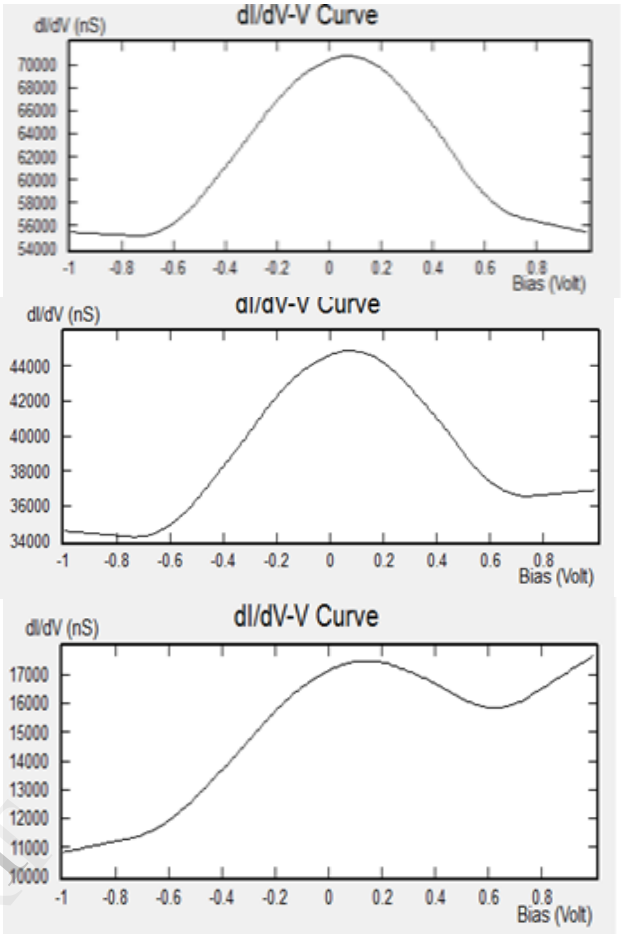


Figure 5: Differential conductance of nanowire containing a) Single CdTe molecule b) 2 CdTe molecules c) 3 CdTe molecules

STRESS:

In order to measure the effect of elongation on the overall stress on the nanowires, we tightly bound the anchoring alligator clips connected to the leads of the metallic electrodes, so that these remain fixed during the equilibrium generated through the transitions of the electrons. With elongation of nanowire, we observed that stress also varied and the nature of the stress observed was compressive. The observed values of stress for different molecular lengths for cadmium selenide and cadmium telluride nanowires have been presented in table3. The elucidated results showed that the as we added second molecule to the nanowires, there was a linear

change in the stress observed, but as the third molecule was added to further increase the length of nanowire, the stress rose exponentially, which indicate a co-relation between the stress and the resistance of the nanowire with increase in molecular length.

Table 3: Molecular Length versus Stress.

Molecular Length(in nm) of nanowire	Stress(in ev/A^{**3}) for CdSe nanowire	Molecular Length(in nm) of nanowire	Stress (in ev/A^{**3}) for CdTe nanowire
1.51	-0.2732	1.62	-0.27036
3.78	-0.2598	4.05	-0.26161
7.18	-0.1849	6.88	-0.18101

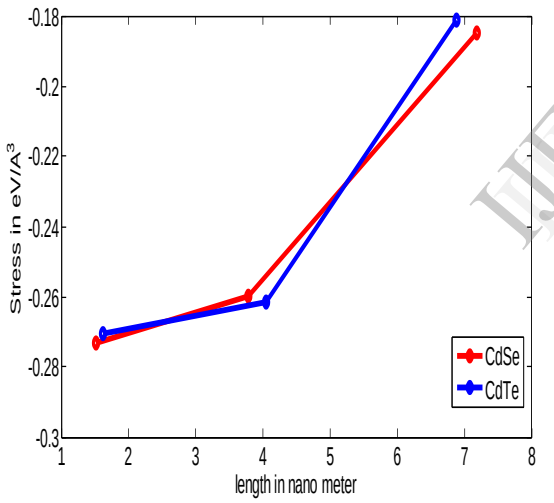


Figure6: Length versus Stress.

With elongation of nanowire there was increment in the values of stress for both cadmium selenide as well as for cadmium telluride nanowires at 1volt of applied bias as shown in figure 6.

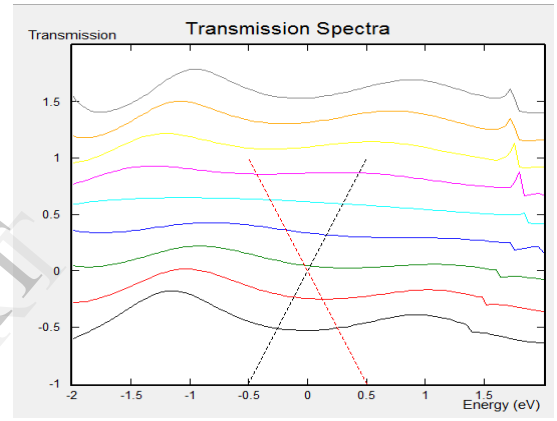
TRANSMISSION SPECTRUM:

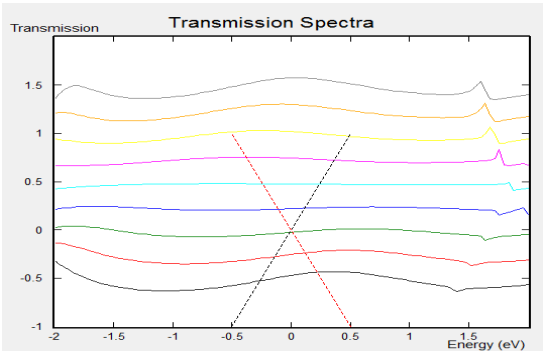
The transmission function is obtained from The Meir–Wingreen transmission formula [18, 19]

$$T(\varepsilon) = \mathrm{Tr}[G^r(\varepsilon)\Gamma_L(\varepsilon)G^a(\varepsilon)\Gamma_R(\varepsilon)] \quad \ldots\ldots\ldots (5)$$

$$G^r(\varepsilon)=[(E + i\,\eta)S-H_0+V_{xc} -\Delta V_H[G]-\textstyle\sum_L (E)]-\sum_R (E) - \sum_{XC}[G]\,(E)]^{-1} \quad \ldots\ldots\ldots\ldots (6)$$

The retarded Green's function of the extended molecule is calculated from Where *S*, H_0, and *Vxc* are the overlap matrix, Kohn–Sham Hamiltonian and the local xc-potential in the atomic orbital basis, respectively; η is a positive infinitesimal. The lead self-energy, Σ*L*/*R*, incorporates the coupling to the left and right electrodes and is obtained by standard techniques.





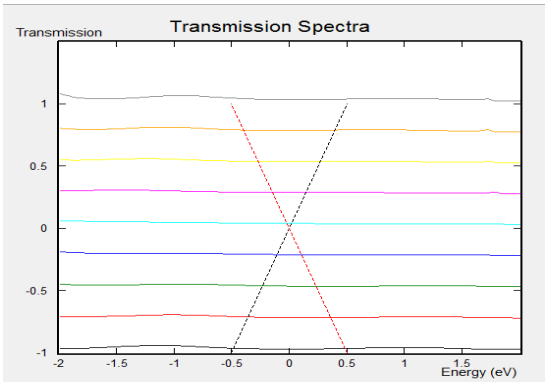
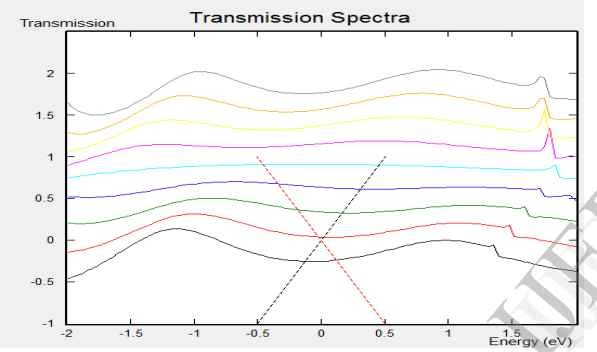
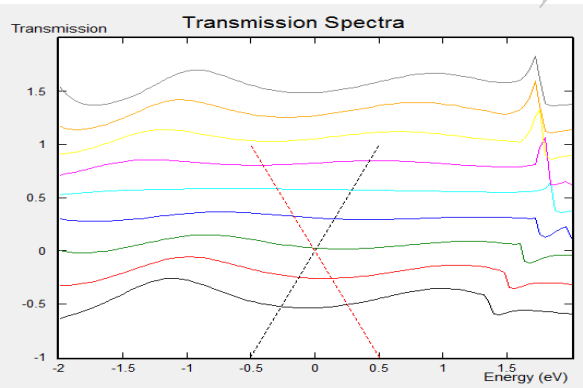


Figure 7: Transmission spectrum of nanowire containing a) Single CdSe molecule b) 2 CdSe molecules c) 3 CdSe molecules.

Lastly, we investigated the effect on the transmission spectrum of the nanowires. We observed that the flatness increased with increase in the length of cadmium selenide as well as for cadmium telluride nanowires with elongation of nanowire as shown in figure5 and 6. Figure 5a and 6a represents transmission spectra of Cadmium Selenide nanowire and cadmium telluride nanowire respectively constituting single molecule, We observed more transmission peaks which represents narrow energy gap between HOMO and LUMO levels whereas in figure 5b,c and 6b, c more flatness was seen that indicated higher HOMO-LUMO gap.





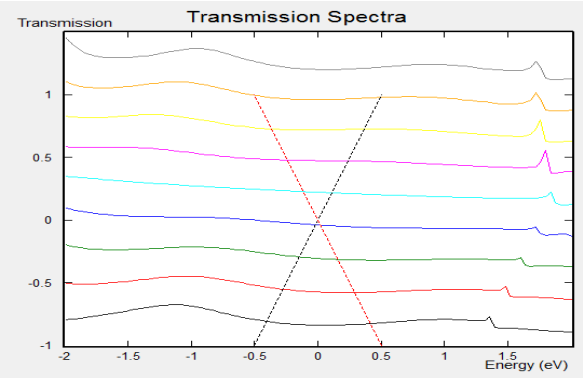


Figure8: Transmission spectrum of nanowire containing a) single CdTe molecule b) 2 CdTe molecules c) 3 CdTe molecules.

CONCLUSION:

The pronounced molecular length dependence of transport properties of nanowires was observed. We investigated that if the length of nanowires was elongated by adding more molecules, these caused the current and conductance to decrease linearly with the percentage increase in bond length. The differential conductance curve exhibited lifting of the Coulomb blockade and Kondo assisted tunnelling. The observed values of the conductance were much below the quantum conductance thus indicating a limit of weak coupling regime and hence tunneling contacts. In comparison to CdSe nanowires, the transport behaviour of the CdTe nanowires exhibited improved metrics. Both nanowires performed clear switching between "ON" and "OFF" within the applied bias range of -0.6 V to 0.6 V. Increased molecular length led to variation in the stress on the both nanowires, though the stress was more dominant on CdTe nanowires. The increased molecular length indicated less perturbations leading to enhanced flatness of transmission spectrum and thus limited electron conduction. Thus, we attributed the decreased conductance upon stretching to the change of the HOMO-LUMO energy gap. The results showed a striking variation of the transport characteristics depending on the geometry of the molecular system.

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