Length-Dependant Tunneling And Hopping Mechanism In Molecular Wires

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Abstract

The temperature-dependant electron transport characteristics of three molecular wires of different molecular lengths belonging to the family of conjugated benzene molecules were studied. In this article, the conductance values for three molecular wires consisting of different number of benzene rings and amounting to different lengths at different temperature were calculated. The percentage change in conductance values were plotted with respect to temperature for each molecular wire in this research work. We concluded that the longest molecular wire of benzene having molecular length of 17.055A^0 showed the most pronounced effect of temperature on conductance, even though this value was much smaller than the value exhibited by shortest molecular wire of length 5.003A^0. The results demonstrated that the shorter wires showed highly length dependence and temperature invariant conductance, whereas the longest wire exhibited weak length dependant and temperature variant behaviour. This electron transport behaviour was observed to be changing from tunnelling in shorter length wires to the hopping in longer length wires.

Keywords: Mesoscopic Systems, Resonant Tunneling, Thermionic emission, Hopping, Coulomb blockade.

1. Introduction

Ongoing investigations of electrical transport in molecules have been motivated by the discovery of intriguing transport phenomenon including Coulomb blockades [1-4], Kondo resonances [4-7], current rectification [8, 9] switching [10, 11] and negative differential resistance [12-14]. In a recent publication, Selzer [15] has revealed that it was possible to measure the temperature dependence of the current-voltage (I–V) response of a single molecule immobilised in a break junction. It was shown that electron transport in a ‘‘molecular wire’, characterised by a conjugated π system and having a relatively rigid-rod structure, could be switched from coherent super-exchange tunnelling at low temperatures to incoherent temperature dependent hopping at higher temperatures. Thermionic emission may occur upon injection of an electron from a conductor into a molecular monolayer. The applied field lowers the activation barrier; resulting in a dependence on both *V* and *d*. “Hopping” consists of thermally activated electron transfer between sites in the monolayer, and yields essentially ohmic behaviour at a given temperature often with d^{-1} dependence [16-19]. Electron transmission occurs when the applied field and temperature are sufficient to permit electrons to overcome coulomb blockade. In order to analyse ambient temperature effects on single molecule conductance, we recorded and analysed data over the temperature range between 0 K and 1500 K. The present work demonstrates the importance of conformational effects on molecular conductance in this temperature range and attempts to quantify these effects through single molecule measurements. We illustrated that thermal effects become significant at ambient temperatures and can be described in terms of the temperature dependence of conformer distribution and a tunneling barrier model.

2. Modelling and Simulation

Three molecular wires consisting of one benzene ring, two benzene rings and finally three benzene rings terminated with the thiol linker group stringed between the two semi-infinite gold electrodes of [1,1,1] orientation as shown in figure 1. The molecular length in its epoch for single benzene molecule was taken as 5.003A^0 whereas for second and third epoch were 11.33 A^0 and 17.055 A^0 respectively. As the length increased for these three epochs, we observed the effect of variation in molecular length of molecular junctions thus formed on the conductance as the temperature was varied from 0K to 1500K. The corresponding values of current and conductance were observed and plotted.

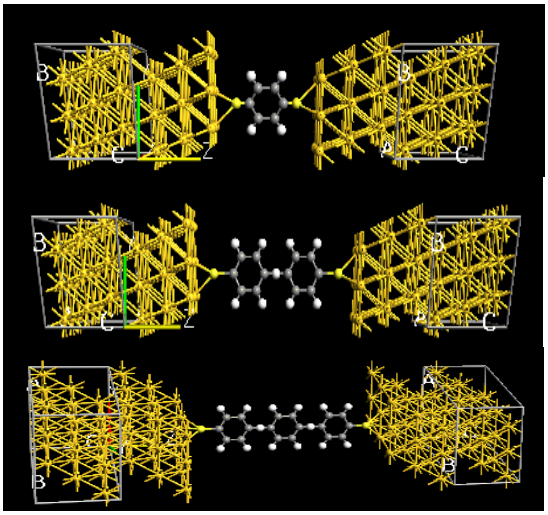


Figure 1: (a) Molecular wire of 1 Benzene ring (b) Molecular wire consisting of two Benzene rings (c) Molecular wire consisting of three Benzene rings coupled to Gold Electrodes with Sulphur as an anchoring atom.

As the geometric optimization of the system comprising of the molecular wire stringed to metallic electrodes through the end group linker is most important for the proper prediction of the electron transport characteristics, we performed these optimizations initially with Gaussian-03 program package [20]. The self-consistent calculations were performed till the stress as well as the force on the constrained atoms reached $0.1eV/A^0$. The quantum mechanical First-principle transport calculations of conductance for a two-probe system were performed for the mesh cut-off of 100 Hartrees using Atomistix Tool Kit and its graphical interface employing semi-empirical Extended Huckle Device Theory and all the calculations were completed within the bias voltage range of -2 V to 2 V.

3. Results and Discussions

The conductance of all three molecular wires consisting of one benzene ring, two benzene rings and three benzene rings coupled to Gold electrodes through thiol end group linker was measured under bias voltage 0V. The observed values of the conductance took into consideration quantum interference, whether constructive or destructive. We detected that conductance decreased with increase in length of molecular wire as shown in table 1.

The envisaged conductance decreased sharply from 287.678nS for $5.003A^0$ to 15.532nS for 11.33 A^0 and then linearly to a negligible value of 0.2485nS for 17.055 A^0. This decrease in conductance with increasing length was based on the following numerical expression [21-25]:

$$J \alpha e^{-\beta.d} \qquad (1)$$

where J is the conductance, β is the decay constant and d is the length of molecule. The decaying conductance with length is shown in figure 2.

Table1: Variation of Conductance with length of molecular Wire

Molecular Wire	Length(A^0)	Conductance(nS)
1Benzene ring	5.003	287.678
2Benzene rings	11.3362	15.532
3Benzene rings	17.0554	0.2485

To explain the electron transport mechanism, the tunnelling theory was introduced. At low bias, the value of β can be expressed approximately by:

$$B= (2(2m\varphi)^{1/2})/h \qquad (2)$$

Where φ is the energy difference between Fermi level of electrodes or HOMO-LUMO level of conjugated molecules. From the expression (2), it is clear that decay constant is relevant with molecule orbitals and the decay constant of conjugated molecules ranges from 0.1 to 0.4 per angstrom.

$$\beta= -0.19 + 0.32(E_g)_{\infty}^{1/2} \qquad (3)$$

As band gaps increase, the dependence of conductance per molecule versus molecular length becomes more and more strong. The foremost momentous result that we concluded in this simulation work is the temperature dependence conduction. The conductance values were observed

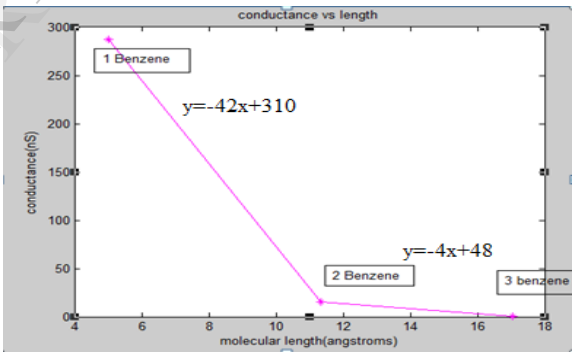


Figure 2: Molecular Length versus Conductance

at different temperature values ranging from 0K to 1500K for bias voltage 1V. As the observed values of conductance were found less than the quantum conductance as predicted by Landauer, we could say without any doubt that the coupling between the molecular wires and the metallic electrodes was weak coupling and hence there couldn't be any electron transport due to conduction and the only probability of charge transport would be through tunnelling or hopping. The shortest wire demonstrated tunnelling while the electron transport through longer wires was only due to hopping. The corresponding values of conductance for molecular wires consisting of single, two and three benzene rings at bias voltage 1V have been reported in table 2. From figure 3 shown below, we analysed that the variations in conductance became

prominent as the number of benzene rings increased. Hence we can say that the conductance of the longer molecular wires having two or three rings of benzene showed strong dependence on temperature variations when compared to the shortest molecular wire having one benzene ring only. One smart discovery from this simulation was the reporting of greater tunnelling resistance as the length of the molecular wire increased. Though the modelling was carried for up to three benzene rings, but we could predict without any doubt that the same behaviour would be there even if we simulate the longer molecular wires having more than three benzene rings. The characteristics in the figure 3 confirmed that the resistances of longer molecules varied inversely (Conductance improved) with respect to the rise in the temperature. We noticed that the conductance of the shortest molecular wire consisting of one benzene ring virtually remained constant throughout the entire temperature range, while the variation in the conductance of the longer molecular wires was substantial. We also observed that percentage change in conductance was more dominant in longest molecular wire as compared to its shorter counterparts. Such phenomenon implied that the hopping mechanism is thermal activated transmission. There was a clear shift from tunnelling mechanism to hopping mechanism for longer molecules. Segong Ho Choi group [26] carried out the research work on the temperature-dependent resistance for isolated and positively charged junctions. The charge hopping rate(K_{et}) is expressed by the following equation (4)

$$K_{et} \alpha \exp(-(\lambda + \Delta G^0)^2 / 4\lambda K_B T \quad (4)$$

Where λ is the reorganization energy, k_B is the Boltzmann constant and T is the temperature, ΔG^0 is the thermodynamic driving force, which is considered to be the variation energy of the first approximation.

Table 2: Temperature (Kelvin) Versus Conductance of different Molecular Wires

Temp. (K)	Conductance (μS) 1 Benzene Ring	Conductance (nS) 2 Benzene Rings	Conductance (nS) 3 Benzene Rings
0	19.5462	13.0	0.290
50	19.6459	13.35	0.299
100	19.646	13.53	0.3046
200	19.652	13.64	0.307
300	19.66	13.71	0.309
500	19.6776	13.91	0.313
700	19.8011	14.24	0.322
900	19.952	14.99	0.348
1100	20.147	17.18	0.422
1300	20.369	22.48	0.592
1500	20.604	32.4	0.913

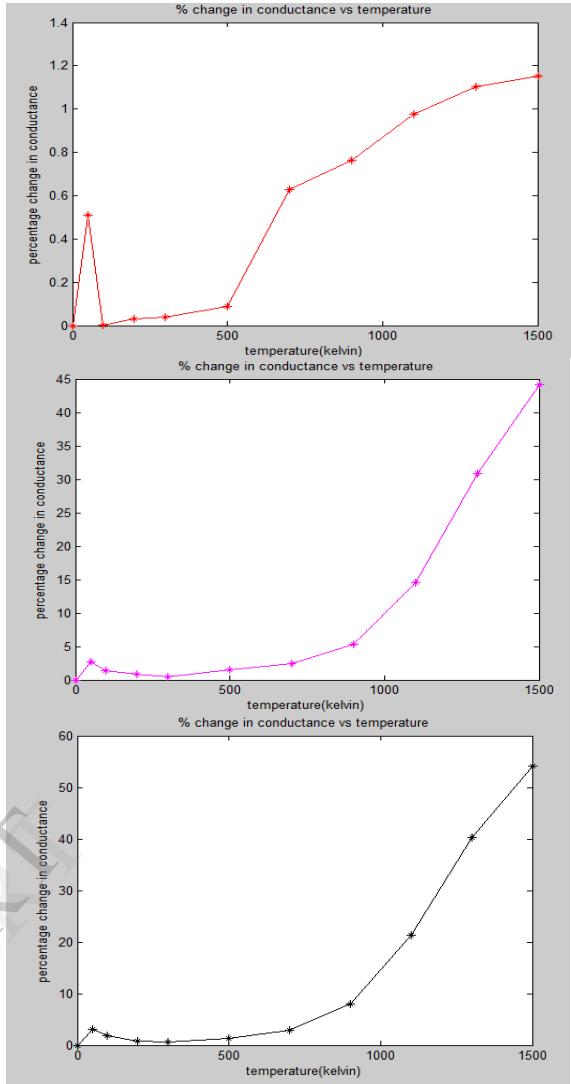
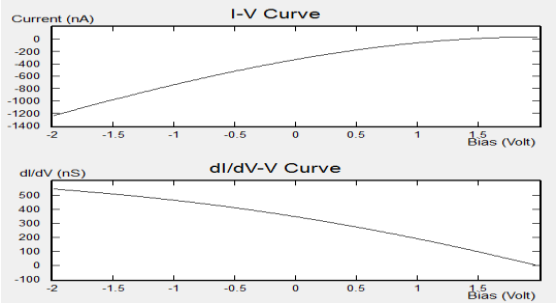


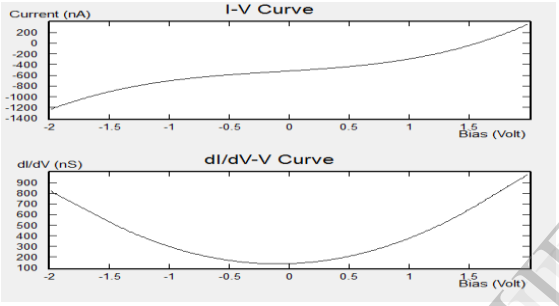
Figure 3: Percentage change in conductance with temperature variations for the molecular wires consisting of: A) Single Benzene ring b) Two Benzene rings c) Three Benzene rings

From figure 3, we observed that there is less than 1% net difference in conductance in case of molecular wire consisting of single benzene ring whereas this effect increased by 44% in the molecular wire consisting of two benzene rings and the notable increase of 54% in the longest molecular wire consisting of three benzene rings. The electron transport characteristics in terms of I-V curves and differential conductance-voltage curves are shown in figure 4. The longest molecular wire consisting of three benzene rings for the bias voltage range from -2V to2Vwas considered for transport characteristics at different temperature values for further elucidation. We noticed that dI/dV and I-V curve at temperature 1500K gave the highest value as compared to that at 900K,1100K and 0K. The differential conductance at 1500K was reported as2400nS which reduced to 1500nS at 1100K whereas that

for 900K was 1000nS which further reduced to 0nS for 0K at 2V bias voltage. The close observation of all the I-V characteristic curves indicated hopping with the range extending the limit as the temperature increased towards 1500 K. The magnitude of the maximum conductance increased with increase in temperature and that was supported by the fact that the electron transport was affected by molecular structure i.e. the energy band gap.



a)



b)

Figure 4 a: Transport curves at 0
Figure 4 b: Transport curves at 900 K

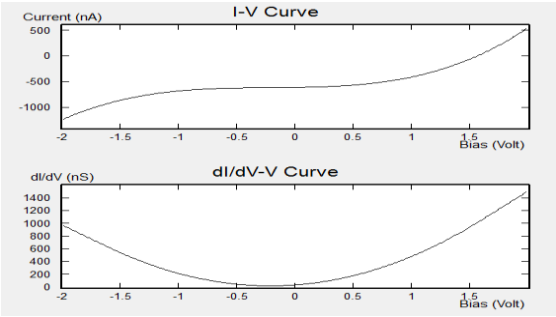


Figure 4 c: Transport curves at 1100 K.

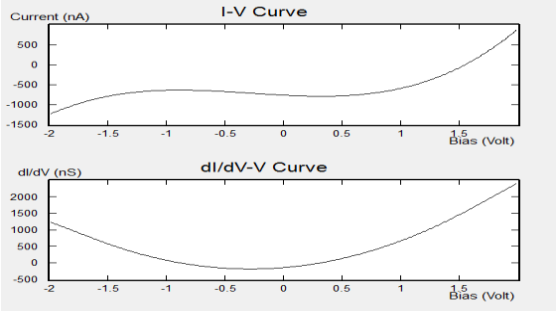


Figure 4 d: Transport curves at 1500K

Also, we observed conductance decreasing with increased bias voltage in dI/dV characteristics for 0K temperature range. Moreover, we noticed that differential conductance revealed similar kind of parabolic curves for 900K and 1500K temperatures where the differential conductance firstly decreased during negative bias voltage range whereas increased during positive bias voltage ranges. The results further confirmed that the conductance becoming lowest at zero bias for higher temperature ranges exhibited increased coulomb interaction. From figure 5, we noticed the effect of increasing temperature from 0K to 1500K for a molecular wire having three benzene rings, where we observed that the conductance at 1500K is maximum recorded as 2740nS whereas that for 0K is minimum recorded as 0.865nS. The increasing order of conductance with temperature is: 0K<300K<900K<1500K. Hence, we conclude that there exists a very strong direct relationship between temperature and the conductance of molecular devices.

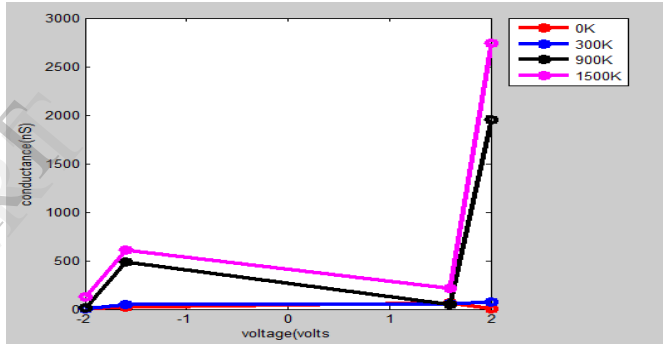


Figure5: Conductance versus Bias voltage

4. Conclusion

The pronounced temperature dependence of the conductance of molecular wires consisting of variable number of rings of aromatic molecule benzene was observed. The results showed a prominent impact of the increase in temperature upon conductance of the molecular wires of differing lengths. The conductance of the molecular wires decreased with increase in length. The dependency of the electron transport on molecular length varied with temperature and reflected the different localization properties of the molecular spectral regimes. Short length molecules showed less change in conduction with changing temperature whereas longer ones showed more change in conduction. Hence, we conclude that the thermal conduction observed in longer length molecular wires contributed higher conductance at nano scale up to great extent, while shorter molecular wires showed least impact of the change in temperature on conductance.

5. Acknowledgement

The authors acknowledge the support by C.S.I.R. and AICTE under Grant No. 22(0519)10/EMR-II.

6. References

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