

List of Figures

1.1	An ideal Self Assembled monolayer based on alkanethiols assembled on gold electrode. (source: page 240, in Electroanalytical chemistry: a series of advances, vol 19. by A. J. Bard and I. Rubinstein)	17
2.1	Schematic of a gated molecular transistor in an electrochemical environment (see ref.[1])	21
2.2	Simple schematic of a molecular wire stretched between two electrode with an redox center interacting with the polarization of the surrounding solvent.	23
2.3	Potential energy surfaces in the case of weak coupling and at the equilibrium potential for the redox system; system parameters: $\epsilon_1 = 0.8$ eV, $v = 0.01$ eV, $\epsilon_r = \lambda = 0.3$ eV. The insert shows the occupation $\langle n_r \rangle$ of the redox center.	29
2.4	Current-potential curves in the case of weak coupling; system parameters: $\epsilon_1 = 1.2$ eV, $v = 0.01$ eV.	30
2.5	Transition probability as a function of the energy ϵ of the tunneling electron for various values of ϵ_r ; the solvent coordinate q was set to zero. System parameters: : $\epsilon_1 = 0.2$ eV, $v = 0.1$ eV.	31
2.6	Current-potential curves for various values of ϵ_r . System parameters: : $\epsilon_1 = 0.2$ eV, $v = 0.1$ eV.	32
2.7	Current-potential curves for small coupling to the leads. System parameters: $\Delta = 0.1$ eV, $\epsilon_r = 0.5$ eV, $v = 0.1$ eV, $\epsilon_1 = -0.2$ eV (left curve) and $\epsilon_1 = 0.3$ eV (right curve).	33

2.8	Current at constant bias $V = 0.1$ V as a function of the overpotential η for various values of ϵ_1^0 , the value of ϵ_1 for vanishing overpotential; $v = 0.1$ eV.	34
3.1	Rate Vs. applied Voltage. The energy units are in terms of eV. with the value of the parameters used indicated beneath the graph	43
3.2	Rate Vs. Applied Voltage profile for the case when the relation $\epsilon_1 - \epsilon_r = 2\lambda$ is satisfied. The value of parameters used are shown beneath the graph	43
3.3	Plot for Rate Vs. $1/T$ at zero bias. The Y-axis is plotted on logarithmic scale. The value of the parameters are used are above.	44
3.4	Rate Vs. Voltage for different value of v_1	45
3.5	Rate Vs. Energy difference between the redox and bridge energies	46
3.6	Comparison of Rate Vs. Energy difference between the redox and bridge for various value value of re-organisation energy	46
4.1	Comparison of density of states of the adsorbate for weakly coupled regime at low ($\theta = 0.1$) and high coverage factor ($\theta = 0.9$). The values of parameters (in eV) are as follows: $E_r^r = 0.6, E_{ar}^r(0) = 0.2, E_a^r = 0.4$ and $v = 0.5$ eV.	58
4.2	Comparison of density of states of adsorbates for strong coupling regime at low and high coverage factor. The values of the various parameters employed (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r(0) = 0.75, \Delta_{ } = 1.5, \Delta_{\perp} = 1.5, \mu = 4.5, v = 2.0$	59
4.3	Plots showing the density of states for redox, adsorbate and the Fermi distribution for anodic current under zero overpotential. The weakly coupled regime and low coverage of $\theta = 0.3$ is considered here .The values of parameters (in eV) are as follows: $E_r^r = 0.6, E_{ar}^r(0) = 0.2, E_a^r = 0.4$ and $v = 0.5$ eV	60
4.4	Plots showing the density of states for redox, adsorbate and Fermi distribution for cathodic current at zero overpotential. The values of parameters are same as in 4.3	60

4.5	Plots showing the density of states for redox, adsorbate and the Fermi distribution for anodic current under zero overpotential. The strongly coupled regime and low coverage of $\theta = 0.3$ is considered here. The values of parameters (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r = 0.75$ and $v = 2.0$ eV	61
4.6	Plots showing the density of states for redox, adsorbate and Fermi distribution for cathodic current at zero overpotential. The values of parameters are same as in 4.5	62
4.7	Plots showing the variation of $\Delta\phi$ with respect to θ the coverage factor. The values of re-organisation energies employed were same in both the curves. $E_r = 0.6$ eV, $E_a(0) = 0.4$ eV, $E_{ar}(0) = 0.2$ eV	62
4.8	anodic current vs η for $\alpha = 0.3$. The values of the various parameters employed (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r(0) = 0.75, \Delta_{ } = 1.5, \Delta_{\perp} = 1.5, \mu = 4.5, v = 2.0$	63
4.9	anodic current vs η for $\theta = 0.1$ in the weak coupled regime. The values of parameters (in eV) are as follows: $E_r^r = 0.6, E_{ar}^r(0) = 0.2, E_a^r = 0.4$ and $v = 0.5$ eV.	64
4.10	anodic current vs η for $\theta = 0.3$ in weak coupled regime. The values of parameters (in eV) are as follows: $E_r^r = 0.6, E_{ar}^r(0) = 0.2, E_a^r = 0.4$ and $v = 0.5$ eV.	65
4.11	anodic current vs η for $\theta = 0.7$. The values of parameters (in eV) are as follows: $E_r^r = 0.6, E_{ar}^r(0) = 0.2, E_a^r = 0.4$ and $v = 0.5$ eV.	65
4.12	anodic current vs η for $\theta = 0.9$. The values of parameters (in eV) are as follows: $E_r^r = 0.6, E_{ar}^r(0) = 0.2, E_a^r = 0.4$ and $v = 0.5$ eV.	66
4.13	anodic current vs η for $\theta = 0.1$. The values of the various parameters employed (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r(0) = 0.75, \Delta_{ } = 1.5, \Delta_{\perp} = 1.5, \mu = 4.5, v = 2.0$	66
4.14	anodic current vs η for $\theta = 0.3$. The values of the various parameters employed (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r(0) = 0.75, \Delta_{ } = 1.5, \Delta_{\perp} = 1.5, \mu = 4.5, v = 2.0$	67
4.15	anodic current vs η for $\theta = 0.7$. The values of the various parameters employed (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r(0) = 0.75, \Delta_{ } = 1.5, \Delta_{\perp} = 1.5, \mu = 4.5, v = 2.0$	67

4.16	anodic current vs η for $\theta = 0.9$. The values of the various parameters employed (in eV) are as follows: $E_r^r = 1.0, E_{ar}^r(0) = 0.25, E_a^r(0) = 0.75, \Delta_{ } = 1.5, \Delta_{\perp} = 1.5, \mu = 4.5, \nu = 2.0$	68
4.17	Plots showing the equilibrium current at zero overpotential I_0 vs θ for strong and weak coupled regime. The values of re-organisation energies were selected be the same for both the curves, $E_r = 0.6$ eV, $E_a(0) = 0.4$ eV, $E_{ar}(0) = 0.2$ eV	69