

Contents

Title page	i
Certificate of Approval	iii
Declaration	iv
Certificate by the Supervisor	v
Acknowledgement	vi
List of Symbols	viii
List of Abbreviations	xii
Abstract	xiv
Contents	xv
1 Introduction	1
1.1 Carbon Nanotubes: An Overview	2
1.1.1 Structure of Single Walled Carbon Nanotubes (SWCNT)	3
1.1.2 Solubility and Reactivity of SWCNTs	4

1.1.3	Chemical Modifications of SWCNTs	6
1.2	SWCNT as a Model of Hydrophobic Nanopore	9
1.2.1	Filling of CNT pores by water	11
1.2.2	Structure of water confined to SWCNT	12
1.2.3	Dynamics of water inside SWCNTs	13
1.2.4	Water confined inside functionalized SWCNTs	16
1.3	Modeling Biological Proton Transfer with the Help of SWCNTs	18
1.3.1	Overview of biological proton transfer	18
1.3.2	Proton transfer through carbon nanotubes	23
1.4	Aim of the Thesis	26
2	Theoretical Methods	29
2.1	Density Functional Theory	29
2.2	Basis Sets	34
2.3	Molecular Dynamics Simulation	36
2.3.1	Molecular Mechanical Force Field	37
2.3.2	Periodic Boundary Conditions	39
2.3.3	Solving the equation of motion	39
2.4	Generating Functionalized Carbon Nanotubes in the Gas Phase	40
2.5	Proton Affinity Calculations Using DFT Method	41
2.6	Modeling Proton Transfer Reaction with Empirical Valence Bond (EVB) Theory	45
3	Proton Affinity of Amino Acid Sidechains in Functionalized Single Walled Carbon Nanotubes	51

3.1	Introduction	51
3.2	Models Studied	53
3.3	Results & Discussion	54
3.3.1	Proton affinity of amino acid sidechains inside endohedrally functionalized CNT	55
3.3.2	Proton affinity of amino acid sidechains in exohedrally functionalized CNT	64
3.4	Conclusion	67
4	Structure and Dynamics of Water Confined to Carbon Nanotubes Functionalized with Some Amino Acid Sidechains	73
4.1	Introduction	73
4.2	Details of Molecular Dynamics Simulations of Endohedrally Functionalized CNTs	75
4.3	Results and Discussion	78
4.4	Conclusion	92
5	Free Energies of Proton Transfer Reactions within Hydrophobic Confinement	95
5.1	Introduction	95
5.2	EVB Simulations with Different Endohedrally Functionalized SWCNTs	97
5.3	Results & Discussion	102
5.4	Conclusion	113
6	Free Energies of Proton Transfer by Amino Acid Sidechains Anchored to the Outer Surface of Carbon Nanotubes.	117

6.1	Introduction	117
6.2	Results and Discussion	119
6.3	Conclusion	121
7	Conclusions and Scope of Future Work	125
	References	129
	Appendix	154
	List of publications	160