

Contents

Chapter 1: Introduction	1
1.1. Hazardous Gas Sensing	2
1.2. Carbon Allotropes as Gas Sensors	3
1.3. Novel Carbon Allotropes and Cyclo[n]carbons	4
1.4. New Addition in the Family of Carbon Allotropes: C ₁₈	5
1.5. Research Objectives	7
1.6. Structure of the Thesis	7
Bibliography	9
Chapter 2: Theoretical Framework	11
2.1. Theory of Electronic Structure	12
2.1.1. Quantum Mechanics, Schrödinger Equation	12
2.1.2. Born-Oppenheimer Approximation	13
2.1.3. Hartree-Fock Method	14
2.1.4. Density Functional Theory	15
2.1.5. Kohn-Sham Equations	15
2.2. Exchange-Correlation Functionals	16
2.2.1. Local Density Approximation (LDA)	16
2.2.2. Generalized Gradient Approximation (GGA)	17
2.2.3. Meta-GGA	17
2.2.4. Hybrid Functionals	17
2.3. Basis Sets	18
2.4. Time Dependent Density Functional Theory (TD-DFT)	19
2.5. Properties from DFT for the Present Thesis	20

2.5.1. Vibrational Spectra Calculation	20
2.5.2. Frontier Molecular Orbitals (FMO)	21
2.5.3. Mulliken Charge Analysis	21
2.5.4. Molecular Electrostatic Potential (MESP)	22
2.5.5 Topological Parameters and Quantum Theory of Atoms in Molecules	22
2.5.6. Global Reactivity Parameters	23
2.5.7. Dipole Moments	24
2.5.8. Ultraviolet (UV) Spectra	24
2.6. Gaussian 09 Package	25
Bibliography	26
Chapter 3: Prediction of Pristine C₁₈ Nanocluster as Hazardous Gas Sensor	29
3.1. Introduction	30
3.2. Methodology	31
3.3. Results and Discussion	31
3.3.1. Structural and electronic properties of pristine C ₁₈ nanocluster	31
3.3.2. Adsorption performance of CO, NO and NH ₃ gas molecules adsorbed C ₁₈ nanocluster	33
3.3.3. Electronic properties after the adsorption	35
3.3.4. Electrostatics potential (ESP) analysis	39
3.3.5. Sensing properties of C ₁₈ nanocluster	40
3.3.6. Absorption and Raman spectra	43
3.3.7. Global reactivity indices	45
3.3.8. C ₁₈ nanocluster as compared to other carbon nanomaterials	48
3.4. Conclusion	49
Bibliography	49

Chapter 4: Effect of Boron & Nitrogen Doping on Molecular Adsorption	51
4.1. Introduction	52
4.2. Methodology	52
4.3. Results and Discussion	53
4.3.1. Physical and electronic characteristics of B, N doped C ₁₈ nanoclusters	53
4.3.2. Adsorption study of CO, NO and NH ₃ molecules over C ₁₇ X nanoclusters	55
4.3.3. Electronic properties of CO, NO and NH ₃ adsorbed C ₁₇ X nanoclusters	57
4.3.4. Sensing properties of C ₁₇ X nanoclusters	60
4.3.5. Quantum Chemical Descriptors	61
4.4. Conclusion	62
Bibliography	63
Chapter 5: Transition Metal-decorated C₁₈ as CO, NO & NH₃ Scavenger	65
5.1. Introduction	66
5.2. Methodology	66
5.3. Results and Discussion	67
5.3.1. Structural and Electronic Properties of TM-decorated C ₁₈ Nanocluster	67
5.3.2. Adsorption Properties of TM-decorated C ₁₈ Nanocluster	70
5.3.3. Mulliken Charge Population Analysis	76
5.3.4. Quantum Theory of Atoms in Molecules (QTAIM) Study	77
5.3.5. Reduced Density Gradient and Non Covalent Interactions	78
5.3.6. Analysis of Raman Spectra	82
5.3.7. Sensing Response and Recovery Time	84
5.3.8. Comparison with the Pristine and Doped C ₁₈ Nanoclusters	85
5.4. Conclusion	86
Bibliography	87

Chapter 6: Adsorption of HCN on Al, Si, P-decorated C₁₈ Nanocluster	89
6.1. Introduction	90
6.2. Methodology	90
6.3. Results and Discussion	91
6.3.1. Optimization of HCN molecule and C ₁₈ nanocluster	91
6.3.2. Adsorption properties of HCN molecule over C ₁₈ nanocluster	91
6.3.3. Structural Parameters of Al, Si, and P-decorated C ₁₈ Nanoclusters	93
6.3.4. Electronic Properties of Al, Si, and P-decorated C ₁₈ Nanoclusters	94
6.3.5. Adsorption Properties	97
6.3.6. Mulliken Charge Transfer Analysis	100
6.3.7. Sensing Properties	100
6.4. Conclusion	102
Bibliography	103
Chapter 7: Summary and Future Prospects	105
7.1. Thesis in a nutshell	106
7.2. Functionalization beyond doping and decoration	110
7.2.1. C ₁₈ dimer	110
7.2.2. Decoration of C ₁₈ on 2D monolayers	110
7.3. Other carbon rings	111
Bibliography	111
Curriculum Vitae and List of Publications	