Table of Contents

Contents	*Page*
Abstract	i
List of Abbreviations	vii
List of Symbols	ix
List of Tables	x
List of Figures	xiii
Chapter 1: Introduction	
1.1 Oxides of carbon and nitrogen: threat to environment	1-1
1.1.1 Transition metals in reducing toxic gases	1-3
1.2 Clusters and nanoclusters	1-4
1.2.1 Types of clusters	1-6
1.2.2 Cluster generation in gas phase	1-7
1.2.3 Variation of cluster properties with size	1-8
1.2.4 Importance of metal nanoclusters	1-10
1.2.5 Transition metal clusters	1-11
1.3 Gold nanoclusters	1-12
1.3.1 Aurophilic interactions	1-13
1.3.2 Relativistic Effects	1-13
1.3.3 Catalysis by gold	1-14
1.3.4 Bimetallic nanoclusters of gold	1-15
1.4 VOCs: another threat to environment	1-17
1.4.1 Effects of CFCs on environment	1-18
1.4.2 Effects in Global warming	1-19
1.4.3 Substitutes for CFCs	1-20
1.4.3.1 HCFCs, the first generation replacement of CFCs	1-21
1.4.3.2 HFCs, second generation replacement of CFCs	1-21
1.4.3.3 HFEs, third generation replacement of CFCs	1-21

1.4.4 Generation of alkoxy radicals 1-22
1.4.4.1 Atmospheric Fate of alkoxy radical 1-22
1.4.5 Degradation Products of HFEs 1-23
1.4.6 Importance of atmospheric chemistry of HFEs 1-23
Bibliography 1-25

Chapter 2: Basic Electronic Theory

2.1 Introduction 2-1
2.2 Overview of computational methods 2-1
2.3 Potential energy surface 2-3
2.4 Tools of computational chemistry 2-4
2.4.1 Molecular Mechanics 2-5
2.4.2 Ab initio methods 2-5
2.4.2.1 Hartree-Fock Theory 2-6
2.4.3 Semiempirical methods 2-7
2.4.4 Density Functional Theory 2-8
2.4.5.1 Local Density Approximation (LDA) 2-9
2.4.5.2 Generalized gradient approximation (GGA) 2-10
2.4.5.3 Hybrid Functionals 2-11
2.5 Basis sets 2-11
2.5.1 Slater Type Orbitals 2-12
2.5.2 Gaussian Type Orbitals 2-12
2.5.3 Minimal Basis Sets 2-12
2.5.4 Split Valence Basis Sets 2-13
2.5.5 Polarization Functions 2-13
2.5.6 Diffuse Functions 2-14
2.5.7 Effective Core Potentials 2-14
2.6 Quantum theory of atoms in molecules (QTAIM) 2-14
Bibliography 2-16

Chapter 3: DFT and QTAIM Studies on Structure and Stability of Double Metal Doped Gold Clusters

3.1 DFT studies on double beryllium doped gold clusters 3-3

3.1.1 Introduction 3-3

3.2.2 Computational Details 3-3

3.2.3 Results and discussion 3-5

3.2.3.1 Structural Study of Au_nBe_2 clusters 3-5

3.1.3.2 Stability of Au_nBe_2 clusters 3-9

3.1.3.3 QTAIM analysis 3-13

3.1.3.4 Natural Charge analysis 3-17

3.1.4 Salient observations 3-18

3.2 DFT study on double magnesium doped gold clusters 3-19

3.2.1Introduction 3-19

3.2.2 Computational details 3-19

3.2.3 Results and discussion 3-20

3.2.3.1 Structural study of Au_nMg_2 clusters 3-20

3.2.3.1.1 Neutral clusters 3-24

3.2.3.1.2 Charged Clusters 3-24

3.2.3.2 Stability of Au_nMg_2 clusters 3-25

3.2.3.2.1 Binding energies per atom 3-25

3.2.3.2.2 Fragmentation energies 3-27

3.2.3.2.3 Second-order difference of energies 3-30

3.2.3.3 Ionization potential and Electron affinity 3-30

3.2.3.4 QTAIM analysis 3-33

3.2.3.5 Natural charge analysis 3-36

3.2.4 Salient observations 3-38

3.3 Effect of double aluminium doping on small gold clusters 3-40

3.3.1 Introduction 3-40

3.3.2 Computational details 3-41

3.3.3 Results and discussion 3-42

3.3.3.1 Structural study of Au_nAl_2 clusters 3-42

3.3.3.1.1 Neutral clusters 3-42
3.3.3.1.2 Charged Clusters 3-42
3.3.3.2 Stability of Au_nAl_2 clusters 3-46
3.3.3.2.1 Binding energies per atom 3-46
3.3.3.2.2 Fragmentation energies 3-48
3.3.3.2.3 Second-order difference of energies 3-50
3.3.3.3 Ionization potential and Electron affinity 3-50
3.3.3.4 QTAIM analysis 3-54
3.3.3.5 Natural Charge Analysis 3-57
3.3.4 Salient observations 3-59
Bibliography 3-61

Chapter 4: Density Functional Study on Catalytic Activity of Anionic Au_2^- and Au-Ag^- Dimer for Nitric Oxide Oxidation

4. 1 Catalytic oxidation of nitric oxide by Au_2^- dimer 4-3
4.1.1 Introduction 4-3
4.1.2 Computational details 4-4
4.1.3 Results and discussion 4-7
4.1.4 Salient observations 4-12
4.2 Catalytic activity of Au-Ag^- for NO oxidation 4-14
4.2.1 Introduction 4-14
4.2.2 Computational details 4-15
4.2.3 Results and discussion 4-16
4.2.3.1 Complexes of Au-Ag^- with O_2 and NO 4-17
4.3.3.2 NO oxidation along Ag sites of Au-Ag^- dimer 4-21
4.2.3.3 NO oxidation along Au sites of Au-Ag- dimer 4-25
4.2.4 Salient Observations 4-27
Bibliography 4-28

Chapter 5: Theoretical Insight on Atmospheric Chemistry of HFE-365mcf3 and HFE-7000 (i-$C_3F_7OCH_3$)

5.1 Atmospheric chemistry of HFE-365MCF3 5-3

5.1.1 Introduction 5-3

5.1.2 Computational details 5-5

5.1.3 Results and discussion 5-6

5.1.3.1 Structure and energetics 5-6

5.1.3.2 Rate constant calculations 5-14

5.1.3.2 Atmospheric consequences 5-16

5.1.3.2.1 Atmospheric lifetime 5-16

5.1.3.3 Atmospheric fate of alkoxy radical 5-17

5.1.4 Salient Observations 5-19

5.2 Atmospheric chemistry of HFE-7000 (i-$C_3F_7OCH_3$) and isofluoro-propyl formate (i-$C_3F_7OC(O)H$) 5-21

5.2.1 Introduction 5-21

5.2.2 Computational details 5-22

5.2.3 Results and discussions 5-23

5.2.3.1 Structure and energetics 5-23

5.2.3.2 Rate constant calculation 5-31

5.2.3 Atmospheric fate of alkoxy radical 5-33

5.2.4 Atmospheric implications 5-35

5.2.4.1 Atmospheric lifetime 5-35

5.2.4.2 Fate of fluorinated ester 5-35

5.2.4 Salient observations 5-37

Bibliography 5-39

Chapter 6: Conclusions and Future Scopes 6-1

6.1 Conclusions 6-1

6.2 Future scopes 6-5

List of Publications xix

List of Conferences Attended xxii

Appendices

A A-1

B B-1