

CONCLUSIONS AND FUTURE SCOPES**6.1 Conclusions**

In the present thesis, we have focused mainly on three goals: firstly to investigate the structure, electronic properties and topology of the double beryllium, magnesium and aluminum doped small Au_n ($n=1-7$) clusters and their comparison with bare gold clusters; secondly to study the catalytic activity of anionic gold and gold-silver dimer for nitric oxide (NO) oxidation; thirdly to study the kinetics and mechanism of atmospheric chemistry of two hydrofluoroethers-HFE-365 and HFE-7000 as well as investigation on the fate of their alkoxy radicals. We have used the most popular computational chemistry tool of recent years-density functional theory (DFT) throughout our study. The QTAIM approach has been applied to study the nature of bonding in the studied clusters. All the calculations have been performed using Gaussian 09 program package whereas for QTAIM analysis we have used AIMALL program.

The thesis begins with a general introduction on the present works. It provides a brief discussion about the automobile exhaust toxic gases mainly on the oxides of carbon and nitrogen. The contribution of them towards global warming makes it necessary to focus on their removal. Transition metals and their nanoclusters show great potential toward the removal of toxic gases. The chapter proceeds with an overview of metal nanoclusters and their various properties with a special concentration on gold nanoclusters. The unique properties of gold like relativistic effect

and aurophilicity are also discussed. The nanosize gold shows remarkable catalytic activity towards various reactions. The chapter also contains a discussion on bimetallic clusters of gold which are more promising than monometallic clusters. Like automobile exhaust gases, the halogenated volatile organic compounds such as CFC, HCFC, HFC are also hazardous to our environment. HFEs which are third generation replacement of CFC are considered in this thesis and we have provided a general understanding of them in the introduction part.

We have discussed various computational methods used in the present thesis in details. The different tools of computational chemistry such as molecular mechanics, HF method, semi-empirical methods have been discussed with special emphasis on DFT. The overview on local density approximations (LDA) and generalized gradient approximations (GGA) as well as various basis sets available in computational chemistry has been also discussed in details. The discussion includes an overview on Bader's quantum theory of atoms in molecules (QTAIM) approach as a part of the present work have used this theory to study the nature of bonding.

The structural and stability of double Be atoms doped Au_n ($n=1-5$) clusters have been studied by using DFT with B3LYP functional. The systematic analysis of both charged as well as neutral clusters are considered together for the first time and a comparison of bare and doped clusters have been made. Almost all the Au_nBe_2 clusters found to adopt planar structures. The stability study reveals that doping of Be atoms can significantly increase the stability of gold clusters. The comparison of stability indicates the greater stability of cationic clusters in comparison to other two types of clusters. The QTAIM analysis has been introduced for the first time in these clusters and it results very small and positive values of electron density, ρ , and its Laplacian, $\nabla^2\rho$ at the Au-Au and Au-Be BCPs. The other two parameters viz local electronic densities, $H(r)$, are all negative and relative kinetic energy density $G(r)/\rho$ has values less than one. These criteria confirm that the covalent interactions are present in both bare as well as doped clusters. The basin paths obtained from QTAIM study clearly supports the interaction between the Au-Au and Au-Be atoms.

The structural and stability of double Mg atoms doped Au_n ($n=1-5$) clusters have been investigated by using DFT with PW91PW91 functional. To generate the

initial structures of the neutral state, classical annealing simulation is used. Most of the clusters adopt planar structures. The relative stabilities as a function of cluster size shows even-odd alternation and doped clusters possess greater stability than the bare counterparts. The vertical electron affinity (VEA) for the doped clusters has low values indicating that they are more stable than the pure clusters. The vertical ionization potential (VIP) values are lower odd numbered clusters than the even clusters which suggest the lower stability of the former one. The QTAIM parameters confirm the presence of covalent interactions in the studied clusters. The observation on natural charge analysis reveal the transfer of charge from Mg to Au atoms.

The effect of double Al doping on Au clusters have been studied using DFT with PW91PW91 functional. Here also classical annealing simulation have been used with the help of Forcite Plus code as encoded in the MATERIAL STUDIO software to generate the initial structures. The structures of doped clusters are found to be different to that of pure clusters indicating the effect of doubly doped Al in the Au clusters. The relative stabilities as a function of clusters size show oscillatory behavior. The binding energy plots clearly suggest the enhanced stability of the doped clusters with higher stability in cationic clusters. The lower values of VEA and higher values of VIP for the even numbered clusters support their higher stability compared to the odd ones. The presence of BCP obtained from QTAIM analysis in all the studied clusters indicates the interaction between the Au and Al atom. The electron density, ρ , and its Laplacian, $\nabla^2\rho$ values suggest the presence of covalent bond in the clusters. The HOMO-LUMO isosurface also support the covalent behaviour of the clusters. Thus overall we can conclude that doping of all the three elements-Be, Mg and Al can significantly improve the stability of the gold clusters.

We have employed DFT with B3LYP functional to observe the catalytic activity of anionic Au₂ dimer (Au₂⁻) toward NO oxidation. Three plausible pathways with detail mechanism are considered for NO oxidation. Thermodynamic calculations at DFT level for free energies and reaction enthalpies are performed to check the feasibility of the pathways. The observation of vibrational frequencies confirms the presence of transition state structures with only one imaginary frequency. The IRC plots for transition states results that the transition state structure connects smoothly the

reactant and the product sides. The construction of energy profile diagram reveal that the pathway III involving O-N-O-O-N-O group like intermediate have lowest energy barrier and hence is the most favorable pathway for NO oxidation.

The catalytic activity of Au-Ag- dimer for NO oxidation has been also studied using the same level of computation. Various possible geometries where the O₂ and NO molecules approach the dimer with different orientations as well as different possible spin combinations are considered. This results that both NO and O₂ prefer to bind with Ag site and O₂ is activated more on binding compare to NO. Here we have considered two plausible pathways for NO oxidation and the pathways are studied along both Au and Ag site. The energetic calculations reveal that pathway II which is initiated by adsorption of O₂ has the lowest energy of activation and thus it is the most prominent pathway for NO oxidation. The comparison of energy barrier along two different sites results the higher activity of Au site compare to the Ag site for NO oxidation. The T1 diagnostic calculations at CCSD(T) level confirm that the transition states obtained in this work do not possess any multi-reference character.

Next we have studied the atmospheric chemistry of HFE-365mcf3 (CF₃CF₂CH₂OCH₃) with OH radical using DFT with meta hybrid M06-2X functional. The H-abstraction reaction by OH radical can proceed from -CH₂ group and -CH₃ group. Both these path proceeds via early transition state structure which is in consonance with Hammond's postulate. The calculated enthalpy of reactions ($\Delta_r H^\circ_{298}$) and reaction free energies ($\Delta_r G^\circ_{298}$) at 298 K indicated that H-abstraction from -CH₂ group may be more prominent. The further energetic study reveals that hydrogen abstraction by OH radical from the -CH₂ group of CF₃CF₂CH₂OCH₃ is more facile than that from the -CH₃ group. This fact is also support from the bond dissociation energy values obtained by using same level of theory. The rate constants for the reactions are calculated by using canonical transition state theory at different temperatures and the values are found to be in close agreement with the experimental reports. Using the value of rate constant, the estimated atmospheric lifetime is found to be 42 days for HFE-365mcf3. The study on fate of the alkoxy radicals generated from the HFE results that the sole atmospheric fate of CF₃CF₂CH₂OCH₂O• radical is reaction with O₂ leading to the formation of CF₃CF₂CH₂OCHO.

The atmospheric chemistry of segregated hydrofluoroether, HFE-7000 ($i\text{-C}_3\text{F}_7\text{OCH}_3$) has been investigated using DFT with M06-2X functional. The geometrical parameters and stereographical orientation suggest that the hydrogen atoms in the -CH_3 group are not equivalent. Therefore, two reaction channels are possible for H-abstraction from $i\text{-C}_3\text{F}_7\text{OCH}_3$ by OH radical. The transition states are characterized by only one imaginary frequency and involve the breaking of C-H bonds and formation of O-H. The elongation of forming bond is found to be larger than that of the breaking bond and it indicates that the barrier of the reaction (R1) is near the corresponding reactants. The IRC calculations provide a smooth transition from reactant to product side. The rate constants at different temperatures are calculated using transition state theory. The calculated rate constant value at 298K is in excellent agreement with experimental results. The estimated lifetime of $i\text{-C}_3\text{F}_7\text{OCH}_3$ is found to be 3.19 years which is in a good agreement with the reported value of 3.7 years. The atmospheric fate of $i\text{-C}_3\text{F}_7\text{OCH}_2\text{O}^\bullet$ radical is found to be reaction with O_2 leading to the formation $i\text{-C}_3\text{F}_7\text{OC(O)H}$. We have also analyzed the fate of fluorinated ester- $i\text{-C}_3\text{F}_7\text{OC(O)H}$ generated from the HFE. Two reaction channels are found to be feasible for $i\text{-C}_3\text{F}_7\text{OC(O)H}$, involving the H-abstraction reaction by Cl and OH radical. The barrier height of Cl-driven reaction results greater than that by OH radical. The OH-driven atmospheric lifetime of $i\text{-C}_3\text{F}_7\text{OC(O)H}$ are computed to be 3.01 years. Our analysis calculate the rate constant for $i\text{-C}_3\text{F}_7\text{OC(O)H}$ with OH radical for the first time.

6.2 Future Scopes

With increasing threat to the environment from factors like global warming and ozone layer depletion, the concern to reduce them are increasing day by day. Transition metal clusters particularly gold nanoclusters can be effectively used in the removal of environmentally toxic gases. Detailed understanding of various reaction mechanism and kinetics has been possible in recent years by the emerging development in computational resources. In the present thesis, we have attempted to provide some important insight on doping of small gold nanoclusters. Most importantly we have investigated the catalytic activity of anionic gold and gold-silver dimer for NO oxidation as well as atmospheric chemistry of two hydrofluoroether. The present work

still can be further extended for future investigations in various directions, some of which are given below:

1. Study on small doped clusters can be extended for larger clusters of gold as well as other other precious metals.
2. There is a possibility for the study of these doubly doped gold clusters for various catalytic reactions.
3. The activity of Au_2^- and Au-Ag^- dimer can be studied for other important reactions like methane activation, water gas shift reaction etc.
4. The NO oxidation reaction can be carried out in other stable gold clusters like Au_6 , Au_8 .
5. The kinetics of HFEs can provide powerful insight in determining the parametrs like ozone depletion potential, global warming potential etc which are very handful considering the envirnmental aspects.