Exploration of Unusual Chemical Bonding in Noble Gas Compounds

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ABSTRACT

Noble gases were considered as highly inert and unreactive in the early days. In 1933, Pauling first predicted that the heavier noble gas atoms, *viz.*, Kr and Xe can form stable molecules with the other elements since their less strongly bound valence electrons are at a large distance from their nuclei and hence more susceptible to chemical bond formation. Successful experimental identification of the first noble gas compound, $XePtF_6$, by Bartlett in 1962 not only validates the Pauling's prediction but also alters the fundamental perception of the "inert" nature of noble gas elements. Although several different kinds of noble gas compounds have been reported, there are few interesting classes of noble gas compounds that attract the scientists to a larger extent in the present era, *viz.*, various kinds of noble gas (Ng) insertion compounds, 'superstrong' van der Waals (vdW) complexes, and entrapment of Ng atoms in various materials. In this article, we aim to review this growing field of noble gas chemistry based on our recent findings on few series of novel Ng insertion compounds, 'superstrong' vdW complexes, and Ng encapsulated molecular cages which are predicted through high level *ab initio* based quantum computational techniques.

Keywords: Noble gas, Chemical bonding, vdW complexes, Stability, DFT, abinitio quantum computations.

Introduction

In general, the bulk properties of the noble gases are mainly dependent by the weak van der Waals forces acting between the atoms. The rise of melting point, boiling point, enthalpy of vaporization, density, and solubility on going from helium to radon is due to the increase in the polarizibility since the attractive force increases with the increase in size of the atoms. The electronic configuration of noble-gas atom was first reported by Kossel[1] and Lewis[2] in 1916 emphasizing the most stable electronic configuration among all the elements exists in nature. Due to full valence electron shell, the Ng atoms are extremely reluctant to form chemical bond with the other elements[3] indicating the inert nature of the noble gas atoms. Mendeleev assigned them as 'Group 0' as a separate group in the periodic table and 'noble gas notation'[4] is broadly used to represent any electronic configuration of any other element in the periodic table.

The remarkable discovery of first noble gas compound, $Xe[PtF_6]$[5] by Bartlett, attracted the scientists to explore the field of noble gas chemistry. The successful identification of the HArF [6] molecule possessing unusual H-Ar covalent bonding by Khriachtchev *et al.* through low temperature matrix isolation infrared spectroscopic technique, has revolutionized the field of 'noble gas chemistry'. Since then, there is a surge to explore the field of noble gas chemistry for both theoreticians and experimentalists and has experienced a renaissance during the past two decades.[7-14] In recent years, a unique category of novel noble gas hydrides of the type HNgY (Ng = Ar, Kr, and Xe; Y = electronegative element or group) has received considerable attention among researchers.[7,8] Various neutral or ionic insertion molecules of noble-gas atoms possessing environmental importance, like HOX [9] (X = F, Cl, Br), H_3O^+ [10] and species with astronomical significance, such as (HCO^+) [11], (Hn_2^+) [12] and so on have been theoretically investigated by us using various computational methods. The first ever noble gas-containing compounds had been detected in space, i.e., noble gas hydride cations ($^{36}ArH^+$) in the Crab Nebula by Barlow and co-workers.[13] Of late, Khriachtchev *et al.*[14] has successfully prepared and characterized one of the Ng insertion molecules, HXeOBr, using IR spectroscopic technique which was theoretically predicted earlier by our group.[9]

The bonding between noble gas and noble metal is completely unusual from the view point of their extreme inert nature. First noble gas-noble metal compounds, $XeAu^+$ and $XeAuXe^+$, were experimentally identified through mass spectrometry in 1998 by Schroder *et al.*,[15] although they were first conceived theoretically by Pyykko, in 1995.[16] Later, Seidel and Seppelt[17] had successfully synthesized the first thermally stable $[AuXe_4][Sb_2F_{11}]_2$ complex containing Ng-noble metal bond. A series of compounds containing Ng-M bond (Ng = Ar, Kr, and Xe; M = Au, Ag, and Cu), *viz.*, NgMX (X =F, Cl, and Br) have been investigated both experimentally as well as theoretically.[18]

A single gold atom can exhibit chemistry analogous to the hydrogen atom found in $SiAu_n$ clusters.[19] By employing this gold-hydrogen analogy, earlier our group have explored the feasibility study of noble gas inserted compounds involving noble metal atoms, *viz.*, MNgF and MNgOH (M = Cu, Ag, and Au; Ng = Ar, Kr, and Xe) using *ab initio* quantum chemical calculations.[20] Recently, Fielicke and co-workers[21] raised a point about the controversial

nature of the noble gas- noble metal bonding by proposing trimeric coinage metal cluster as a prototype system to unravel the nature of Ar- M bonding (M = Ag and Au). Motivated by the aforementioned findings, we have explored the unprecedented enhancement of Ng- M bonding strength in NgM_3^+ (Ng = Ar, Kr, and Xe; M = Cu, Ag, and Au) ions through hydrogen doping by employing various *ab initio* based techniques.[22]

One of the major issues in nuclear fuel reprocessing and reactor accidental scenarios is to manage radioactive fission gases including Xe and Kr. Due to the extreme inert nature of noble gases, it is very difficult to trap the radioactive noble gases in suitable matrix by van der Waals interactions using simple physisorption process. Theoretical modelling is necessary to select a suitable metal-organic framework (MOF) based materials required for the adsorption/separation of radioactive noble gas due to its high intake capacity, better selectivity and tunable chemical properties. In recent times, scientists have exhaustively studied the adsorption of Ng atom with a large number of MOF systems, viz., Sb-MOF-2,[23] Sb-MOF-1,[24] M-MOF-74,[25] etc. Very recently, our group has reported theoretically the enhancement of the adsorption of fission gases Xe and Kr on doped graphene, graphyne and graphidiyne.[26] Moreover, enhancement of Ng adsorption on doped MoS_2 monolayer and confined induced adsorption of Ng on MOF MFM-300 has been found very recently by us and found to be promising.[27]

As far as the nuclear fuel is concerned, the reactivity of noble gas atoms towards the uranium atoms is one of the most important aspects in nuclear reactor. In 2002, Andrews and co-workers have found first Ng-U (Ng = Ar, Kr, Xe) bonding in CUO molecule formed from the reaction of laser-ablated U atoms with CO in low temperature noble gas matrices through IR spectroscopic techniques.[28] Unusual IR shift in the U-O and U-C stretching modes confirms the generation of CUO·Ng molecules where U-Ar bond length and binding energy have been found to be 3.16 Å and 3.2 kcal mol^{-1}, respectively.[28] Subsequently, several $CUONg_nNg'_m$ molecules have been prepared and characterized experimentally supported by theoretical calculations.[29] Evidence for direct U-Ar bonding has also been reported by the same group of scientists for investigating the electronic structure of the UO_2 molecule at low temperature Ng matrices through IR spectroscopy with the formation of UO_2Ar, $UO_2(Ar)_5$,[30] and $UO_2(Ng)_4$ (Ng = Ne, Ar).[31]

Recently, Chattaraj and co-workers have studied confinement-induced binding of noble gas atoms within magic BN-fullerenes like $B_{12}N_{12}$ and $B_{16}N_{16}$[32] and BN doped carbon nanotubes.[33] Moving one step forward, we have also explored the structure and stability of the Ng encapsulated inorganic fullerene, viz., plumbasspherene

($Ng@Pb_{12}^{2-}$) and stannaspherene ($Ng@Sn_{12}^{2-}$) followed by molecular dynamic simulations.[34] The superelectrophilic behaviour of $B_{12}Cl_{11}$,[35] $B_{12}(CN)_{12}^{2-}$ and its fragment $[B_{12}(CN)_{11}]^-$ ion[36] is confirmed by their spontaneous covalent bonding with Ng atoms and the formation of thermodynamically stable $[NgB_{12}Cl_{11}]^-$ (Ng = Kr, Xe) and $[NgB_{12}(CN)_{11}]^-$ (Ng = Ar) compounds. Very recently, for the first time we have predicted thermodynamically stable dianionic noble gas compounds, viz., $[NgBeB_{11}(CN)_{11}]^{2-}$ (Ng = Ar, Kr, Xe),37 and $B_{12}Ng_{12}F_{12}^{2-}$ (Ng = Kr, Xe).[34]

A Typical Bonding in Novel Class of Noble Gas Insertion Compounds

Motivated from the discovery of HArF by Räsänen and co-workers,[6] we have predicted interesting noble gas insertion compounds by using ab initio quantum chemical techniques, viz., protonated nitrogen cations ($HNgN_2^+$),[12] formyl cations ($HNgCO^+$),[11] thioformyl cations ($HNgCS^+$)[39] (Fig.1(i)), hydride ions of boron ($HNgBF^+$),[40] protonated silicone monoxide cations ($HNgOSi^+$)[41] (Fig. 1(ii)), hypohalous acids (HXeOX; X = F, Cl, Br),[9] hydroxides of icosagens (HYO-HOY; Y = B, Al),[42] and hydronium ions ($HNgOH_2^+$)[10] (Fig.1(iii)),. Apart from the noble gas hydrides, we have also explored the possibility for the existence of noble gas halo compounds, viz., fluoro(sulphido)boron (FNgBS),[43] halocarbenes (FNgCX; X = F, Cl, Br, I)[44] (Fig.1(iv)), formyl cations ($XNgCO^+$; X = F, Cl).[45] We have also predicted the metastable metal-noble gas complexes, viz., XM-Ng-F (X = H, F; M = Be, Mg),[46] F-Ng-MF_2 (M = B, Al).[47] Exploiting the gold-hydrogen analogy, Ng insertion compounds involving most unusual noble gas-noble metal bonding, viz., MNgF and MNgOH (M = Cu, Ag, and Au; Ng = Ar, Kr, and Xe) have been predicted by us in the recent past.[20] All these compounds possess closed-shell geometries and they have been found to be singlet in their respective potential energy surfaces.

The CCSD(T) computed H- Ng bond length values have been found to be 0.766- 1.620 Å in $HNgCS^+$,[39] 0.764- 1.610 Å in $HNgCO^+$,[11] 0.765- 1.607Å in $HNgN_2^+$,[12] 0.771- 1.620Å in $HNgBF^+$,[40] 0.751- 1.615Å in $HNgOSi^+$ [41] and 0.754- 1.609 Å in $HNgOH_2^+$ [10] ions on going from He to Xe whereas the corresponding H–Ng bond lengths are from 0.824 to 1.680 Å in HNgF species and from 0.776 to 1.607 Å in bare H- Ng^+ ions.[48-50] Due to the close proximity of the H- Ng bond lengths, the comparable H- Ng bond strength with HNgF and bare HNg^+ ions indicates that there exists a strong bonding between the H and Ng atom in all the predicted ions. On going from He to Xe, the Ng- C bond lengths (2.036- 2.872 Å) in $HNgCS^+$ ions are found to be smaller than Ng- B (2.240- 3.090 Å) in $HNgBF^+$, Ng- N (2.138- 3.093 Å) in $HNgN_2^+$ and Ng- C (2.221- 3.124 Å) in $HNgCO^+$ bond lengths as obtained by CCSD(T) method.
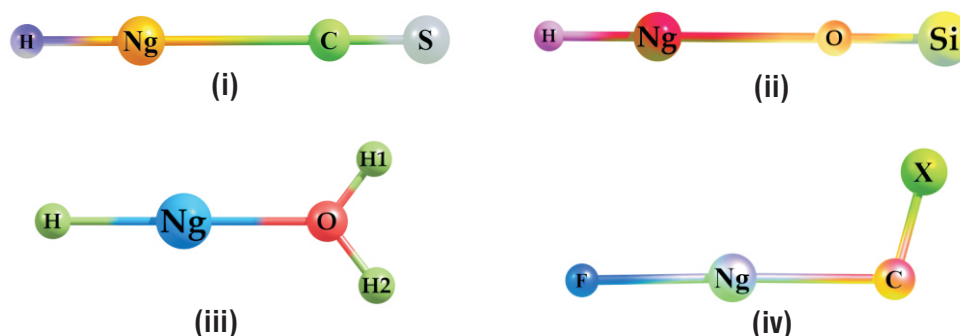

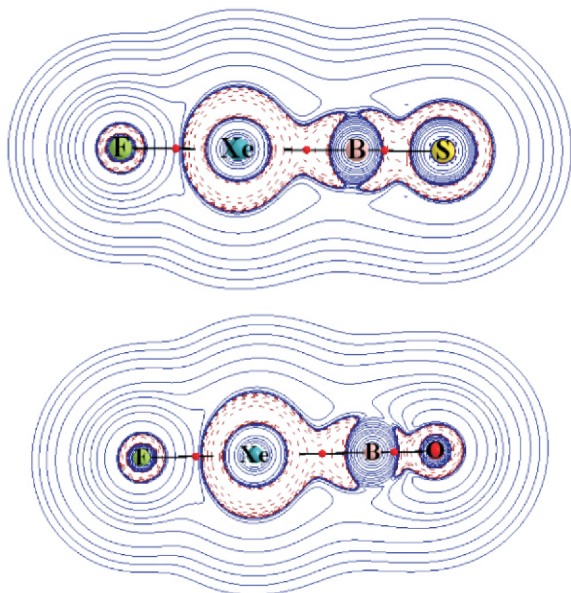**Fig.1:** Optimized minima structures of (I) $HNgCS^+$, (ii) $HNgOSi^+$, (iii) $HNgOH_2^+$, and (iv) FNgCX compounds.

The contour lines corresponding to the Laplacian ($\nabla^2\rho$) distribution (Fig.2) show more or less a uniform charge accumulation around the noble gas-boron-sulfur region in the FNgBS molecules; however, it is somewhat nonuniform in the case of FNgBO systems. Nevertheless, charge concentration in the Ng-B bonding region indicates that the Ng-B bond is rather covalent in nature whereas B-S bond is found to be more covalent than the B-O bond.

Stimulated by the open shell noble gas insertion compound with a doublet ground electronic state HXeO ($^2\Sigma$),[51] ^{2}HXeCC[52] and ^{3}FN–XeF$^+$,[53] for the first time we have predicted the neutral Ng insertion compound in the triplet electronic state, ^{3}FNgY (Ng = Kr, Xe; Y = N, P).[54] Subsequently, we have reported the neutral Ng insertion compound with heavier pnictides, ^{3}FNgY (Ng = Kr, Xe; Y = As, Sb, Bi) with triplet state.[55] Similar to the singlet Ng hydrides, we have also predicted the first Ng hydrides, *i.e.*, Ng inserted ketenyl cations (^{3}HNgCCO$^+$)[56] in the triplet ground state. For all the predicted ^{3}FNgY and ^{3}HNgCCO$^+$ species, significantly higher singlet-triplet energy gaps would prevent intersystem crossing (ISC) even at a very low temperature.

All the predicted species are found to be thermodynamically stable with respect to all possible 2-body and 3-body dissociation channels, except the dissociation path leading to the respective global minimum products. Nevertheless, all these compounds are found to be kinetically stable with finite barrier heights corresponding to their transition states, which are connected to their respective global minima products. The atoms-in-molecules (AIM) analysis strongly reveals that there exists conventional chemical bonding with the noble gas atom in all the predicted compounds.

'Superstrong' vdW Complexes with Ng: H Doping in NgM$_3^+$ (M = Noble Metal)

Following the footsteps of Fielicke and co-workers,[21] we have explored the exceptional enhancement of Ng-M bonding strength in NgM$_3^+$ (Ng = Ar, Kr, Xe; M = Cu, Ag, Au) ions through hydrogen doping by employing various *ab initio* based techniques.[22] The precursor ions, *viz.*, Au$_3^+$, Au$_3$H$^+$, and AuH$_2^+$ exhibit a nonlinear planar structure for the minima. Now the interaction of the Ng atom with these ions leads to the formation of strongly bonded NgAu$_3^+$, NgAu$_2$H$^+$, and NgAuH$_2^+$ complexes, as depicted in Fig. 3 which shows the variation of Ar-Au bond lengths in these complexes. The decrease in the Ar-Au bond length value from 2.605 Å in ArAu$_3^+$ to 2.518 Å in ArAu$_2$H$^+$ and 2.429 Å in ArAuH$_2^+$, respectively, as obtained by CCSD(T) indicates that the Ng-Au interaction is increased considerably in ArAuH$_2^+$ species. It implies that the Ng-Au bond strength is enhanced drastically with the doping of two hydrogen atoms in a pure Au trimer cation. In this context it is important to note that the CCSD(T) computed Ng-Au bond length values in NgAu$^+$ are generally larger (2.537, 2.553, and 2.617 Å in ArAu$^+$, KrAu$^+$, and XeAu$^+$, respectively) than that in the NgAuH$_2^+$ complexes, which indicate that the Ng-Au bond strength is greater in the latter complexes.
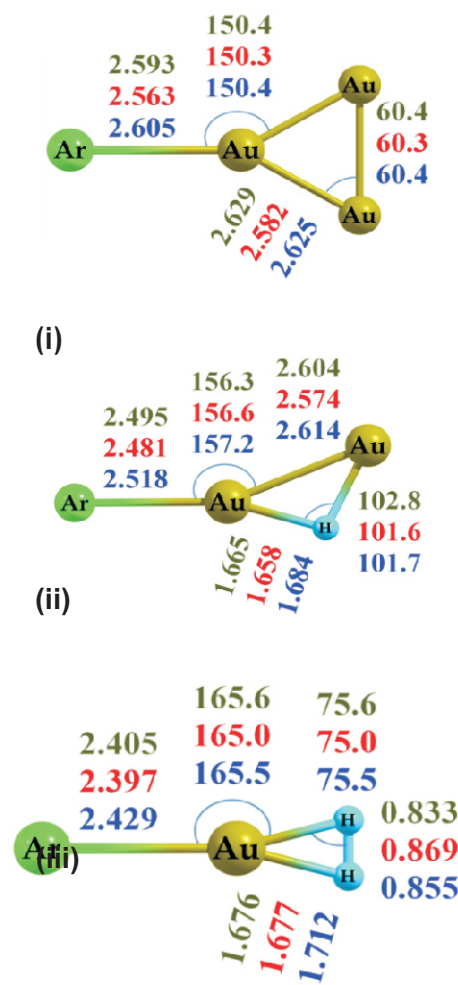
Table 1 lists all the bond dissociation energy, stretching frequency and force constant values for the Ng-Au bond in NgAu$_3^+$, NgAu$_2$H$^+$, and NgAuH$_2^+$ complexes. As far as binding energy is concerned, the Ng-Au bonding interaction has been found to be increased by 2.26 times for Ar, 1.99 times for Kr, and 1.75 times for Xe complexes in going from NgAu$_3^+$ to NgAuH$_2^+$ complex as shown in the Table 1. The Ng-Au binding energy in NgAuH$_2^+$ ions are even more stronger than the corresponding energy in NgAuF and NgAu$^+$

Table 1. CCSD(T) Computed Bond Dissociation Energy (BE in kJ mol^{-1}) and MP2 Calculated Stretching Frequency (ν in cm^{-1}) and Force Constant (k in Nm^{-1}) Values for Ng-Au Bond in NgAu$_3^+$, NgAu$_2$H$^+$ and NgAuH$_2^+$ Species.

Ions	BE (Ng-Au)			ν (Ng-Au)			k (Ng-Au)		
	Ar	Kr	Xe	Ar	Kr	Xe	Ar	Kr	Xe
NgAu$_3^+$	31.9	50.7	81.2	120.5	116.7	114.1	39.4	60.3	81.0
NgAuH$_2^+$	47.5	69.3	102.4	142.2	126.3	116.4	63.4	81.1	95.6
NgAuH$_2^+$	72.0	100.7	142.0	223.2	183.0	166.2	97.8	115.2	125.3

which are found to be 46.0, 44.1 kJ mol^{-1} in Ar, 64.4, 73.5 kJ mol^{-1} in Kr, and 92.4, 121.6 kJ mol^{-1} in Xe containing complexes, respectively, at the same level. The MP2/DEF2 computed Ng-Au stretching vibrational frequency value changes from 120.5 to 223.2 cm^{-1} in Ar, 116.7 to 183.0 cm^{-1} in Kr, and 114.1 to 166.2 cm^{-1} in Xe containing complexes on going from NgAu$_3^+$ to NgAuH$_2^+$ species, respectively, and the corresponding force constant values are changed from 39.4 to 97.8 N m^{-1} in Ar, 60.3 to 115.2 N m^{-1} in Kr, and 81.0 to 125.3 N m^{-1} in Xe containing complexes (Table 1). Both the Ng-Au stretching frequency and force constant values strongly reveals that the Ng-Au bonding strength is greatly enhanced with the hydrogen doping in pure Au trimers which is found to be in concurrence with the optimized structures and energetics.

The unprecedented enhancement of noble gas-noble metal bonding strength in NgM$_3^+$ (Ng = Ar, Kr, and Xe; M = Cu, Ag, and Au) ions through hydrogen doping have been explored by using various *ab initio* based techniques. The concept of gold-hydrogen analogy has been used to evolve this pronounced effect of hydrogen doping in Au trimers leading to the strongest Ng-Au bond in NgAuH$_3^+$ species, as revealed from the calculated values of Ng-Au bond length, bond energy, vibrational frequency and force constant. Similar trends have been found in the case of Ng-Ag and Ng-Cu complexes. The enhancement of Ng-M bonding interaction in Ng-MH$_2^+$ (Ng = Ar, Kr, and Xe; M = Cu, Ag, and Au) as compared to that in Ng-M$_3^+$ can be attributed to considerable increase in the Ng-M covalency as revealed from the electron density based topological properties and energy decomposition analysis. Calculated values of HOMO and LUMO energies, and partial atomic charges further indicate that an enhancement in the charge-induced dipole interaction is also responsible for the surprisingly high Ng-M bonding interaction in Ng-MH$_2^+$ species.
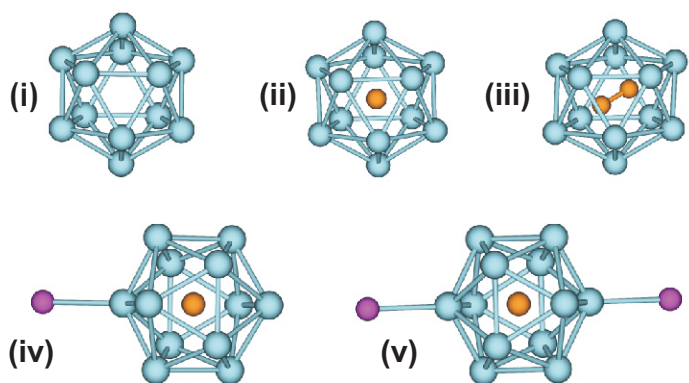

Fig.4: Optimized geometry of the (i) bare Pb$_{12}^{2-}$, (ii) Ng@Pb$_{12}^{2-}$, (iii) Ng$_2$@Pb$_{12}^{2-}$, (iv) Ng@KPb$_{12}^-$, and (v) Ng@K$_2$Pb$_{12}$.

Endohedral Encapsulation of Ng in Molecular Cages

In recent times, we have explored the possibility of the existence of noble gas encapsulated inorganic fullerene clusters by evaluating the stability of the Ng encapsulated endohedral Zintl ions, Ng@M$_{12}^{2-}$ (Ng = He, Ne, Ar, and Kr; M = Sn and Pb)[34] through density functional theory. Figure 4 depicts that the Ng@M$_{12}^{2-}$ cluster exhibits Ih symmetry while the D5d symmetry has been assigned to Ng$_2$@M$_{12}^{2-}$.

The cage diameter for Sn$_{12}^{2-}$ has been expanded from 6.061 Å to 6.111-6.555 Å while it is expanded from 6.303 Å to 6.344-6.764 Å in the Pb$_{12}^{2-}$ cage after the encapsulation of the Ng atoms. The
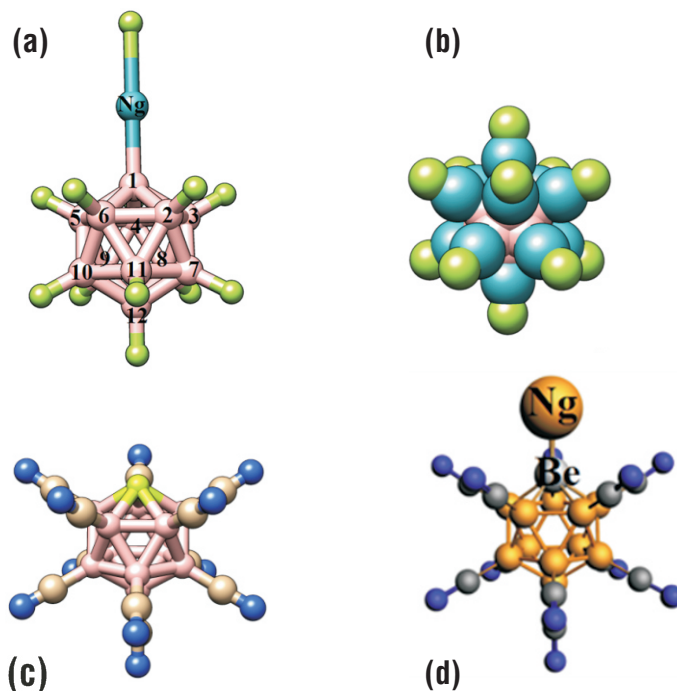

Fig.5: Optimized structures of (a) B$_{12}$NgF$_{12}^{2-}$, (b) B12Ng12F$_{12}^{2-}$, (c) BeB$_{11}$(CN)$_{11}^{2-}$, and (d) NgBeB$_{11}$(CN)$_{11}^{2-}$

B3LYP/def-TZVP computed Pb-Pb and Ng-Pb distances have been found to be in the range of 3.335-3.556 Å and 3.172-3.382 Å, respectively. A remarkable observation is that the He-He bond length (1.561 Å) in the He$_2$@Pb$_{12}^{2-}$ cluster is considerably shorter than that in the free He-He dimer (3.852 Å). The B3LYP/def-TZVP calculated binding energy are -15.2 to -147.2 kcal mol^{-1} in Ng@Pb$_{12}^{2-}$ clusters (Ng = He - Kr), while the same have been found to be 116.6 to 24.5 kcal mol^{-1} in Ng@KPb$_{12}^{2-}$ clusters and 199.4 to 105.9 kcal mol^{-1} in Ng@K$_2$Pb$_{12}$ clusters (Ng = He - Ar). These binding energy values clearly indicate that the Ng@Pb$_{12}^{2-}$ are thermodynamically unstable clusters while potassium salt of these are found to be stable. The kinetic stability of the Ng@Pb$_{12}^{2-}$ clusters has been studied through ab initio molecular dynamics simulation. Therefore, the Ng@M$_{12}^{2-}$ clusters are kinetically stable and thermodynamically unstable whereas the K$^+$ salt of Ng@M$_{12}^{2-}$ clusters are found to be both kinetically as well as thermodynamically stable.

Very recently, for the first time we have predicted a theromodynamically stable dianionic noble gas compound, viz., [NgBeB$_{11}$(CN)$_{11}$]$^{2-}$ (Ng = Ar, Kr, Xe).[37] Since the electron affinity of noble gas atoms is negative, therefore, a Ng atom can bind with the anions or dianions which are supposed to be superelectrophilic in nature due to the presence of a high positive charge on the free B or Be atom in these anions.[37]

Subsequently, we have further reported the unprecedented stabilization of multiply charged anion, $B_{12}F_{12}^{2-}$, through insertion of Ng atoms into B–F bonds, resulting in the formation of stable icosahedral $B_{12}Ng_{12}F_{12}^{2-}$ anions[38] (Fig.5) where the HOMO is stabilized significantly and the binding energy of the second excess electron is increased remarkably. Unprecedented stability enhancement with Ng insertion might be due to a strong covalent B–Ng bond, increased charge delocalization and increased electrostatic interaction between the oppositely charged centers.

In a nutshell, various high level quantum computational techniques provide all possible future directions to explore the different aspects of selective complexation and cluster formation using a specific noble gas atom with several interesting molecular systems utilizing various fundamental chemical concepts. Herein, the progress in the investigation of a novel class of chemically bound Ng compounds is reviewed. Reported work in the literature indicates that the field of noble gas chemistry is at an early developmental stage with a large number of open questions on the astonishing properties and the synthetic mechanisms of the Ng molecular systems, which put forward a real challenge to the contemporary researchers. Moreover, investigations of noble gas compounds would be highly promising not just from the view point of fundamental chemical bonding but also for the design of new materials to trap radioactive noble gases in nuclear establishments.

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