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Theoretical prediction of noble gas inserted halocarbenes: FNgCX (Ng = Kr, and Xe; X = F, Cl, Br, and I)

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ABSTRACT

A new series of neutral noble gas inserted compounds involving halocarbenes, mainly, FNgCX (Ng = Kr, and Xe; X = F, Cl, Br, and I) has been predicted through various *ab initio* quantum chemical techniques such as MP2, DFT, CCSD(T) and MRCI. The structure, stabilities, charge distribution, harmonic vibrational frequencies and topological properties of these compounds have been investigated. It is found that the predicted species are energetically stable with respect to all the plausible 2-body and 3-body dissociation pathways, with the exception of the 2-body channel that leads to the global minimum products (FCX + Ng). Despite this, existence of finite barrier heights indicates that these compounds are kinetically stable with respect to global minimum products. The computational results indicate that it might be possible to prepare and characterize the most stable singlet state of FNgCX molecules under cryogenic conditions through suitable experimental technique(s).

1. Introduction

Carbenes have been an important subject of interest for experimentalists and theoreticians for well over half a century, and continue to be studied in a wide array of chemical reactions. They have been extensively researched as free radicals due to the significant difference in reactivity between their low-lying singlet ($\sigma^2\pi^0$) and triplet ($\sigma^1\pi^1$) ground states, despite their energetic closeness [1–4]. The simplest of these molecules, CH_2, shows greater stability in its triplet state [5], which is understood simply as a result of higher coulombic repulsion energy between the nonbonding electrons in the singlet state as compared to the triplet state. In CF_2, however, the singlet state is more stable due to stabilization of σ molecular orbital and/or destabilization of 2p-π atomic orbital on C atom where the molecule adopts sp^2 hybrid structure [6]. The nature of interaction of such species is greatly determined by the relative stability of the singlet and triplet state [7–14]. The carbene, 2,5-diazacyclopentadienylidene, for instance, is known to form an adduct with Xe when produced in matrix isolation. This species has been characterized spectroscopically and is found to have a significantly high electrophilic reactivity along with a singlet ground state [15,16].

Halogenated carbenes are very important reactive molecular species playing vital roles in large number of chemical reactions; viz., these are the most possible photoproducts of halons and chlorofluorocarbons (CFCs) which have large ozone depletion potentials (ODPs) due to destruction of ozone layer in the stratosphere, and the halocarbenes are also very important intermediates in several organic synthesis as well as in the gas-phase combustion reactions [17,18]. In fact, it has been estimated that the bromine containing halocarbons are 60 times more destructive to the ozone layer than the corresponding chlorine counterpart [19–21]. The larger values of ODPs demand further investigation of the photoproducts of halons and CFCs, i.e., halocarbenes. For this purpose, halocarbenes are the most significant specified species among all the carbenes in the frontier area of research [22–27].

Here, we look into parent molecules of the type FCX, where X = F, Cl, Br and I, forming FNgCX upon insertion of noble gas atom, Ng = Kr and Xe. In this context, it may be noted that we have tried the argon inserted halocarbenes (FArCX, X = F, Cl, Br and I), but none of these compounds are stable with respect to 3-body dissociated products. Noble gases used to be considered as highly unreactive species until 1962, when Bartlett discovered the first stable noble gas compound $XePtF_6$ [28,29] affirming Pauling's hypothesis

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of formation of chemical bond between xenon and oxygen or fluorine atoms in 1933 [30]. Consequently, to explore the xenon chemistry, extensive research has been devoted to prepare and characterize several xenon–fluorine species [31–34]. The outstanding breakthrough by Räsänen and co-workers [35,36], with the discovery of first covalently bonded argon compound, HArF led to an entirely new direction of research in noble gas chemistry. This marked the beginning of the study of a large number of neutral and ionic noble gas containing chemical species discovered in succeeding decades [37–81]. Accordingly, an in-depth study has been carried out in order to understand the nature of bonding that exists in the metastable noble gas inserted chemical species. Plenty of ionic and neutral noble gas inserted chemical compounds have been predicted theoretically with various computational techniques through insertion of a noble gas atom into ions/molecules having environmental or astronomical impacts, such as HCO^+ [60], HCS^+ [74], $HOSi^+$ [78], HOX (X = F, Cl, Br) [56], and H_3O^+ [71] etc. Further, theoretical prediction of such molecules using quantum chemical calculations has proven to be useful in determining their stability and hence synthesizing these compounds experimentally. For instance, HXeOBr has been successfully prepared by Khriachtchev et al. [64], which was theoretically predicted by our group previously [56]. In addition to the insertion type of compounds, Grochala and co-workers have investigated noble gas oxide molecule inside a dipolar cavity consisting of alkali metal fluoride molecules [67,75].

Studies with organo-xenon derivatives involving a Xe–C bond have significantly increased in the past decade and extensive research been done on synthesising such molecules [41,42,45,57,69,70]. Thus, several compounds containing Xe–C bond, such as HXeCN [39], HXeCCH [44,46,66], HXeCCXeH [44], HXeCCF [63], $HXeC_3N$ [58], and $HXeC_4H$ [47] have been identified in the solid phase under a cryogenic environment. Moreover, a gate to organo-krypton chemistry has been opened with the discovery of HKrCCH by Khriachtchev et al. [82–84]. Subsequently more compounds possessing Kr–C bonds have been prepared and characterized through matrix isolation technique followed by *ab initio* calculations [63,85]. Of late, a new class of noble gas inserted compounds having the general formula 'XNgY', where X and Y are two separate electronegative fragments, such as ClXeCN and BrXeCN [68] have emerged, which are associated with a Ng–C bond as well. Very recently, FXeCN, FXeNC and FKrCN have been prepared and characterized by Khriachtchev and co-workers by UV photolysis of FCN in the Xe and Kr matrices and subsequent thermal annealing [79]. Prediction of molecules $Xe(CF_3)_2$ [48], $FXeCF_3$ [48], and $FKrCF_3$ [50] involving F–Ng and Ng–C bonds has motivated us to investigate species having similar fragments. Extensive theoretical studies have also been carried out on xenon and krypton's interactions with other members of the tetragen series. The compounds $FKrSiF_3$ [50], $FKrGeF_3$ [50], and $FNgEF_3$ (where E = Sn, Pb; Ng = Kr–Rn) [80] have been investigated following their carbon counterpart. While FXeSiF [43], FXeGeF [73], and FNgEF (where E = Sn, Pb; Ng = Kr–Rn) [80] have already been studied, the corresponding molecules with carbon are curiously missing. Further, compounds containing F–C bonds (organofluroine compounds) are known to have diverse applications in pharmaceuticals, refrigerants and catalysis [86]. To the best of our knowledge noble gas inserted halocarbene molecules have not been reported till date.

In this work, we have systematically obtained optimized structures, dissociation energies, charge distributions, harmonic vibrational frequencies and atoms-in-molecules (AIM) bonding parameters of FNgCX species. These have been investigated through quantum computational methods such as Møller-Plesset perturbation theory (MP2), density functional theory (DFT), and coupled-cluster theory (CCSD(T)). The change in the aforementioned parameters based on a periodic variation of the substituted halogen has been presented in a comprehensive yet concise manner. Further, the multi-reference computational approach has also been employed for each molecule so as to ensure the consistency of the single reference based methods in predicting the various properties of these compounds. Furthermore, it remains to be seen how the singlet-triplet energy gap of the FCX (X = F, Cl, Br and I) molecule is changed upon insertion of a noble gas atom.

2. Computational methodology

Ab initio and density functional theory based calculations have been performed using GAMESS [87] and MOLPRO 2012 [88] programs. The minima and transition state geometries of FNgCX have been optimized using *ab initio* and density functional theory based methods including Møller–Plesset second-order perturbation theory (MP2) [89], density functional theory (DFT) with Becke 3-parameter exchange and Lee–Yang–Parr correlation (B3LYP) [90,91] functional and dispersion corrected omega separated form of Becke's 1997 hybrid functional with short-range HF exchange (ωB97X-D) functional [92], and coupled cluster theory with the inclusion of single and double excitations and an estimate of connected triples (CCSD(T)) [93]. C_s point group has been used for optimizing the minima structures of FNgCX on the singlet as well as triplet potential energy surfaces whereas the most stable transition state structures contain no symmetry. For the ωB97X-D and MP2 calculations the def2-TZVPD basis sets designed by Weigend and Ahlrichs [94] for I and Xe atoms [95] with 28 core electrons each and all-electron def2–TZVPD basis sets for the C, F, Cl, Br, and Kr atoms [96] have been used. This combination of basis set will henceforth be referred as B1. Moreover, we have used valence only aug-cc-pVTZ-PP basis sets with Stuttgart small core effective potentials (ECP10MDF for Br and Kr atoms, and ECP28MDF for I and Xe atoms) [97], and the aug-cc-pVTZ basis sets for the C, F, and Cl atoms for the CCSD(T) calculations. This grouping of basis set is denoted as B2. Vibrational analysis has been carried out through MP2/B1, ωB97X-D/B1 and CCSD(T)/B2 level of theory whereas Mulliken population analysis have been performed with B1 basis set using MP2 and ωB97X-D methods. The natural bond orbital (NBO) analysis of all minima structures has been performed using MP2 and B3LYP methods with B2 basis set taking CCSD(T) optimized geometries. Furthermore, to obtain a clear insight into the nature of chemical bonding that exists between different atoms quantitatively, the AIM (atoms-in-molecule) analysis has been carried out using MP2, B3LYP, and ωB97X-D methods with B1 basis set utilizing AIMPAC program for bond critical point (BCP) properties and Multiwfn program [98] for local electron energy density critical point (HCP) properties. In addition, the multi-reference configuration interaction method [99,100] (MRCI) has been employed for single point energy calculation using MP2/B1 optimized geometries of all the predicted FNgCX species with MOLPRO 2012 program. To generate the reference space through CASSCF [101] calculations for each system, 20 valence electrons and 13 valence orbitals have been considered.

3. Results and discussions

3.1. Structural parameters of FNgCX species

The optimized geometries of all Ng inserted FCX molecules, where X = F, Cl, Br and I are nonlinear and planar with C_s symmetry for both singlet and triplet potential energy surfaces. The structural parameters including bond lengths and bond angles of ^{3}FNgCX molecules optimized using MP2/B1, B3LYP/B1, ωB97X-D/B1 and