Research paper

A theoretical evidence for cooperative enhancement in aerogen-bonding interactions: Open-chain clusters of $KrOF_2$ and $XeOF_2$

Mehdi D. Esrafili [a,*], Esmail Vessally [b]

[a] Laboratory of Theoretical Chemistry, Department of Chemistry, University of Maragheh, Maragheh, Iran
[b] Department of Chemistry, Payame Noor University, Iran

ARTICLE INFO

ABSTRACT

The cooperativity of aerogen-bonding interactions is studied in open-chain $(KrOF_2)_{n=2-6}$ and $(XeOF_2)_{n=2-6}$ clusters. The formation mechanism and bonding properties of these clusters are investigated by means of molecular electrostatic potentials, natural bond orbital and noncovalent interaction index analyses. The small variation of average interaction energy from the pentamer to hexamer cluster reveals that cooperativity effects are almost completely saturated in the larger clusters. The cooperative effects in the clusters also make an increase in the average ^{83}Kr or ^{129}Xe chemical shielding isotropies and total spin-spin coupling constants across the aerogen-bonding.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Over the past decades, hydrogen bond interactions have raised a tremendous interest as they play a fundamental role in many field of chemistry and biochemistry [1]. However, with the rapid development of computer technology and advanced experimental techniques, other types of noncovalent interactions, for example, σ-hole bonds [2–8], have attracted considerable attention recently. A σ-hole bond refers to a directional interaction between covalently-bonded Groups 14–18 atoms playing the role of the Lewis acid with a potential electron donor. The Lewis acid properties of these atoms are generally described in terms of the existence of an electron-deficient region (σ-hole) [9–13] that is present on their outer surfaces. This region is often characterized by a positive molecular electrostatic potential (MEP) which accounts for the electrostatic component of σ-hole bonds. Such interactions are referred to the tetrel-bonding [14–17], pnicogen-bonding [18–23], chalcogen-bonding [24–27], halogen-bonding [28–30] and aerogen-bonding [31–33] for the atoms of Groups 14, 15, 16, 17 and 18, respectively. It should be noted that the σ-hole concept cannot completely explain the characteristics of these interactions, since there are numerous theoretical studies [8,19,21,34–36] demonstrating that the charge-transfer interaction is also responsible for the stability and directionality of these interactions as well.

The aerogen bond is the newer member of the family of σ-hole interactions. This bond arises when an aerogen atom (noble gas) acts as an electron-acceptor in a Lewis acid -Lewis base interaction. Bauzá and Frontera [31] first proposed the possibility of formation of this interaction between some noble gas containing molecules and nitrogen bases. Their results clearly indicated that aerogen bonds are quite strong and can be comparable in strength to the hydrogen bonds. Thus, aerogen bonds can be used as a molecular linker in molecular recognition, and material science. Very recently, some theoretical studies have focused on the characteristics of the aerogen-bonding interactions [37–40]. The electron donors of aerogen bonds were lone pairs from molecules such as NH_3 or NCH [31,39,41], although other types of electron donors like π electrons [32,33,37], metal hydrides [42] or even radical species [43] have been also reported. Like other σ-hole bonds, the strength of aerogen bonds depends not only on the nature of aerogen atoms but also to the substitution and cooperative effects.

Cooperativity is perhaps one of the most important concepts in the theory of noncovalent interactions. So far, a few studies have reported the cooperativity in systems where one of the interactions corresponds to the aerogen bond [39,40]. However, to the best of our knowledge, no previous study has considered the cooperativity in linear aerogen-bonded clusters. In this letter, continuing our interest about cooperativity in linear σ-hole interactions [16,44–46], we address the geometry, interaction energies and bonding properties of open-chain clusters of $(ZOF_2)_{n=2-6}$, where Z = Kr and Xe. In order to understand the mechanism of the cooperativity, molecular electrostatic potential (MEP), noncovalent interaction (NCI) index and natural bond orbital (NBO) analyses are performed.

2. Computational details

Full geometry optimizations and the corresponding harmonic frequency calculations were carried out using Gaussian 09 suite of programs [47]. All density functional theory (DFT) calculations were performed with the M06-2X method, since this density functional is able to provide reliable results for the σ-hole bonds [48,49], primarily due to the proper description of charge transfer component in these interactions. The all-electron def2-TZVPPD triple-ζ basis set equipped with two sets of polarization and diffusion functions was used for the description of all atoms, except for Xe atom, where the corresponding relativistic effects were treated through the use a small-core energy-consistent relativistic pseudopotential. The structure of the $(ZOF_2)_{n=2,3}$ clusters was also optimized at the MP2/def2-TZVPPD level. The interaction energy was calculated as the difference of the total energy of the complex and the sum of the isolated monomers in their complex geometry. The basis set superposition error (BSSE) calculated with the counterpoise (CP) method [50] was used to correct the interaction energies. The MEP analysis was performed on the 0.001 electrons/Bohr^3 contour of the electronic density using the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) [51]. The NBO analysis [52] was performed with the help of NBO 5.0 program at the M06-2X/def2-TZVPPD level of theory [53]. The NCI index analysis [54] was carried out using the MultiWFN program [55]. The ^{83}Kr and ^{129}Xe chemical shielding isotropy values as well as spin-spin coupling constant across the aerogen bond interactions were cal-culated at the M06-2X/def2-TZVPPD level using the gauge-included atomic orbital approach [56].

3. Results and discussion

The optimized structures of the linear $(KrF_2O)_{2-6}$ and $(XeF_2O)_{2-6}$ clusters at the M06-2X/def2-TZVPPD level of theory are depicted in Fig. 1. All these clusters have a linear open-chain structure, in which there exists only one Kr$\cdots$O or Xe$\cdots$O interaction between two neighbor monomers. The calculated aerogen bond distances in the binary $KrF_2O\cdots KrF_2O$ and $XeF_2O\cdots XeF_2O$ complexes are 2.847 and 2.889 Å, respectively. These are shorter than the sums of the van der Waals radii of the atoms involved ($r_{vdw,Kr}$ = 2.02 Å, $r_{vdw,Kr}$ = 2.16 Å, $r_{vdw,O}$ = 1.55 Å) [57], which imply that there exists an attractive interaction between the interacting molecules. Fig. 1 also indicates that Z$\cdots$O binding distances in the $(ZF_2O)_n$ clusters become shorter when the number of the monomer increases in the cluster. In particular, the increasing the size of the each cluster brings about a sizable reduction in the Z$\cdots$O binding distances between the central units. This indicates that the strength of the aerogen bonds formed between the interior units of each cluster is larger than those of terminal ones. For example, the calculated Xe$\cdots$O binding distance between the interior units of $(XeF_2O)_6$ cluster is 0.147 Å (5%) shorter than the corresponding distance in $(XeF_2O)_2$ complex. Therefore, the progressive enhancement in the Z$\cdots$O shrinkage with the number of monomers in the clusters reveals the marked cooperative nature of the geometry changes
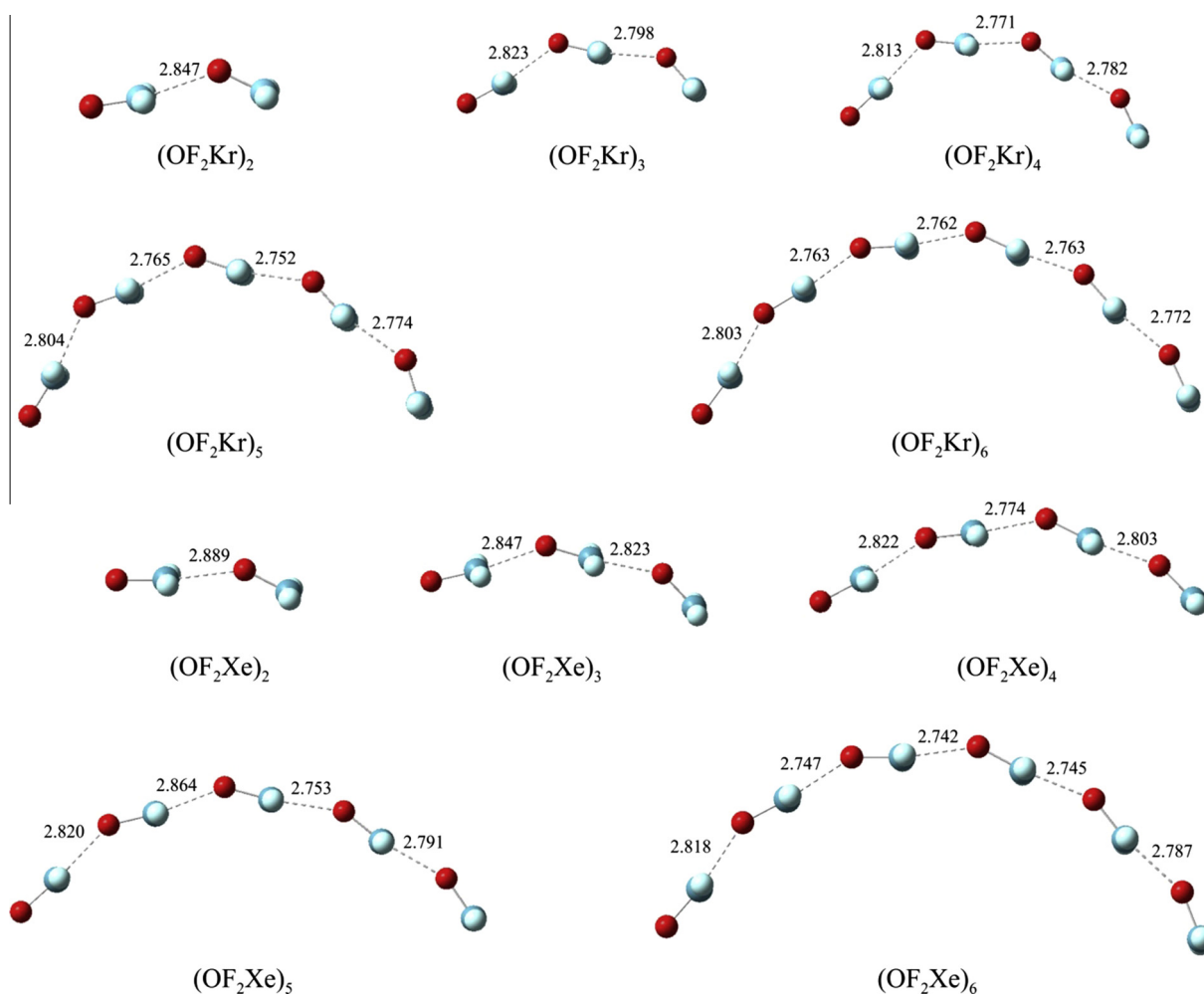

Fig. 1. Optimized structure of open-chain $(KrF_2O)_{n=2-6}$ and $(KrF_2O)_{n=2-6}$ clusters at the M06-2X/def2-TZVPPD level.