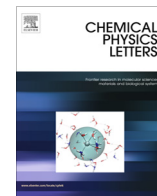




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Research paper

An ab initio study on anionic aerogen bonds

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ABSTRACT

An ab initio study is carried out to investigate the anionic aerogen bonds in complexes of KrO_3 , XeO_3 and XeOF_2 with F^- , Cl^- , Br^- , CN^- , NC^- , N_3^- , SH^- , SCN^- , NCS^- , OH^- and OCH_3^- anions. All of the anionic aerogen bonds analyzed here have a partial covalent character. Charge transfer from the anion to the Kr–O or Xe–O σ^* orbital stabilizes these complexes and leads to a sizable redshift in the corresponding stretching frequencies. The $J(\text{Kr–O})$ or $J(\text{Xe–O})$ spin-spin coupling constants can be regarded as a useful tool for the characterization of strength of the anionic aerogen-bonded complexes.

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1. Introduction

Over the past few decades, finding and explaining novel weak noncovalent interactions have become one of the most active research fields [1–6]. Noncovalent interactions play a critical role in protein folding, stacking of nucleobases, drug binding, self-assembly, and crystal packing processes [7,8]. Until now, many different types of noncovalent interactions have been characterized and investigated by various experiments and theoretical calculations, including hydrogen-bonding [9,10], π - π stacking [11,12] and cation- π [13,14] interactions. Meanwhile, much attention has been recently devoted to σ -hole bonds [15–23] owing to their diverse and potential applications in many fields including supramolecular chemistry, biochemistry and material science. A σ -hole bond is an electrostatically-driven interaction between covalently-bonded Groups 14–18 atoms playing the role of the Lewis acid and an electron-rich site [24,25]. For example, high-level ab initio calculations performed by Bauzá and Frontera [26] have indicated that the aerogen atoms (noble gases) in compounds such as XeO_3 and XeOF_2 are able to interact with potential nitrogen bases, with strength comparable to hydrogen bonds. Such interactions are often named as the aerogen bonds. Recently, the xenon trioxide alkyl nitrile adducts were synthesized and the nature of the aerogen bond was theoretically studied by Schrobilgen and co-workers [27]. The formation of the aerogen bonding in these complexes is attributed to the existence of a positive electrostatic potential area (σ -hole) in the extension of the Xe–O bond, which

is due to the depletion of the electron density in this region. This electrostatic factor is also supplemented by other stabilizing energy terms, like charge-transfer, polarization and dispersion effects [28–30].

One of the interesting aspects of aerogen bonds, like other σ -hole interactions, is their directional tunability which exhibits a great promise for the fabrication and modeling of novel materials with desired functions and properties. There are many factors which influence the strength and bonding properties of aerogen-bonded complexes. These include the nature of the aerogen atom, the nature of the electron-donor, substituent effects on the Lewis acid and the Lewis base, and the cooperativity with other intermolecular interactions [26,28–33]. The Lewis base moiety in aerogen-bonding can be any electron-rich site, like lone-pair electrons [26,32], π -electrons [28,30,31,33], metal hydrides [34] or even radical species [35]. Bauzá and Frontera [26] have also reported a theoretical evidence for the formation of aerogen bonding interaction with the halide ions (Cl^- and Br^-) acting as the Lewis base. Note that the latter interaction has some similar features with the anion- π interaction, in which the anion species interacts with a positive region of electrostatic potential on the π -system. Both these interactions can be classified as the charge-assisted interactions and may be regarded as potential noncovalent interactions for the crystal packing and designing of anion receptors.

In this work, using high-level ab initio calculations, the geometries and interaction energies of anionic aerogen bonds between some aerogen containing molecules (KrO_3 , XeO_3 and XeOF_2) and a series of anions (F^- , Cl^- , Br^- , CN^- , NC^- , N_3^- , OH^- , SH^- , OCH_3^- , NCS^- and SCN^-) are investigated. We also discuss the bonding properties

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of the resulting complexes by a vast number of methods including molecular electrostatic potential (MEP), electron localization function (ELF), quantum theory of atoms in molecules (QTAIM), non-covalent interaction (NCI) index and natural bond orbital (NBO) methods. We hope that the results of this study to be useful for a better understanding and future applications of the aerogen-bonding and noble gas chemistry.

2. Computational details

All ab initio calculations were carried out using the Gaussian 09 suite of programs [36]. MP2 calculations were performed for the geometry optimizations and the subsequent frequency calculations of all systems considered here. The all-electron aug-cc-pVTZ basis set was used for all atoms, except Xe, for which the aug-cc-pVTZ-PP [37] basis set was employed. Only one minimum structure was obtained for the complexes under study, except for the thiocyanate and cyanide anions, in which two stable structures were found depending on the nature of the interacting atom. The interaction energies were estimated at the MP2/aug-cc-pVTZ(-PP) and CCSD(T)/aug-cc-pVTZ(-PP) levels with corrections for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise method [38]. The ELF [39] and NCI index [40] analyses were performed with the help of MultiWFN [41] using the wavefunctions generated at the MP2/aug-cc-pVTZ(-PP) level. The MEPs were computed on the 0.001 au contour of the electronic density by means of the Wave Function Analysis–Surface Analysis Suite [42]. The NBO analysis [43] was performed with the help of NBO 5.0 program [44]. The ^{83}Kr and ^{129}Xe chemical shielding isotropy values as well as spin-spin coupling constants were calculated with the gauge-included atomic orbital approach [45].

3. Results and discussion

It is better to analyze the MEP maps for the isolated KrO_3 , XeO_3 and XeOF_2 molecules since the areas of the positive MEPs are

related to the nucleophilic attack sites while the negative potential areas are attributed to the electrophilic attack. Fig. 1 shows the MEP maps of the isolated KrO_3 , XeO_3 and XeOF_2 molecules. The isosurface of the electron density of 0.001 au was chosen here according to the suggestion of Bader [46]. From Fig. 1, it is seen that there is a distinct positive region (σ -hole) in the extension of the Kr–O or Xe–O bond(s) of these molecules, which is due to the depletion of the electron density in this region. Thus, the aerogen atoms in these molecules may act as the Lewis acid in the extension of Kr–O or Xe–O bond(s), forming aerogen bonds. Note that the maximum positive electrostatic potential of XeO_3 is larger than that of KrO_3 (Fig. 1), which may suggest the stronger aerogen-bonding interactions for the former complexes than for the latter ones. This finding is also supported by the ELF analysis of these molecules, as shown in Fig. 1. The ELF plots clearly indicate the localization of the lone pair domain at the Kr or Xe atom as well as a high degree of electron density deficiency around these atoms. The latter demonstrates the strong tendency of these molecules to form aerogen bond interactions with the potential electron donors.

The minimum electrostatic potential ($V_{s,\text{min}}$) values associated with the anion species considered here are collected in Table 1. It is evident that the absolute value of $V_{s,\text{min}}$ becomes larger in the order of $\text{SCN}^- < \text{NCS}^- < \text{Br}^- = \text{N}_3^- < \text{CN}^- < \text{HS}^- < \text{Cl}^- < \text{NC}^- < \text{OCH}_3^- < \text{F}^- < \text{OH}^-$. Note that for the thiocyanate anion, the negative MEPs are found at the sulfur and nitrogen atoms, which indicates the dual role of this anion as a Lewis base. Interestingly, the calculated $V_{s,\text{min}}$ value at the nitrogen atom (-126 kcal/mol) is more negative than that of at the sulfur one (-96 kcal/mol). Hence, there could be a directional and electrostatically-driven interaction between the positive σ -hole on the aerogen atom of KrO_3 , XeO_3 and XeOF_2 molecules the negative MEP site of these anions, and the corresponding interaction is called anionic aerogen bond.

Table 1 lists the calculated binding distances and BSSE-corrected interaction energies of anionic aerogen-bonded complexes studied here. The optimized structures are depicted in Fig. S1 of Supporting Information. From Table 1, it is seen that the aerogen bond distances in these complexes span a large range,

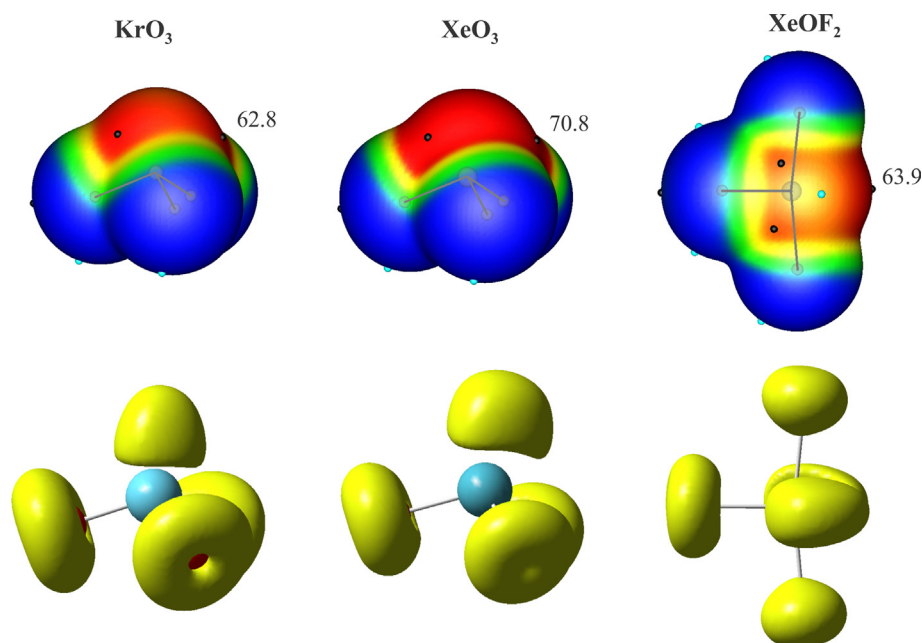


Fig. 1. Calculated MEP (above) and ELF (below) isosurfaces of the isolated KrO_3 , XeO_3 and XeOF_2 monomers. The color code for MEP plots, in kcal/mol, is: red > 40 ; $40 > \text{yellow} > 20$; $20 > \text{green} > 0$ and blue < 0 . The locations of the σ -holes at Z (Kr, Xe) associated with the Z–O bond are indicated with black circles, and their values are given in kcal/mol. The isosurface values of the MEP and ELF maps are 0.001 and 0.75 au, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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