



Research paper

Comparative study of hydrogenated and lithiated superhalogens



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ABSTRACT

The structural features, properties and stability of two kinds of representative superhalogen compounds, namely hydrogenated superhalogens and lithiated superhalogens, are theoretically studied in detail, providing further insight into the behavior of superhalogens. According to topological analysis of the electron localization function, most of superhalogen clusters as a whole combine with Li atom through ionic bond (s). In contrast, the H atom tends to bind with superhalogen by covalent bond although a portion of the superhalogens are broken upon hydrogenation. In addition, the electric properties of these superhalogen compounds are also obtained and compared with those of traditional acid and salt molecules.

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1. Introduction

Superhalogens are an important subset of superatom clusters, which represent a class of molecules that possess larger electron affinities (EAs) than those of halogen atoms (3.40–3.62 eV) [1] in the periodic table. So far many researches have been devoted to characterizing various superhalogen species since they were introduced by Boldyrev and Gutsev in 1981 [2]. The most prominent group of superhalogen is of the XY_{k+1} type (where X is a main group or transition metal atom, Y is a halogen atom, and k is the maximal formal valence of X) [2], which has been well-studied during the past 30 years [3,4]. For example, the existence of superhalogen anions XY_2 (X = Li, Na; Y = Cl, Br, I) [5] was experimentally confirmed by Wang's group in 1999. They also investigated superhalogen anions XY_3 (X = Be, Mg, Ca; Y = Cl, Br) by combining photoelectron spectroscopy and theoretical methods [6]. Anusiewicz et al. theoretically studied the T_d -symmetric XY_4 (X = B, Al; Y = F, Cl) superhalogen anions and obtained their vertical electron detachment energies (VDEs) (6.22–9.79 eV) [7]. Considerable VDE values were also predicted to be 8.54 eV [8] and 9.43 eV [9] for the SiF_5 and PF_6 anions, respectively. Later, diverse new-type superhalogens had been reported, for example, binuclear superhalogen anions X_2Y_5 (X = Be, Mg; Y = F, Cl) [10–12] and superhalogens SO_3F , SO_2F_3 and SOF_5 with mixed ligands [13]. Recent works have also revealed the existence of halogen-free superhalogens, including BO_2 , AlO_2 [14], NO_3 , PO_3 [2], etc., whose VDEs

(4.00–5.30 eV) are larger than those of halogens but less than those of traditional superhalogens.

As a special kind of chemical species, superhalogens may help to develop new research areas where strong oxidizing agents are required. As previously reported, they can oxidize counterparts with relatively high ionization potentials (IPs), such as noble gas atom [15], O_2 [16], benzene [17], and water [18] molecules. They can be used to access the high oxidation states of metal atoms [19,20], which are inaccessible in conventional chemistry. Other important applications of superhalogens include: tuning electronic and magnetic properties of traditional materials as dopants [21,22], constructing organic superconductors [23], designing halogen-free electrolytes for lithium-ion batteries [24] and magnesium batteries [25], and being utilized as ligands for constituting hyperhalogens with higher EAs, etc. Besides, the possibility of synthesizing a peculiar class of salts with superalkali and superhalogen as building blocks, referred to as supersalts, has been proposed [26–29]. Undoubtedly, superhalogens are of great importance in many scientific fields and have attracted increasing attention in recent years.

Considering the high EA feature of superhalogens and their resemblance to halogen atoms, they may not only combine with alkali metal atom to form salts but also combine with H atom to form acids. In this letter, we focused on this idea and studied structures, properties and stability of two kinds of representative superhalogen compounds, namely hydrogenated superhalogens and lithiated superhalogens. To provide comprehensive insight into the behavior of superhalogens, we not only considered the basic XY_{k+1} type superhalogens such as XY_2 (X = Li, Na; Y = F, Cl), XY_3 (X = Be, Mg; Y = F, Cl), XY_4 (X = B, Al; Y = F, Cl), SiF_5 , and PF_6 , but

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also took various new-type superhalogens into account, including binuclear superhalogens X_2Y_5 ($X = \text{Be}, \text{Mg}; Y = \text{F}, \text{Cl}$), halogen-free superhalogens BO_2 , AlO_2 , NO_3 , PO_3 and ClO_4 [30], and superhalogens SO_3F , SO_2F_3 and SOF_5 with mixed ligands. Our main objectives are (1) comparing the structural features of these two kinds of superhalogen compounds and characterizing their respective bonding natures, (2) exploring the chemical stability of these species by examining their possible dissociation channels and corresponding dissociation energies, and their HOMO-LUMO gaps as well, (3) presenting the electric properties (first hyperpolarizabilities, polarizabilities and the dipole moments) of these species.

2. Computational methods

The computations were performed using Dunning's augmented correlation consistent polarized valence double zeta basis set, aug-cc-pVDZ [31]. The optimum configurations and vibrational frequencies for the studied superhalogen compounds were obtained by the second-order MP2(FC) [32] method. The electric properties and natural bond orbital (NBO) [33] charges of these compounds were also obtained using the MP2 electron densities. The calculations of the electric properties relied on the finite-field approach [34]. The total static dipole moment μ_0 , the mean polarizability α_0 , and the mean first hyperpolarizability β_0 are defined as

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (1)$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3)$$

where

$$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}), \quad i, j, k = x, y, z$$

The interaction energies (E_{int}) between H/Li and superhalogens subunits were calculated at the CCSD(T)/aug-cc-pVDZ level. We used the counterpoise (CP) procedure to eliminate the basis set superposition error (BSSE) effect given by Eq. (4):

$$E_{\text{int}} = E_{\text{AB}}(X_{\text{AB}}) - E_{\text{A}}(X_{\text{AB}}) - E_{\text{B}}(X_{\text{AB}}) \quad (4)$$

where the same basis set, X_{AB} , was used for the subunit energy (E_{A} and E_{B}) calculations as for the complex energy (E_{AB}) calculation.

All the calculations in this work were carried out by using the GAUSSIAN 09 program package [35]. The dimensional plots of molecular configurations were generated with the GaussView program (Gaussian, Inc. Pittsburgh, PA).

3. Results and discussion

3.1. Geometrical features of hydrogenated superhalogens and lithiated superhalogens

The optimized geometries of the H(Li)-superhalogens compounds (superhalogens = LiF_2 , LiCl_2 , NaF_2 , NaCl_2 , BeF_3 , BeCl_3 , MgF_3 , MgCl_3 , BF_4 , BCl_4 , AlF_4 , AlCl_4 , Mg_2F_5 , Mg_2Cl_5 , Be_2F_5 , Be_2Cl_5 , SiF_5 , PF_6 , SO_3F , SO_2F_3 , SOF_5 , BO_2 , AlO_2 , NO_3 , PO_3 , ClO_4) are shown in Figs. S1–S8, respectively, in supporting information. Several representative superhalogen anions and their corresponding compounds are summarized in Fig. 1. Herein, r_1 denotes the length of X-Y (central atom-ligand) bond which directly interacts with the H/Li atom, and θ represents the Y-X-Y bond angle where the two Y atoms interact with the H/Li atom. According to the computational results, both hydrogenation and lithiation lead to decreased θ angles and increased r_1 lengths of the XY_{k+1} type superhalogens whereas result in decreased r_1 length of binuclear superhalogens.

As can be seen from the figures in supporting information, for the XY_{k+1} type superhalogens, their geometrical integrity basically retains upon lithiation. In contrast, most of them are broken down after hydrogenation, and the resulting compounds can be regarded as dimer molecules. For binuclear superhalogens, halogen-free

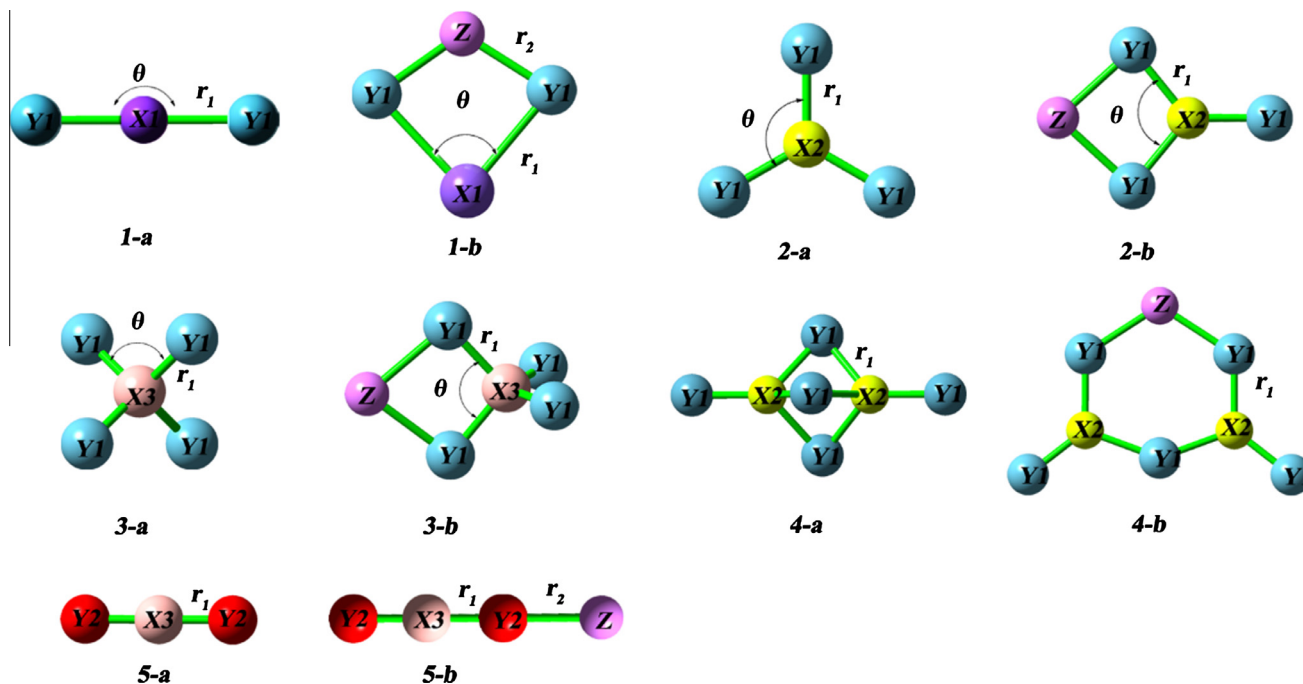


Fig. 1. The schematic structures of representative (a) superhalogen anions and (b) their hydrogenated and lithiated compounds ($X1 = \text{Li}, \text{Na}$; $X2 = \text{Be}, \text{Mg}$; $X3 = \text{B}, \text{Al}$; $Y1 = \text{F}, \text{Cl}$; $Y2 = \text{O}$; $Z = \text{H}, \text{Li}$). r and θ denote bond lengths and bond angles, respectively.

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