

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/223022984>

An ab initio study on MgX_3^- and CaX_3^- superhalogen anions ($\text{X}=\text{F}, \text{Cl}, \text{Br}$)

ARTICLE in CHEMICAL PHYSICS · JUNE 2003

Impact Factor: 1.65 · DOI: 10.1016/S0301-0104(03)00208-8

CITATIONS

48

READS

105

4 AUTHORS, INCLUDING:



Iwona Wanda Anusiewicz

University of Gdansk

52 PUBLICATIONS 1,137 CITATIONS

SEE PROFILE



Iwona Dąbkowska

University of Gdansk

4 PUBLICATIONS 106 CITATIONS

SEE PROFILE



Piotr Skurski

University of Gdansk

141 PUBLICATIONS 3,382 CITATIONS

SEE PROFILE

An ab initio study on MgX_3^- and CaX_3^- superhalogen anions ($\text{X} = \text{F}, \text{Cl}, \text{Br}$)

Iwona Anusiewicz^{a,b}, Monika Sobczyk^{a,b}, Iwona Dąbkowska^a, Piotr Skurski^{a,b,*}

^a Department of Chemistry, University of Gdańsk, Sobieskiego 18, Gdańsk 80-952, Poland

^b Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

Received 24 February 2003

Abstract

The vertical electron detachment energies (VDEs) of twenty MX_3^- ($\text{M} = \text{Mg}, \text{Ca}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$) anions were calculated at the OVGF level with the 6-311++G(3df) basis sets. The largest vertical electron binding energy was found for MgF_3^- system (8.793 eV). All negatively charged species possess the VDEs that are larger than 5.9 eV and thus may be termed *superhalogen* anions. The strong dependence of the VDE of the MX_3^- species on the ligand–central atom (M–X) distance and on the partial atomic charge localized on Mg or Ca was observed and discussed, as well as the other factors that may influence the electronic stability of such anions.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Superhalogen; Anions; Vertical electron detachment energy

1. Introduction

The electron affinities (EAs) of molecules are of interest not only in areas where gas-phase ions are encountered, e.g., negative-ion analytical mass spectrometry, gas-phase radiation chemistry, and electron capture detector gas chromatography, but also in the much wider field of condensed-phase chemistry [1]. Since molecular systems exhibiting extremal characteristics are of particular interest from both theoretical and practical points of view, the molecules possessing large EAs have been ex-

tensively studied in the past, primarily by Gutsev and Boldyrev [2].

It is well known that halogen atoms possess the highest electron affinities among the elements (fluorine 3.40 eV, chlorine 3.62 eV) [3]. However, the EA of a polyatomic system may exceed the 3.62 eV limit due to collective effects. Such species are of a great importance in chemistry since they can be used for the oxidation of counterpart systems with relatively high ionization potentials (such as O_2 , Xe) and allow the synthesis of unusual chemical compounds (e.g., involving noble gases atoms). In addition, molecules possessing high EAs are widely used in the production of organic superconductors [4,5]. Although such species have been attracting chemists' attention since early 60s, it was only in 1981 when Gutsev and Boldyrev

* Corresponding author.

E-mail addresses: piotr@chem.univ.gda.pl, piotr@chemik.chem.univ.gda.pl (P. Skurski).

proposed to term them *superhalogens* and introduced a simple formula for one class of these compounds, MX_{k+1} , where M is a main group or transition metal atom, X is a halogen atom, and k is the maximal formal valence of the atom M [2]. It was a milestone work since Gutsev and Boldyrev not only provided theoretically estimated electron binding energies of superhalogen-based anions but they also pointed out a few main reasons as being responsible for the increase of the vertical electron detachment energy (VDE) in MX_{k+1}^- relative to X^- , such as: (i) delocalization of the extra electron over $k+1$ halogen atoms instead of one, (ii) nonbonding character of the highest occupied molecular orbital (HOMO), (iii) coordination of X^- anion to the electropositive ion M^{k+} (electrostatic effect), and (iv) stabilizing electron relaxation and correlation effects [2].

Since early 80s, many other theoretical efforts have been undertaken to estimate the VDEs of various anions having superhalogens as their neutral parents (see [6–10] and references cited therein). In 1999 a dramatic progress has been made in the investigating superhalogen systems due to the joined theoretical and experimental effort that resulted in an excellent report comprising of the first experimental photoelectron spectra of superhalogens (measured by the Wang's group) together with their theoretical interpretations provided by Boldyrev and coworkers [11]. In particular, the photoelectron spectra of MX_2^- (where M = Li, Na, and X = Cl, Br, I) anions have been obtained and assigned on the basis of ab initio outer valence Green function (OVGF) calculations. An excellent agreement between experimentally and theoretically estimated values of VDEs has been achieved and all the anions have proven to be superhalogen-based species since their electron binding energies were found to be greater than 3.62 eV (see [11] for details).

Recently, the Schaefer's group studied the EAs of arsenic fluorides AsF_n ($n = 1-6$) which resulted in reporting the AsF_6^- anion to possess a very large VDE (VDE = 7.95–10.54 eV, depending on the density functional method used) [12].

It should be noted that although there are many theoretical results for superhalogens anions available, most of them were obtained in the 80s when

the computational resources limited the level of calculations. In particular, early discrete-variational X_α -method calculations led to underestimated values of the VDEs of many superhalogen anions, although it should be stated that the main goal of these investigations was to prove that such species are indeed exhibiting extremely large electron binding energies rather than to provide precise vertical detachment energies [2,6]. We faced this problem (inaccuracy of VDEs or lack thereof) recently while studying a completely different class of molecular systems in which we encountered MX_3^- anions (where M = Be, Mg, Ca; X = F, Cl, Br) that were involved in complexes with certain cations (e.g., H_3O^+) as their counterparts [13]. In fact, one would wonder if attaching of an extra electron to ($\text{H}_3\text{O}^+/\text{MX}_3^-$) species leads to the anion of Rydberg or dipole-bound nature. In order to understand this phenomenon better, we performed a literature search for relatively accurate VDEs of MX_3^- superhalogen anions. Unfortunately, the results we found were either old (and thus not accurate) or incomplete (i.e., not containing “mixed” species, such as BeFCl_2^- , BeFClBr^- , MgFCl_2^- , or CaCl_2Br^- for example). This lack of data has motivated us to take a closer look at the various superhalogen anions of this type and to calculate possibly accurate values of their VDEs.

In the preceding paper we described the vertical electron binding energies for BeX_3^- superhalogen anions [14] calculated at the OVGF/6-311++G(3df) and CCSD(T)/6-311++G(3df) levels. All the negatively charged species studied were derived from their neutral parent radicals and have proven to exhibit a “superhalogen” nature which means their electron binding energies were found to significantly exceed the EA of chlorine (3.62 eV). It was concluded the OVGF/6-311++G(3df) treatment produces reliable estimates of the previously studied superhalogen anions and the following vertical detachment energies of 10 BeX_3^- (X = F, Cl, Br) species considered were found to be: 7.630 eV (BeF_3^-), 6.239 eV (BeF_2Cl^-), 6.166 eV (BeCl_2F^-), 6.171 eV (BeCl_3^-), 5.585 eV (BeF_2Br^-), 5.715 eV (BeFClBr^-), 5.803 eV (BeCl_2Br^-), 5.602 eV (BeBr_2F^-), 5.692 eV (BeBr_2Cl^-), and 5.647 eV (BeBr_3^-).

In this contribution, we present our ab initio results for 20 negatively charged species exhibiting

“superhalogen nature” and having Mg or Ca as the metal component (in MX_3^-). We believe that the vertical electron binding energies we provide in this work might be found useful for experimental chemists, especially those who design new materials in which the strong electron acceptors are involved.

2. Methods

Since our main goal was to calculate the VDEs for the MX_3^- anions ($\text{M} = \text{Mg, Ca}$; $\text{X} = \text{F, Cl, Br}$) we limited our geometry optimization calculations to the closed-shell anionic species for which we also obtained harmonic vibrational frequencies at their minimum energy structures. For this purpose we applied second-order Møller–Plesset (MP2) perturbational method with the 6-311++G(d) basis sets [15,16]. Providing reliable VDEs of the MX_3^- anions requires using more accurate treatment thus we decided to perform both *direct* and *indirect* calculations of the electron binding energies. A *direct* scheme was based on applying the OVGF method [17–21] while the latter (*indirect*) approach consisted in subtracting the anion energies from those of the neutral (both calculated at the same level of theory which was MP2 level in our case). The OVGF approximation remains valid only for outer valence ionizations for which the pole strengths (PSs) are greater than 0.80–0.85 [22]. For all states studied here, the PSs are sufficiently large to justify use of the OVGF method (the smallest PS found for the states studied in this work is 0.91). The core electrons were kept frozen in treating the electron correlation.

As far as the basis sets are concerned, we applied the 6-311++G(3df) basis sets [15,16] while estimating VDEs at various levels since analogous basis sets have recently been used by others for LiX_2^- and NaX_2^- ($\text{X} = \text{F, Cl, Br, I}$) superhalogen anions and provided an excellent agreement between such calculated and experimentally measured VDEs [11].

In order to determine the usefulness and accuracy of our theoretical treatment for calculating the VDEs of superhalogen anions we performed test calculations of the VDEs of previously studied anions exhibiting similar (i.e., superhalogen)

nature. In particular, we estimated the VDEs for LiCl_2^- and NaCl_2^- anions, whose experimentally measured VDEs have been recently published [11]. We concluded, that the VDEs of LiCl_2^- (5.98 eV) and NaCl_2^- (5.89 eV) calculated at the OVGF level with the 6-311++G(3df) basis set are in excellent agreement with the experimental values of 5.92 ± 0.04 eV (for LiCl_2^-) and 5.86 ± 0.06 eV (for NaCl_2^-) [11]. The observation that the differences between our VDEs calculated at the OVGF/6-311++G(3df) level and the experimental vertical electron binding energies are almost within the experimental uncertainties range reported by Wang et al. [11], supports this conclusion.

All calculations were performed with the GAUSSIAN 98 program [23] on Intel Pentium IV computers and an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals (MOs) were generated with the MOLDEN program [24].

3. Results

3.1. The MP2 equilibrium geometries and vibrational frequencies

The MP2 minimum energy structures of the superhalogen anions MgX_3^- and CaX_3^- ($\text{X} = \text{F, Cl, Br}$) are characterized in Tables 1 and 2 where the corresponding harmonic vibrational frequencies are also collected. Since for each negatively charged system studied in this work all the Hessian matrix eigenvalues were found positive and we are confident that these structures correspond to the minima on the MP2 ground-state anion potential energy surface.

We found all the MX_3^- ($\text{M} = \text{Mg, Ca}$; $\text{X} = \text{F, Cl, Br}$) anions to be planar and possess D_{3h} (MgF_3^- , MgCl_3^- , MgBr_3^- , CaF_3^- , CaCl_3^- , CaBr_3^-), C_{2v} (MgF_2Cl^- , MgCl_2F^- , MgF_2Br^- , MgCl_2Br^- , MgBr_2F^- , MgBr_2Cl^- , CaF_2Cl^- , CaCl_2F^- , CaF_2Br^- , CaCl_2Br^- , CaBr_2F^- , CaBr_2Cl^-), and C_s (MgFClBr^- , CaFClBr^-) symmetry. This finding is consistent with the earlier calculations performed by others for MgF_3^- , MgCl_3^- , CaF_3^- , and CaCl_3^- in which planar D_{3h} -symmetry geometries were either found [25] or assumed [2,26].

Table 1

The MP2 geometrical parameters, corresponding harmonic vibrational frequencies, and the OVGf/6-311++G(3df) VDEs together with the corresponding PSs for the MgX_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) anions studied in this work

Species and symmetry point group	VDE (eV) OVGf/6-311++G(3df) (PS)	Geometry	Vibr. freq. (cm^{-1})
$\text{MgF}_3^- \text{D}_{3h}$	8.793 (0.95)	$R(\text{Mg-F}) = 1.853$ $\angle(\text{FMgF}) = 120.00$	$\nu_{1,2} = 183 (e')$ $\nu_3 = 248 (a'_2)$ $\nu_4 = 467 (a'_1)$ $\nu_{5,6} = 655 (e')$
$\text{MgF}_2\text{Cl}^- \text{C}_{2v}$	6.665 (0.91)	$R(\text{Mg-F}) = 1.844$ $R(\text{Mg-Cl}) = 2.299$ $\angle(\text{FMgF}) = 121.72$ $\angle(\text{FMgCl}) = 119.138$	$\nu_1 = 135 (b_2)$ $\nu_2 = 170 (a_1)$ $\nu_3 = 224 (b_1)$ $\nu_4 = 353 (a_1)$ $\nu_5 = 572 (a_1)$ $\nu_6 = 672 (b_2)$
$\text{MgCl}_2\text{F}^- \text{C}_{2v}$	6.648 (0.91)	$R(\text{Mg-F}) = 1.836$ $R(\text{Mg-Cl}) = 2.286$ $\angle(\text{FMgCl}) = 120.79$ $\angle(\text{ClMgCl}) = 118.41$	$\nu_1 = 111 (a_1)$ $\nu_2 = 146 (b_2)$ $\nu_3 = 199 (b_1)$ $\nu_4 = 313 (a_1)$ $\nu_5 = 449 (b_2)$ $\nu_6 = 642 (a_1)$
$\text{MgCl}_3^- \text{D}_{3h}$	6.684 (0.91)	$R(\text{Mg-Cl}) = 2.275$ $\angle(\text{ClMgCl}) = 120.00$	$\nu_{1,2} = 106 (e')$ $\nu_3 = 176 (a'_2)$ $\nu_4 = 280 (a'_1)$ $\nu_{5,6} = 462 (e')$
$\text{MgF}_2\text{Br}^- \text{C}_{2v}$	6.058 (0.92)	$R(\text{Mg-F}) = 1.841$ $R(\text{Mg-Br}) = 2.473$ $\angle(\text{FMgF}) = 122.91$ $\angle(\text{FMgBr}) = 118.54$	$\nu_1 = 120 (b_2)$ $\nu_2 = 153 (a_1)$ $\nu_3 = 214 (b_1)$ $\nu_4 = 288 (a_1)$ $\nu_5 = 562 (a_1)$ $\nu_6 = 680 (b_2)$
$\text{MgFClBr}^- \text{C}_s$	6.172 (0.91)	$R(\text{Mg-F}) = 1.830$ $R(\text{Mg-Cl}) = 2.281$ $R(\text{Mg-Br}) = 2.458$ $\angle(\text{FMgCl}) = 121.88$ $\angle(\text{FMgBr}) = 119.95$ $\angle(\text{ClMgBr}) = 118.17$	$\nu_1 = 94 (a')$ $\nu_2 = 134 (a')$ $\nu_3 = 190 (a'')$ $\nu_4 = 263 (a')$ $\nu_5 = 421 (a')$ $\nu_6 = 643 (a')$
$\text{MgCl}_2\text{Br}^- \text{C}_{2v}$	6.273 (0.91)	$R(\text{Mg-Cl}) = 2.271$ $R(\text{Mg-Br}) = 2.446$ $\angle(\text{ClMgCl}) = 120.91$ $\angle(\text{ClMgBr}) = 119.54$	$\nu_1 = 89 (b_2)$ $\nu_2 = 97 (a_1)$ $\nu_3 = 166 (b_1)$ $\nu_4 = 237 (a_1)$ $\nu_5 = 416 (a_1)$ $\nu_6 = 468 (b_2)$
$\text{MgBr}_2\text{F}^- \text{C}_{2v}$	6.085 (0.91)	$R(\text{Mg-F}) = 1.833$ $R(\text{Mg-Br}) = 2.452$ $\angle(\text{FMgBr}) = 121.00$ $\angle(\text{BrMgBr}) = 118.00$	$\nu_1 = 76 (a_1)$ $\nu_2 = 127 (b_2)$ $\nu_3 = 181 (b_1)$ $\nu_4 = 229 (a_1)$ $\nu_5 = 373 (b_2)$ $\nu_6 = 641 (a_1)$
$\text{MgBr}_2\text{Cl}^- \text{C}_{2v}$	6.182 (0.91)	$R(\text{Mg-Cl}) = 2.268$ $R(\text{Mg-Br}) = 2.442$ $\angle(\text{BrMgCl}) = 120.54$	$\nu_1 = 73 (a_1)$ $\nu_2 = 86 (b_2)$ $\nu_3 = 154 (b_1)$

Table 1 (continued)

Species and symmetry point group	VDE (eV) OVGF/ 6-311++G(3df) (PS)	Geometry	Vibr. freq. (cm ⁻¹)
		$\angle(\text{BrMgBr}) = 118.92$	$\nu_4 = 203 (a_1)$ $\nu_5 = 379 (b_2)$ $\nu_6 = 449 (a_1)$
MgBr_3^- D_{3h}	6.144 (0.91)	$R(\text{Mg}-\text{Br}) = 2.439$ $\angle(\text{BrMgBr}) = 120.00$	$\nu_{1,2} = 67 (e')$ $\nu_3 = 144 (a'_2)$ $\nu_4 = 171 (a')$ $\nu_{5,6} = 383 (e')$

Bond lengths (R) in Å, valence angles (\angle) in degrees, VDEs in eV.

The magnesium–fluorine and calcium–fluorine bond length for the optimized anions are within the 1.830–1.853 Å and 2.069–2.125 Å range, respectively, and we found the largest Mg–F and Ca–F separations for MgF_3^- and CaF_3^- species (see Tables 1 and 2). Data collected in Table 1 demonstrate that the Mg–X distance gradually decreases when X atoms in MgX_3^- are subsequently substituted with the less electronegative Y atoms, whereas the reverse is observed when Y is more electronegative than X. One may notice the same tendency for the Ca–X distance in CaX_3^- species (see Table 2). To illustrate, the shortening of the Mg–F bond length by ca. 0.01–0.02 Å accompanies subsequent substitution of fluorine atoms with chlorine ones in MgF_3^- . Similarly, the 0.01–0.03 Å elongation of the Mg–Br distance is observed when bromine atoms in MgBr_3^- are subsequently replaced with fluorine atoms (see Table 1). As far as the superhalogen anions containing Ca are concerned, the subsequent substitution of F atoms with Cl atoms in CaF_3^- leads to the shortening of the Ca–F bond by 0.024–0.047 Å while the elongation of the Ca–Br bond length in CaX_3^- (by 0.034–0.071 Å) is observed when the bromine atoms are replaced with fluorine atoms (see Table 2).

Even though the reported geometry differences seem relatively small, it should be noted that they could play an important role in superhalogen species because the halogen–central atom distance significantly influences the VDE of such anions, as was previously concluded by Gutsev and Boldyrev [2]. Moreover, it was found on the basis of the simple electrostatic model consisting of F^- anion and the positive charge $+q$ separated by the 3.0

a.u. distance, that the electron binding energy of F^- increases by approximately 1 eV when q increases by 0.1 a.u. [2]. Since the superhalogen anions, such as MgX_3^- or CaX_3^- , may be considered as the neutral MX_2 systems (where M is Mg or Ca) with the X^- attached, one may expect the strong dependence of the partial atomic positive charge localized on the central atom (Mg or Ca) on the VDE of such an anion. The significance of these effects for MX_3^- (M = Mg, Ca; X = F, Cl, Br) anions is discussed in the following section.

As far as the MP2 harmonic vibrational frequencies are concerned, they are collected in Table 1 (for MgX_3^- species) and Table 2 (for CaX_3^- species). For each anion, there are three soft vibrational frequencies that correspond to valence angle deformation modes (ν_1, ν_2) and umbrella (inversion) mode (ν_3), and three frequencies (ν_4, ν_5 , and ν_6) corresponding to M–X stretching modes. The frequency of the umbrella mode decreases when the fluorine atoms in MgF_3^- are subsequently replaced with the chlorine and bromine atoms (see ν_3 in Table 1) and the same tendency we observe for CaF_3^- (see ν_3 in Table 2). The frequency of the in-phase Mg–F stretching mode in MgF_3^- (see ν_4 in Table 1) increases when the F atoms are substituted with one (in MgF_2Cl^-) or two (in MgCl_2F^-) Cl atoms (see ν_5 and ν_6 in Table 1 for MgF_2Cl^- and MgCl_2F^- , respectively). Similarly, the frequency of the in-phase Ca–F stretching mode in CaF_3^- (see ν_4 in Table 2) increases when the fluorine atoms are substituted with one (in CaF_2Cl^-) or two (in CaCl_2F^-) chlorine atoms (see Table 2, ν_5 and ν_6 for CaF_2Cl^- and CaCl_2F^- , respectively).

Table 2

The MP2 geometrical parameters, corresponding harmonic vibrational frequencies, and the OVGF/6-311++G(3df) VDEs together with the corresponding PSs for the CaX_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) anions studied in this work

Species and symmetry point group	VDE (eV) OVGF/ 6-311++G(3df) (PS)	Geometry	Vibr. freq. (cm^{-1})
$\text{CaF}_3^- \text{D}_{3h}$	8.620 (0.95)	$R(\text{Ca}-\text{F}) = 2.125$ $\angle(\text{FCaF}) = 120.00$	$\nu_{1,2} = 133 (e')$ $\nu_3 = 136 (a_2')$ $\nu_4 = 409 (a_1')$ $\nu_{5,6} = 491 (e')$
$\text{CaF}_2\text{Cl}^- \text{C}_{2v}$	6.440 (0.91)	$R(\text{Ca}-\text{F}) = 2.101$ $R(\text{Ca}-\text{Cl}) = 2.616$ $\angle(\text{FCaF}) = 119.82$ $\angle(\text{FCaCl}) = 120.09$	$\nu_1 = 102 (b_2)$ $\nu_2 = 128 (a_1)$ $\nu_3 = 124 (b_1)$ $\nu_4 = 280 (a_1)$ $\nu_5 = 466 (a_1)$ $\nu_6 = 510 (b_2)$
$\text{CaCl}_2\text{F}^- \text{C}_{2v}$	6.606 (0.91)	$R(\text{Ca}-\text{F}) = 2.078$ $R(\text{Ca}-\text{Cl}) = 2.589$ $\angle(\text{FCaCl}) = 119.66$ $\angle(\text{ClCaCl}) = 120.68$	$\nu_1 = 82 (a_1)$ $\nu_2 = 113 (b_2)$ $\nu_3 = 113 (b_1)$ $\nu_4 = 259 (a_1)$ $\nu_5 = 335 (b_2)$ $\nu_6 = 509 (a_1)$
$\text{CaCl}_3^- \text{D}_{3h}$	6.732 (0.91)	$R(\text{Ca}-\text{Cl}) = 2.561$ $\angle(\text{ClCaCl}) = 120.00$	$\nu_{1,2} = 80 (e')$ $\nu_3 = 100 (a_2'')$ $\nu_4 = 243 (a_1')$ $\nu_{5,6} = 346 (e')$
$\text{CaF}_2\text{Br}^- \text{C}_{2v}$	5.908 (0.92)	$R(\text{Ca}-\text{F}) = 2.096$ $R(\text{Ca}-\text{Br}) = 2.791$ $\angle(\text{FCaF}) = 119.77$ $\angle(\text{FCaBr}) = 120.12$	$\nu_1 = 90 (b_2)$ $\nu_2 = 117 (a_1)$ $\nu_3 = 119 (b_1)$ $\nu_4 = 220 (a_1)$ $\nu_5 = 468 (a_1)$ $\nu_6 = 513 (b_2)$
$\text{CaFClBr}^- \text{C}_s$	6.122 (0.92)	$R(\text{Ca}-\text{F}) = 2.074$ $R(\text{Ca}-\text{Cl}) = 2.582$ $R(\text{Ca}-\text{Br}) = 2.761$ $\angle(\text{FCaCl}) = 119.69$ $\angle(\text{FCaBr}) = 119.74$ $\angle(\text{ClCaBr}) = 120.57$	$\nu_1 = 70 (a')$ $\nu_2 = 105 (a')$ $\nu_3 = 108 (a'')$ $\nu_4 = 210 (a')$ $\nu_5 = 318 (a')$ $\nu_6 = 512 (a')$
$\text{CaCl}_2\text{Br}^- \text{C}_{2v}$	6.308 (0.91)	$R(\text{Ca}-\text{Cl}) = 2.554$ $R(\text{Ca}-\text{Br}) = 2.733$ $\angle(\text{ClCaCl}) = 119.99$ $\angle(\text{ClCaBr}) = 120.01$	$\nu_1 = 66 (b_2)$ $\nu_2 = 74 (a_1)$ $\nu_3 = 95 (b_1)$ $\nu_4 = 201 (a_1)$ $\nu_5 = 316 (a_1)$ $\nu_6 = 349 (b_2)$
$\text{CaBr}_2\text{F}^- \text{C}_{2v}$	6.097 (0.91)	$R(\text{Ca}-\text{F}) = 2.069$ $R(\text{Ca}-\text{Br}) = 2.754$ $\angle(\text{FCaBr}) = 119.78$ $\angle(\text{BrCaBr}) = 120.44$	$\nu_1 = 57 (a_1)$ $\nu_2 = 99 (b_2)$ $\nu_3 = 103 (b_1)$ $\nu_4 = 183 (a_1)$ $\nu_5 = 275 (b_2)$ $\nu_6 = 516 (a_1)$
$\text{CaBr}_2\text{Cl}^- \text{C}_{2v}$	6.270 (0.91)	$R(\text{Ca}-\text{Cl}) = 2.548$ $R(\text{Ca}-\text{Br}) = 2.726$ $\angle(\text{BrCaCl}) = 120.01$	$\nu_1 = 55 (a_1)$ $\nu_2 = 66 (b_2)$ $\nu_3 = 90 (b_1)$

Table 2 (continued)

Species and symmetry point group	VDE (eV) OVGF/ 6-311++G(3df) (PS)	Geometry	Vibr. freq. (cm ⁻¹)
		$\angle(\text{BrCaBr}) = 119.99$	$\nu_4 = 175 (a_1)$ $\nu_5 = 282 (b_2)$ $\nu_6 = 338 (a_1)$
$\text{CaBr}_3^- \text{ D}_{3h}$	6.238 (0.91)	$R(\text{Ca-Br}) = 2.720$ $\angle(\text{BrCaBr}) = 120.00$	$\nu_{1,2} = 51 (e')$ $\nu_3 = 85 (a_2'')$ $\nu_4 = 150 (a')$ $\nu_{5,6} = 284 (e')$

Bond lengths (R) in Å, valence angles (\angle) in degrees, VDEs in eV.

3.2. VDEs

The VDEs of MX_3^- ($M = \text{Mg}, \text{Ca}$; $X = \text{F}, \text{Cl}, \text{Br}$) anions calculated at the OVGF/6-311++G(3df) level are collected in Tables 1 and 2 while those obtained at the SCF and MP2 levels with the 6-311++G(3df) basis sets are shown in Table 3 for comparison.

As it was concluded in [14] we consider the VDEs calculated at the OVGF level with the 6-311++G(3df) basis sets as the most reliable since they are in a very good agreement with the

experimentally measured values (see Section 2). Therefore, let us begin with the discussion of such obtained VDEs of the superhalogen anions studied in this work.

First, we want to stress that all the calculated VDEs greatly exceed the EA of the chlorine atom (3.62 eV) and thus the studied MgX_3^- and CaX_3^- species should be classified as the superhalogen anions. The largest VDE among systems considered was found for the MgF_3^- (8.793 eV) and for CaF_3^- (8.620 eV). These VDEs are similar to those obtained by Weikert and Cederbaum [25] who used the third-order algebraic diagrammatic construction (ADC(3)) Green's function approach. The VDEs of the remaining anions are always larger than 5.9 eV (see Tables 1 and 2). The correlation between the VDEs (collected in Tables 1 and 2 for MgX_3^- and CaX_3^- species, respectively) and the chemical constitution, geometrical parameters, or partial atomic charges [27] is not straightforward, however, a few tendencies could be noticed:

(i) In the MgF_3^- – MgCl_3^- – MgBr_3^- series the VDE decreases with an increase of the atomic number of the halogen atoms (i.e., the lowest VDE corresponds to MgBr_3^-). It is consistent with the partial atomic charge on magnesium (q^{Mg}) becoming less positive ($q^{\text{Mg}} = 1.496, 1.055$, and 0.874 a.u. for MgF_3^- , MgCl_3^- , and MgBr_3^- , respectively). Similar tendency can be observed in the CaF_3^- – CaCl_3^- – CaBr_3^- series in which the VDE also decreases with the decrease of the positive partial atomic charge on calcium ($q^{\text{Ca}} = 1.666, 1.366$, and 1.243 a.u. for CaF_3^- , CaCl_3^- , and CaBr_3^- , respectively).

(ii) The analysis of the results calculated for MgF_3^- , MgF_2Cl^- , and MgF_2Br^- indicates that

Table 3

The VDEs (in eV) of all superhalogen anions studied in this work calculated at the SCF, MP2, and OVGF level with the 6-311++G(3df) basis sets

	VDE (eV)		
	SCF	MP2	OVGF
MgF_3^-	7.902	7.677	8.793
MgF_2Cl^-	5.485	6.556	6.665
MgCl_2F^-	6.117	6.534	6.648
MgCl_3^-	6.500	6.513	6.684
MgF_2Br^-	5.046	5.961	6.058
MgFClBr^-	5.171	6.091	6.172
MgCl_2Br^-	5.275	6.202	6.273
MgBr_2F^-	5.614	5.999	6.085
MgBr_2Cl^-	5.725	6.104	6.182
MgBr_3^-	5.980	6.032	6.144
CaF_3^-	7.633	7.358	8.620
CaF_2Cl^-	5.242	6.332	6.440
CaCl_2F^-	6.133	6.463	6.606
CaCl_3^-	6.544	6.522	6.732
CaF_2Br^-	4.894	5.814	5.908
CaFClBr^-	5.098	6.026	6.122
CaCl_2Br^-	5.276	6.214	6.308
CaBr_2F^-	5.678	5.996	6.097
CaBr_2Cl^-	5.847	6.165	6.270
CaBr_3^-	6.059	6.097	6.238

replacing the fluorine atom in MgF_3^- with Cl or Br also leads to lower VDE (by 2.128 and 2.735 eV, respectively, see Table 1) which is accompanied again by the decrease of the q^{Mg} ($q^{\text{Mg}} = 1.375$ a.u. for MgF_2Cl^- and 1.348 a.u. for MgF_2Br^-). We observe the same situation for CaF_3^- in which one F atom is replaced with Cl or Br leading to CaF_2Cl^- or CaF_2Br^- , respectively. Specifically, the VDE of CaF_3^- (8.620 eV, see Table 2) decreases by 2.180 eV when one fluorine atom is replaced with chlorine and by 2.712 eV when the F atom is replaced with bromine. This is consistent with the partial atomic charge on calcium (q^{Ca}) becoming less positive ($q^{\text{Ca}} = 1.666$, 1.564, and 1.549 a.u. for CaF_3^- , CaF_2Cl^- and CaF_2Br^- , respectively).

(iii) If one compares the results for MgCl_3^- with these obtained when one or two chlorine atoms are replaced with the F or Br atoms, it seems that similar tendencies are preserved (i.e., the decrease of the VDE accompanies the decrease of the q^{Mg}). For example, $q^{\text{Mg}} = 0.991$ a.u. for MgCl_2Br^- and 1.055 a.u. for MgCl_3^- while the VDE of the latter exceeds that of the former by 0.411 eV (see Table 1). Similar observation can be made for the anions containing calcium, for example, the VDEs found for CaCl_2Br^- and CaCl_3^- are 6.308 and 6.732 eV, respectively (see Table 2) while the partial atomic charge on Ca atom is 1.345 a.u. for CaCl_2Br^- and 1.366 a.u. for CaCl_3^- .

(iv) The shortening of the Mg–F bond length observed when the fluorine atoms in MgF_3^- are being subsequently substituted with chlorine (which leads to MgF_2Cl^- and MgCl_2F^-) or bromine (which leads to MgF_2Br^- and MgBr_2F^-) is consistent with the decrease of the VDE (see Table 1). The same tendency can be observed for the Ca–F bond length (see Table 2) when fluorine atoms in CaF_3^- are subsequently replaced with chlorine atoms (which leads to CaF_2Cl^- and CaCl_2F^-) or with bromine atoms (which leads to CaF_2Br^- and CaBr_2F^-).

These conclusions are in agreement with the general predictions formulated previously for the superhalogen anions [2,6]. In particular, the observation that smaller “size” of the halogen ligands usually leads to larger VDEs is confirmed by our results. Moreover, it seems clear that the partial atomic charge localized on the central atom (Mg or Ca in our case) as well as the ligand–central

atom separations are strongly related to the VDE of the resulting anion.

In order to support our discussion we present the three-dimensional pictures of the HOMO for six chosen anions: MgF_3^- , MgCl_2F^- , MgFClBr^- , CaF_3^- , CaCl_2F^- , and CaFClBr^- (see Fig. 1). It is shown that in each case the HOMO is composed purely of ligand atomic orbitals (AOs) while the contributions from the central atom (Mg or Ca) are absent. As a consequence, the HOMO is a nonbonding MO with respect to the ligand–central atom interaction. This finding is consistent with the prediction formulated by Gutsev and Boldyrev [2] who suggested that the species for which the HOMO has such character should possess relatively high VDE values.

The calculations of the vertical electron binding energies, although doable for MX_3^- ($\text{M} = \text{Mg}, \text{Ca}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$) anions, can be found very expensive and time consuming for larger systems when performed at the OVGF and especially at the CCSD(T) level with large basis sets. Therefore, we decided to verify if any lower-level theoretical treatment could be found sufficient for approximate estimating the VDEs for superhalogen anions. Since it was not our goal to undertake any systematic studies in this matter, we limit our discussion to the results obtained at the SCF, MP2, and OVGF levels with the 6-311++G(3df) basis sets. We performed a similar comparison (although more extensive) previously, while studying BeX_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) superhalogen anions [14] hence the numerical tests presented in this contribution were undertaken to confirm the conclusions formulated earlier. The VDEs calculated at these levels for the 20 anions studied in this work are collected in Table 3.

According to our conclusions (see Section 2 of this contribution and [14]) the most reliable VDEs of the superhalogen anions are those calculated at the OVGF/6-311++G(3df) level and therefore we use these values as the reference while analyzing the VDEs obtained at different levels.

At the first glance it seems clear that the VDEs of the 20 anions studied in this work are underestimated at both the SCF and MP2 levels of theory (with respect to the OVGF values). In most cases the VDEs obtained with the SCF method are smaller than those calculated with at the MP2 level.

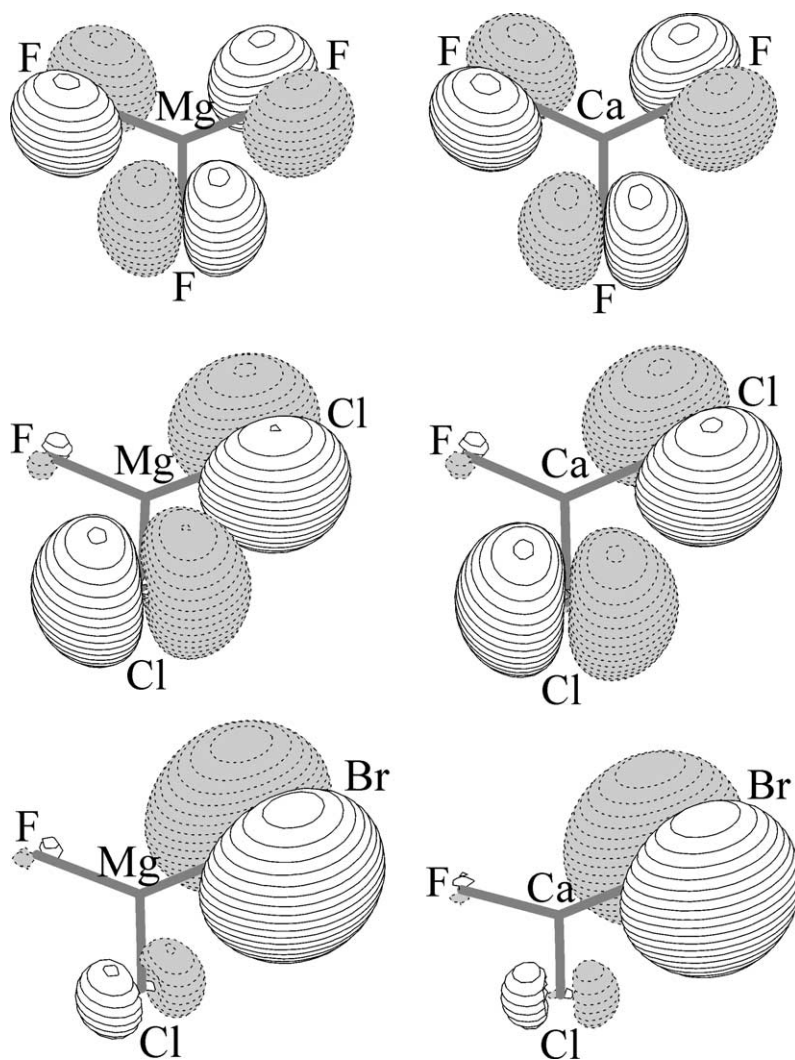


Fig. 1. The HOMO of the MgF_3^- (top left), MgCl_2F^- (middle left), MgFClBr^- (bottom left), CaF_3^- (top right), CaCl_2F^- (middle right), and CaFClBr^- (bottom right), superhalogen anions (plotted with $0.02 \text{ bohr}^{-3/2}$ contour spacing).

As it was previously observed for BeX_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) species [14], the MP2 treatment leads to quite reliable estimates of the VDEs and the differences between the electron binding energies calculated at the MP2 and OVGF level are within the 0.071–0.210 eV range (except for two cases, i.e., MgF_3^- and CaF_3^- , for which these deviations are significant, see Table 3). The observations that (i) the VDEs of the superhalogen anions calculated at the MP2 level are always underestimated with respect to those obtained at the more accurate OVGF

level, and (ii) in most cases the VDEs calculated with the MP2 method are reliable, allow for an easy and fast estimate of the electronic stability of a superhalogen anion when neither experimental nor theoretical results are available.

We therefore conclude that the OVGF method should be considered as the most reliable for predicting VDEs of superhalogen anions. For any crude or preliminary estimates, however, we recommend applying the MP2 method which should result with underestimated VDEs.

4. Summary

The VDEs of the superhalogen anions MgX_3^- and CaX_3^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) were calculated at the OVGF/6-311++G(3df) level. All the negatively charged species studied in this work were derived from their neutral parent radicals and have proven to exhibit a “superhalogen” nature which means their electron binding energies were found to significantly exceed the EA of chlorine (3.62 eV). It was concluded the OVGF/6-311++G(3df) treatment produces reliable estimates of the previously studied superhalogen anions and the following vertical detachment energies of 20 MX_3^- ($\text{M} = \text{Mg}, \text{Ca}; \text{X} = \text{F}, \text{Cl}, \text{Br}$) species considered in this work were found to be: 8.793 eV (MgF_3^-), 6.665 eV (MgF_2Cl^-), 6.648 eV (MgCl_2F^-), 6.684 eV (MgCl_3^-), 6.058 eV (MgF_2Br^-), 6.172 eV (MgFClBr^-), 6.273 eV (MgCl_2Br^-), 6.085 eV (MgBr_2F^-), 6.182 eV (MgBr_2Cl^-), and 6.144 eV (MgBr_3^-) for the species containing Mg atom, and 8.620 eV (CaF_3^-), 6.440 eV (CaF_2Cl^-), 6.606 eV (CaCl_2F^-), 6.732 eV (CaCl_3^-), 5.908 eV (CaF_2Br^-), 6.122 eV (CaFClBr^-), 6.308 eV (CaCl_2Br^-), 6.097 eV (CaBr_2F^-), 6.270 eV (CaBr_2Cl^-), and 6.238 eV (CaBr_3^-) for the species containing Ca.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (KBN) Grant No. DS/8371-4-0137-3 and the NSF Grants 9618904 and 9982420. The computer time provided by the Academic Computer Centre of the Stanislaw Staszic University of Mining and Metallurgy in Cracow (Grant No. KBN/SGI2800/UGdański/050/2002 to Iwona Anusiewicz) and the Center for High Performance Computing at the University of Utah is also gratefully acknowledged.

References

- [1] P. Kebarle, S. Chowdhury, *Chem. Rev.* 87 (1987) 513.
- [2] G.L. Gutsev, A.I. Boldyrev, *Chem. Phys.* 56 (1981) 277.
- [3] H. Hotop, W.C. Lineberger, *J. Phys. Chem. Ref. Data* 14 (1985) 731.
- [4] N. Bartlett, *Proc. Chem. Soc.* (1962) 218.
- [5] F. Wudl, *Acc. Chem. Res.* 17 (1984) 227.
- [6] G.L. Gutsev, A.I. Boldyrev, *Russ. Chem. Rev.* 56 (1987) 519.
- [7] G.L. Gutsev, R.J. Bartlett, A.I. Boldyrev, J. Simons, *J. Chem. Phys.* 107 (1997) 3867.
- [8] M.K. Scheller, L.S. Cederbaum, *J. Chem. Phys.* 100 (1994) 8934.
- [9] J.V. Ortiz, *Chem. Phys. Lett.* 214 (1993) 467.
- [10] J.V. Ortiz, *J. Chem. Phys.* 99 (1993) 6727.
- [11] X.-B. Wang, C.-F. Ding, L.-S. Wang, A.I. Boldyrev, J. Simons, *J. Chem. Phys.* 110 (1999) 4763.
- [12] W. Xu, G. Li, G. Yu, Y. Zhao, Q. Li, Y. Xie, H.F. Schaefer III, *J. Phys. Chem. A* 107 (2003) 258.
- [13] A. Sawicka, I. Anusiewicz, P. Skurski, J. Simons, *Int. J. Quantum Chem.* 92 (2003) 367.
- [14] I. Anusiewicz, P. Skurski, *Chem. Phys. Lett.* 358 (2002) 426.
- [15] A.D. McLean, G.S. Chandler, *J. Chem. Phys.* 72 (1980) 5639.
- [16] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, *J. Chem. Phys.* 72 (1980) 650.
- [17] V.G. Zakrzewski, J.V. Ortiz, J.A. Nichols, D. Heryadi, D.L. Yeager, J.T. Golab, *Int. J. Quantum Chem.* 60 (1996) 29.
- [18] J.V. Ortiz, *J. Chem. Phys.* 89 (1988) 6348.
- [19] L.S. Cederbaum, *J. Phys. B* 8 (1975) 290.
- [20] V.G. Zakrzewski, J.V. Ortiz, *Int. J. Quantum Chem.* 53 (1995) 583.
- [21] V.G. Zakrzewski, J.V. Ortiz, *Int. J. Quantum Chem., Quantum Chem. Symp.* 28 (1994) 23.
- [22] V.G. Zakrzewski, O. Dolgounitcheva, J.V. Ortiz, *J. Chem. Phys.* 105 (1996) 5872.
- [23] M.J. Frisch et al., *GAUSSIAN 98*, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.
- [24] G. Schaftenaar, J.H. Noordik, *J. Comput.-Aided Mol. Des.* 14 (2000) 123.
- [25] H.-G. Weikert, L.S. Cederbaum, *J. Chem. Phys.* 99 (1993) 8877.
- [26] G.L. Gutsev, A.I. Boldyrev, *Chem. Phys. Lett.* 84 (1981) 352.
- [27] The partial atomic charges were fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme as described in B.H. Besler, K.M. Merz, Jr., P.A. Kollman, *J. Comput. Chem.* 11 (1990) 431.