Theoretical Search for Anions Possessing Large Electron Binding Energies

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The vertical electron detachment energies (VDE) of several anions were calculated at the OVGF level with 6-311++G(d) basis sets. The negatively charged species studied were chosen based on the observation that the largest electron binding energies for such systems are expected to be found for the anions whose neutral parents are polynuclear superhalogens. The largest vertical electron binding energy of 12.63 eV was found for $Ta_3F_{16}^-$, and this is the largest excess electron binding energy of a molecular system reported in the literature thus far. Moreover, the VDEs of 12.63 and 12.20 eV calculated for $Ta_3F_{16}^-$ and $As_3F_{16}^-$, respectively, exceed the upper limit for the excess electron binding energy (thought to be 12 eV). Several other anions were also found [at the OVGF/6-311++G(d) level] to possess very large VDEs (i.e. $Al_2Br_7^-$: 7.08 eV, $Al_2Cl_7^-$: 7.75 eV, $Al_2F_7^-$: 11.16 eV, $P_2F_{11}^-$: 10.95 eV, $V_2F_{11}^-$: 10.98 eV, $As_2F_{11}^-$: 11.43 eV, and $Ta_2F_{11}^-$: 11.84 eV).

1. Introduction

The electron affinities 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 extreme characteristics are of particular interest from both theoretical and practical points of view, the molecules possessing large electron affinities (EA) have been extensively studied in the past, primarily by Gutsev and Boldyrev.

It is well-known that halogen atoms possess the highest electron affinities among the elements (fluorine 3.40 eV, chlorine 3.62 eV).[2] However, the EA of a polyatomic system may exceed the 3.62 eV limit due to collective effects. Such species are of great importance in chemistry since they can be used for the oxidation of counterpart systems with relatively high ionisation potentials (such as O_2, Xe) and allow the synthesis of unusual chemical compounds (e.g. those involving noble gases atoms). In addition, molecules possessing high electron affinities are widely used in the production of organic super-conductors.[3,4]

Such species have been attracting the attention of chemists since the early 60's; however, the term *superhalogens* for these species was proposed by Gutsev and Boldyrev as late as 1981. Further, they 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.[5] This work was of great importance since Gutsev and Boldyrev not only provided theoretically estimated electron binding energies of superhalogen-based anions, but they also explained the reason for the increase in the vertical electron detachment energy (VDE) of MX_{k+1}^- relative to X^-. These reasons include: (i) the delocalisation of the extra electron over $k+1$ halogen atoms instead of one only, (ii) the nonbonding character of the highest occupied molecular orbital (HOMO), (iii) the coordination of the X^- anion to the electropositive ion M^{k+} (electrostatic effect), and (iv) the stabilising electron relaxation and correlation effects.[5]

Since the early 80's many other theoretical studies have been undertaken to estimate the VDEs of various anions having superhalogens as their neutral parents (see refs.[6–9] and references cited therein). Major progress was made in 1999 in the investigations involving superhalogen systems due to the joined theoretical and experimental studies. This resulted in an excellent report comprising the first experimental photoelectron spectra of superhalogens (measured by Wang's group), together with theoretical interpretations provided by Boldyrev and Simons.[10] In particular, the photoelectron spectra of the anions MX_2^- (where M = Li, Na, and X = Cl, Br, I) 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 been proven to be superhalogen−based species since their electron binding energies were found to be greater than 3.62 eV (see ref.[10] for details).

Recently, Schaefer's group studied the electron affinities of arsenic fluorides AsF_n (n = 1−6), from which they deduced that the AsF_6^- anion has a very large vertical elec-

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tron detachment energy (VDE = 7.95−10.54 eV, depending on the density functional method used).[9]

It should be noted that although there are many theoretical results for superhalogen anions available, most were obtained in the 80's when computational resources limited the level of the calculations. In particular, early discrete−variational X_a-method (DV-X_a) calculations led to underestimated values of the VDEs of many superhalogen anions. However, it should be stated that the main goal of these investigations was to prove that such species indeed exhibit extremely large electron binding energies, rather than to provide precise vertical detachment energies.[5,6]

The problem of estimating the maximum possible electron binding energy for a molecular system was raised by Gutsev and Boldyrev in the 80's.[6] Naturally, these two authors began their theoretical search for the species possessing extremely large VDE values by investigating the superhalogen anions. From their experience in examining such negatively charged molecules, they concluded that the anion should contain the maximum possible number of fluorine atoms as ligands. This issue has also been discussed by Kalcher and Sax,[12] who investigated the relationship between the EA of a molecule M and the ionisation potential (IP) of the same molecule. On the basis of the observation that the IP of a given molecule always exceeds its own EA, and that the IPs of some molecules (such as fluorides like CF_4, SiF_4, SF_6, etc.) are found to be in the range 15−17 eV, they concluded that the EA value in that range (i.e. 15−17 eV) should be considered as the upper limit for the electron affinity characterising the neutral molecular system. However, Kalcher and Sax admitted that neither theoretical nor experimental evidence could be provided for such high values.[12] In fact, this idea had been proposed earlier by Gutsev and Boldyrev who based their analysis on the anionic daughters of the MF_6 superhalogens in which the extra electron resides in a nonbonding orbital which is delocalised over all F ligands.[6,13] These authors observed that the EAs of such systems depend primarily on the F_k ligand framework (rather than the nature of the transition metal centre), and estimated that the maximum EA (EA_{max}) for $k = 2$ is 5.5 eV, $EA_{max} = 6.5$ eV for $k = 6$, and that the limiting EA value (i.e. for $k = \infty$) is 10−12 eV.[13]

The estimate of the maximum value possible for the EA, made originally by Gutsev and Boldyrev, is of great importance for studying the properties of the chemical species in general, and for designing novel super-conductors in particular. However, it should be stressed that despite determining the 12 eV limit, there is no evidence that any of the known (reliable) EA values approaches this ultimate theoretical value. In particular, the early calculations (using discrete-variational X_a-method) performed on As_2F_{11} and P_2F_{11} resulted in an EA of 8.6 eV (for both cases).[6] To the best of our knowledge, the only known VDE that approaches the 12 eV limit is that estimated by Boldyrev and Simons[14] for TeF_7^- (11.9 eV); however, it corresponds to the result calculated at the Koopmans' Theorem (KT)[15] level, which is not very accurate.[16]

In this paper we present the results of our theoretical search for anions that possess extremely large (i.e. approaching the 12 eV limit or above) electron binding energies. While performing our search, we followed the very interesting and valuable suggestions on designing such species described by Gutsev and Boldyrev,[6] which, in fact, allowed us to find the anions that exhibit such large VDEs. In particular, we focused our studies on the various polynuclear superhalogen anions, for which we calculated VDE values that may possibly be accurate.

2. Methods

Since our main goal was to calculate the vertical electron detachment energies for several anions, 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 the Hartree−Fock Self-Consistent Field method (SCF). Since the SCF method does not include electron correlation effects, we decided to test if this affects the equilibrium geometries of the anions studied. Therefore, for two cases (i.e. $Al_2F_7^-$ and $Al_2Cl_7^-$) we performed geometry optimization calculations (followed by the calculations of harmonic vibrational frequencies) at the second-order Møller−Plesset (MP2) perturbational level. We concluded that the equilibrium structures obtained with the SCF method are very similar to those calculated at the MP2 level (the average differences in bond lengths and valence angles did not exceed 0.2 Å and 0.5 deg, respectively). Since the possible inaccuracies in our vertical electron detachment energies (caused by using the SCF rather than MP2 geometries) was considered to be most important, we verified that our best VDE estimates (i.e. calculated with the outer valence Green function method) for $Al_2F_7^-$ and $Al_2Cl_7^-$ differ by less than 0.05 eV (which corresponds to 1% of the total VDE value) when obtained using the SCF and MP2 equilibrium anionic structures. Therefore, we concluded that using the SCF rather than MP2 geometries does not cause any significant errors in the systems studied in this work.

In order to obtain reliable vertical electron detachment energies of the superhalogen anions, a more accurate treatment of the data is required, thus we decided to perform both *direct* and *indirect* calculations of the electron binding energies. A *direct* scheme was based on applying the outer valence Green function (OVGF) method,[17,18] while the latter (*indirect*) approach involved subtracting the anion energies from those of the neutral species (both calculated at the same level of theory). In the *indirect* approach, we used the MP2 perturbational method. The core electrons were frozen when treating the electron correlation.

We applied the 6-311++G(d) basis sets[19,20] for the calculations of the equilibrium geometries and harmonic frequencies, and for estimating the vertical electron detachment energies at various levels, since analogous basis sets have recently been used for the BeX_3^- superhalogen anions

(X = F, Cl, Br), which have provided reliable VDEs for these species.[21] However, it is important to note that applying the OVGF method with the 6-311++G(3df) basis sets would most likely provide better vertical electron detachment energies [as described in ref.[10] for LiX_2^- and NaX_2^- (X = F, Cl, Br, I), and in ref.[21] for BeX_3^- (X = F, Cl, Br)], since the OVGF/6-311++G(3df) treatment was found to produce an excellent agreement between such calculated and experimentally measured VDEs. Since the species studied in this work are relatively large (i.e. containing up to 19 heavy atoms) we had to employ the 6-311++G(d) basis set rather than the 6-311++G(3df) basis set. On the basis of our previous results [obtained for the BeX_3^- superhalogen anions (X = F, Cl, Br)],[21] we expect our final VDEs to be underestimated by less than 0.2 eV (which corresponds to ca. 1−2% of the vertical electron detachment energies).

All calculations were performed with the GAUSSIAN98 program[22] on Intel Pentium IV computers and an SGI Origin2000 numerical server.

3. Results

The theoretical and experimental results involving the superhalogen anions available in the literature relate mostly to *mononuclear systems* (i.e. those involving one central atom and several halogen ligands).[5−14,21] As we stated in Section 1, the mononuclear anionic system most likely possessing the largest vertical electron detachment energy that has been found thus far is TeF_7^-, for which the VDE of 11.9 eV was estimated (at the KT level) by Boldyrev and Simons.[14] Since the VDE of the superhalogen anion increases with the number of halogen ligands involved, one could explore this route in order to search for systems that maximise the VDE. However, one should recall that the TeF_7^- anion contains seven halogen atoms, and it is clear that attempts to search for another mononuclear anion involving larger number of ligands would be extremely difficult due to central atom valence saturation and topological limitations. Moreover, it has been shown that mononuclear species containing larger number of ligands, such as MnF_8^- or TcF_8^-, possess VDEs that are actually *smaller* than those of the anions MX_6^- or MX_7^- (the VDE values for MnF_8^- and TcF_8^- were found to be 6.7 and 5.8 eV, respectively).[6] Therefore, it seemed natural to examine whether the polynuclear superhalogen anions could exist as (geometrically and electronically) stable species since this would provide more than one central atom and hence would greatly increase the maximum number of halogen atoms in the system. This idea had been originally investigated as early as in 1987 by Gutsev and Boldyrev.[6] They proposed a few polynuclear superhalogen anions and estimated their VDEs.

The polynuclear superhalogen anions proposed by Gutsev and Boldyrev involved phosphorus, aluminium, arsenic, and vanadium as the central atoms and fluorine atoms as the ligands. On the basis of the DV-X_a calculations, they estimated the following electron binding energies: 8.6 eV

Table 1. The SCF geometrical parameters and the MP2 and OVGF estimates of the vertical electron detachment energies (VDE) for dinuclear superhalogen anions studied in this work [calculated with the 6-311++G(d) basis sets]. Bond lengths (*R*) in Å, valence angles (∠) in degrees, vertical electron detachment energies in eV

Species (symmetry)	VDE [eV] 6-311++G(d)	Geometry
$Al_2F_7^-$ (D_{3d})	MP2 9.84 OVGF **11.16**	*R*(Al−F) = 1.667 ∠(FAlF1) = 104.96 ∠(AlF1Al) = 180.0 *R*(Al−F1) = 1.779 ∠(FAlF) = 113.58
$Al_2Cl_7^-$ (C_2)	MP2 7.56 OVGF **7.75**	*R*(Al−Cl1) = 2.126 *R*(Al−Cl4) = 2.313 ∠(Cl3AlCl4) = 105.97 *R*(Al−Cl2) = 2.121 ∠(Cl1AlCl3) = 112.56 ∠(AlCl4Al) = 123.09 *R*(Al−Cl3) = 2.133 ∠(Cl2AlCl3) = 114.44
$Al_2Br_7^-$ (C_2)	MP2 6.96 OVGF **7.08**	*R*(Al−Br1) = 2.298 *R*(Al−Br4) = 2.493 ∠(Br2AlBr3) = 114.29 *R*(Al−Br2) = 2.288 ∠(AlBr4Al) = 118.93 ∠(Br1AlBr3) = 112.39 *R*(Al−Br3) = 2.305 ∠(Br3AlBr4) = 106.34
$P_2F_{11}^-$ (C_1)	MP2 9.66 OVGF **10.95**	*R*(P1F2) = 1.835 *R*(P3F13) = 1.571 ∠(F2P1F7) = 85.60 *R*(P1F4) = 1.569 *R*(P3F2) = 1.834 ∠(P1F2P3) = 168.19 *R*(P1F6) = 1.571 *R*(P3F5) = 1.569 ∠(F5P3F10) = 94.05 *R*(P3F10) = 1.573 *R*(P3F12) = 1.573 ∠(F2P3F13) = 86.23 *R*(P1F7) = 1.572 ∠(F4P1F6) = 94.11 ∠(F2P3F12) = 85.27 *R*(P1F8) = 1.571 ∠(F2P1F9) = 85.57 ∠(F2P3F11) = 86.27 *R*(P1F9) = 1.572 ∠(F2P1F8) = 86.26 ∠(F2P3F10) = 85.58 *R*(P3F11) = 1.571 ∠(F2P1F6) = 86.22
$V_2F_{11}^-$ (D_{4h})	MP2 8.67 OVGF **10.98**	*R*(V−F1) = 1.691 ∠(F1VF) = 94.03 ∠(VF2V) = 180.0 *R*(V−F) = 1.723 ∠(FVF2) = 85.96 *R*(V−F2) = 1.950 ∠(FVF) = 89.72
$As_2F_{11}^-$ (D_{4h})	MP2 9.86 OVGF **11.43**	*R*(As−F1) = 1.695 ∠(F1AsF) = 93.84 ∠(AsF2As) = 180.0 *R*(As−F) = 1.696 ∠(FAsF2) = 86.16 *R*(As−F2) = 1.903 ∠(FAsF) = 89.74
$Ta_2F_{11}^-$ (D_{4h})	MP2 9.79 OVGF **11.84**	*R*(Ta−F1) = 1.855 ∠(F1TaF) = 94.35 ∠(TaF2Ta) = 180.0 *R*(Ta−F) = 1.877 ∠(FTaF2) = 85.65 *R*(Ta−F2) = 2.066 ∠(FTaF) = 89.67

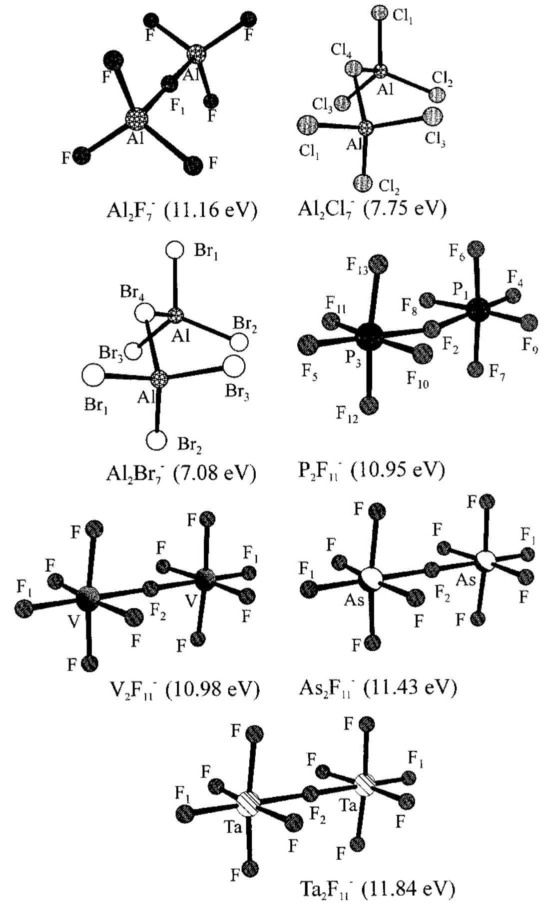
(for $P_2F_{11}^-$), 7.5 eV (for $Al_2F_7^-$), 8.6 eV (for $As_2F_{11}^-$), and 8.0 eV (for $V_2F_{11}^-$).[6] Moreover, Gutsev and Boldyrev concluded that exploring the polynuclear superhalogen species is a promising way of searching for systems with the maximum VDE value. Therefore, we decided to take a closer look at such species to examine whether VDE values that exceed the 12 eV limit (see Section 1) could be found.

3.1. Dinuclear Superhalogen Anions

We begin our discussion with the superhalogen anions that possess two central atoms and consider a few species that have been proposed earlier by Gutsev and Boldyrev (the VDEs of these species could not be estimated accurately in the past due to the rather limited computer resources available at the time).[6] In addition, we examine other ligands of $Al_2X_7^-$, such as chlorine and bromine, to verify (or confirm) whether F ligands indeed lead to the largest vertical electron detachment energies.

3.1.1. Equilibrium Geometries

The parameters defining the geometries corresponding to the minima on the potential energy surfaces for $Al_2F_7^-$, $Al_2Cl_7^-$, $Al_2Br_7^-$, $P_2F_{11}^-$, $V_2F_{11}^-$, $As_2F_{11}^-$, and $Ta_2F_{11}^-$ are presented in Table 1, and the equilibrium structures are depicted in Figure 1. In each case, the two central atoms (M) are linked via a halogen atom (X), and the M−X−M bond could be linear (as in $Al_2F_7^-$, $V_2F_{11}^-$, $As_2F_{11}^-$, and $Ta_2F_{11}^-$), quasi-linear (as in $P_2F_{11}^-$) or bent (as in $Al_2Cl_7^-$ and $Al_2Br_7^-$) (see Figure 1).



$Al_2F_7^-$ (11.16 eV) $Al_2Cl_7^-$ (7.75 eV) $Al_2Br_7^-$ (7.08 eV) $P_2F_{11}^-$ (10.95 eV) $V_2F_{11}^-$ (10.98 eV) $As_2F_{11}^-$ (11.43 eV) $Ta_2F_{11}^-$ (11.84 eV)

Figure 1. The SCF/6-311++G(d) equilibrium structures of the dinuclear superhalogen anions studied in this work. The corresponding OVGF/6-311++G(d) vertical electron detachment energies are given in parenthesis

The Al−F bond lengths in the $-AlF_3$ units in $Al_2F_7^-$ are shorter (by 0.1 Å) than the Al−F distances in the −Al−F−Al− fragment that serves as a bridge between the two subunits in this superhalogen anion. A similar observation can be made in the case of other dinuclear anions containing Al as the central atoms (see Table 1). Specifically, in the case of $Al_2Cl_7^-$ (and $Al_2Br_7^-$), the Al−Cl (Al−Br) bond lengths in the $-AlCl_3$ ($-AlBr_3$) units are shorter by ca. 0.2 Å than the Al−Cl (Al−Br) distances in the −Al−Cl−Al− (−Al−Br−Al−) fragment.

The P−F bonds in the $-PF_5$ subunits of the quasi-linear $P_2F_{11}^-$ structure are also shorter (by ca. 0.25 Å) than the P−F distances in the −P−F−P− fragment (see Table 1). An analogous situation can be observed in the case of all other dinuclear anions (i.e. $V_2F_{11}^-$, $As_2F_{11}^-$, and $Ta_2F_{11}^-$). The V−F bonds in the $-VF_5$ subunits of the $V_2F_{11}^-$ structure are shorter by ca. 0.2 Å than those in the −V−F−V− fragment connecting the two central atoms (see Table 1). A similar elongation (by ca. 0.2 Å) of the M−X distance is observed in $As_2F_{11}^-$ and $Ta_2F_{11}^-$ (see Table 1).

Since the corresponding harmonic vibrational frequencies for all the dinuclear superhalogen anions studied are positive (see Table 2), we conclude that each of these anionic structures is a true minimum on the potential energy surface, and this indicates the geometrical stability of such a system.

3.1.2. Vertical Electron Detachment Energies

The VDEs of all the dinuclear superhalogen anions studied in this work [calculated at the OVGF and MP2 levels with the 6-311++G(d) basis sets] are presented in Table 1. The second-order MP vertical electron detachment energies are usually smaller than those calculated at the OVGF level. This is consistent with the fact that the OVGF method approximately corresponds to the third-order perturbational treatment. Moreover, the largest discrepancies between MP2 and OVGF results were found for the superhalogens anion which had fluorine atoms as ligands.[21] This is also the case for the dinuclear superhalogen anions studied in this work (see Table 1). Therefore, we prefer to use the OVGF values in our discussion (given in this Section) since the OVGF treatment[23] has proven to produce a much better agreement between the calculated and experimentally determined electron binding energies of such species.[21]

Our results obtained for $Al_2X_7^-$ anions (X = F, Cl, Br) support the observation established earlier by others that species with fluorine ligands tend to have the largest VDE values (see Table 1). Indeed, the VDE calculated for $Al_2F_7^-$ is 11.16 eV, while those obtained for the analogous species with chlorine and bromine ligands are smaller (7.75 and 7.08 eV for $Al_2Cl_7^-$ and $Al_2Br_7^-$, respectively). To support this finding we calculated the vertical electron binding energies for mononuclear octahedral superhalogen anions hav-

Table 2. The SCF harmonic vibrational frequencies (in cm^{-1}) for dinuclear superhalogen anions

Al_2F_7		Al_2Br_7				Al_2Cl_7			
ν_1 (a_{1u})	19	ν_1 (a)	12	ν_{15} (b)	213	ν_1 (b)	14	ν_{15} (b)	337
$\nu_{2,3}$ (e_u)	21	ν_2 (b)	12	ν_{16} (b)	286	ν_2 (a)	18	ν_{16} (b)	395
$\nu_{4,5}$ (e_g)	140	ν_3 (a)	27	ν_{17} (a)	347	ν_3 (a)	40	ν_{17} (a)	442
ν_6 (a_{1g})	171	ν_4 (a)	57	ν_{18} (b)	441	ν_4 (a)	91	ν_{18} (b)	550
$\nu_{7,8}$ (e_u)	201	ν_5 (b)	57	ν_{19} (a)	448	ν_5 (b)	91	ν_{19} (a)	554
$\nu_{9,10}$ (e_g)	258	ν_6 (a)	62	ν_{20} (b)	461	ν_6 (a)	99	ν_{20} (b)	570
ν_{11} (a_{2u})	298	ν_7 (b)	77	ν_{21} (a)	463	ν_7 (b)	125	ν_{21} (a)	570
$\nu_{12,13}$ (e_u)	304	ν_8 (a)	95			ν_8 (a)	151		
ν_{14} (a_{1g})	446	ν_9 (b)	104			ν_9 (b)	162		
ν_{15} (a_{2u})	651	ν_{10} (a)	108			ν_{10} (a)	167		
ν_{16} (a_{1g})	697	ν_{11} (b)	115			ν_{11} (b)	182		
ν_{17} (a_{2u})	703	ν_{12} (b)	131			ν_{12} (b)	196		
$\nu_{18,19}$ (e_g)	842	ν_{13} (a)	134			ν_{13} (a)	207		
$\nu_{20,21}$ (e_u)	852	ν_{14} (a)	202			ν_{14} (a)	312		
As_2F_{11}		Ta_2F_{11}		V_2F_{11}		P_2F_{11}			
ν_1 (a_{1u})	13	ν_1 (a_{1u})	13	ν_1 (a_{1u})	25	ν_1 (a)	9	ν_{25} (a)	656
$\nu_{2,3}$ (e_u)	33	$\nu_{2,3}$ (e_u)	43	$\nu_{2,3}$ (e_u)	39	ν_2 (a)	12	ν_{26}(a)	800
ν_4 (a_{1g})	152	$\nu_{4,5}$ (e_g)	102	ν_4 (b_{2u})	130	ν_3 (a)	26	ν_{27} (a)	812
$\nu_{5,6}$ (e_g)	165	ν_6 (b_{2u})	111	$\nu_{5,6}$ (e_g)	136	ν_4 (a)	135	ν_{28} (a)	881
ν_7 (b_{2u})	219	ν_7 (b_{1g})	119	ν_7 (b_{1g})	137	ν_5 (a)	167	ν_{29} (a)	944
ν_8 (b_{1g})	224	ν_8 (a_{1g})	123	ν_8 (a_{1g})	153	ν_6 (a)	216	ν_{30} (a)	1011
$\nu_{9,10}$ (e_u)	276	$\nu_{9,10}$ (e_u)	184	$\nu_{9,10}$ (e_u)	213	ν_7 (a)	222	ν_{31} (a)	1011
ν_{11} (a_{2u})	303	ν_{11} (a_{2u})	211	ν_{11} (a_{2u})	281	ν_8 (a)	287	ν_{32} (a)	1043
$\nu_{12,13}$ (e_g)	331	$\nu_{12,13}$ (e_g)	219	$\nu_{12,13}$ (e_g)	282	ν_9 (a)	292	ν_{33} (a)	1043
$\nu_{14,15}$ (e_u)	388	ν_{14} (a_{1g})	261	$\nu_{14,15}$ (e_u)	350	ν_{10} (a)	348		
$\nu_{16,17}$ (e_g)	415	$\nu_{15,16}$ (e_u)	262	$\nu_{16,17}$ (e_g)	352	ν_{11} (a)	351		
ν_{18} (b_{1u})	419	$\nu_{17,18}$ (e_g)	266	ν_{18} (a_{1g})	366	ν_{12} (a)	432		
ν_{19} (b_{2g})	420	ν_{19} (b_{1u})	308	ν_{19} (b_{1u})	380	ν_{13} (a)	432		
ν_{20} (a_{1g})	435	ν_{20} (b_{2g})	311	$\nu_{20,21}$ (e_u)	381	ν_{14} (a)	486		
$\nu_{21,22}$ (e_u)	441	$\nu_{21,22}$ (e_u)	337	ν_{22} (b_{2g})	382	ν_{15} (a)	488		
ν_{23} (a_{2u})	531	ν_{23} (a_{2u})	541	ν_{23} (a_{2u})	496	ν_{16}(a)	547		
ν_{24} (b_{2u})	635	ν_{24} (b_{2u})	634	ν_{24} (b_{2u})	610	ν_{17} (a)	547		
ν_{25} (b_{1g})	640	ν_{25} (b_{1g})	638	ν_{25} (b_{1g})	617	ν_{18} (a)	585		
ν_{26} (a_{1g})	722	$\nu_{26,27}$ (e_g)	648	ν_{26} (a_{2u})	728	ν_{19} (a)	585		
ν_{27} (a_{2u})	730	ν_{28} (a_{1g})	668	ν_{27} (a_{1g})	733	ν_{20} (a)	595		
ν_{28} (a_{2u})	757	$\nu_{29,30}$ (e_u)	670	$\nu_{28,29}$ (e_g)	751	ν_{21} (a)	600		
ν_{29} (a_{1g})	768	ν_{31} (a_{2u})	671	ν_{30} (a_{2u})	792	ν_{22} (a)	600		
$\nu_{30,31}$ (e_g)	795	ν_{32} (a_{1g})	760	$\nu_{31,32}$ (e_u)	795	ν_{23} (a)	625		
$\nu_{32,33}$ (e_u)	810	ν_{33} (a_{2u})	763	ν_{33} (a_{1g})	814	ν_{24} (a)	650		

ing phosphorus as a central atom. The results shown in Tables 3 and 4 indicate that the VDE of PF_6^- is relatively large (9.4 eV) and decreases when the F ligands are replaced with Cl or Br ligands. In addition, our earlier results obtained for BeX_3^- (X = F, Cl, Br),[21] as well as the results obtained by others,[5−7] support this conclusion. Hence, we decided not to calculate the electron binding energies for other species containing either Cl or Br ligands, since it can be predicted that such anions would have smaller VDEs than the corresponding species containing fluorine atoms as the ligands.

Table 3. The SCF geometrical parameters and the MP2 and OVGF estimates of the vertical electron detachment energies (VDE) for mononuclear superhalogen anions studied in this work [calculated with the 6-311++G(d) basis sets]. Bond lengths (*R*) in Å, vertical electron detachment energies in eV

Species (symmetry)	VDE [eV] 6-311++G(d)	Geometry
PF_6^-	MP2 8.49	*R*(P−F) = 1.603
(O_h)	OVGF **9.43**	
PCl_6^-	MP2 5.94	*R*(P−Cl) = 2.168
(O_h)	OVGF **7.55**	
PBr_6^-	MP2 5.30	*R*(P−Br) = 2.374
(O_h)	OVGF **6.66**	

Table 4. The SCF harmonic vibrational frequencies (in cm^{-1}) for mononuclear superhalogen anions

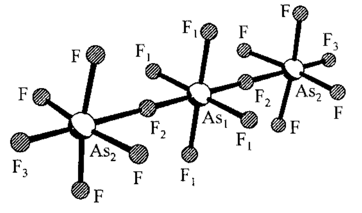
PBr_6		PCl_6		PF_6	
$\nu_{1,2,3}$ (t_{2u})	99	$\nu_{1,2,3}$ (t_{2u})	172	$\nu_{1,2,3}$ (t_{2u})	333
$\nu_{4,5,6}$ (t_{2g})	145	$\nu_{4,5,6}$ (t_{2g})	256	$\nu_{4,5,6}$ (t_{2g})	504
$\nu_{7,8}$ (e_g)	157	$\nu_{7,8}$ (e_g)	271	$\nu_{7,8,9}$ (t_{1u})	600
$\nu_{9,10,11}$ (t_{1u})	174	$\nu_{9,10,11}$ (t_{1u})	305	$\nu_{10,11}$ (e_g)	603
ν_{12} (a_{1g})	215	ν_{12} (a_{1g})	377	ν_{12} (a_{1g})	787
$\nu_{13,14,15}$(t_{1u})	387	$\nu_{13,14,15}$(t_{1u})	481	$\nu_{13,14,15}$(t_{1u})	943

One should also notice that the VDE of $Al_2F_7^-$ calculated at the OVGF/6-311++G(d) level differs significantly from the electron binding energy determined by Gutsev and Boldyrev (7.5 eV).[6] We believe that our OVGF value of 11.16 eV, even if slightly overestimated, is much closer to the true vertical electron detachment energy of this anion. The VDE calculated for the $P_2F_{11}^-$ superhalogen anion (10.95 eV) is slightly smaller than that of $Al_2F_7^-$ (see Table 1). On the basis of the discussion given in the preceding paragraphs, we do not expect the VDE to increase when the fluorine atoms in $P_2F_{11}^-$ are replaced by other halogen atoms. However, we have verified that replacing the phosphorus atoms (the central atoms) by other elements, such as V, As, or Ta, may lead to larger electron binding energies. In particular, the VDE for the superhalogen anion $V_2F_{11}^-$ [calculated at the OVGF/6-311++G(d) level] approaches the value of 11 eV (10.98 eV, see Table 1), while the vertical electron detachment energy of $As_2F_{11}^-$ is even larger and equals to 11.43 eV. The largest VDE for a dinuclear superhalogen anion was found for $Ta_2F_{11}^-$ (11.84 eV). We considered this finding to be promising because the VDE of dinuclear $Ta_2F_{11}^-$ (11.84 eV) approaches the value of 12 eV (which is supposed to be the VDE limit according to the recent studies[6,12,13]), and one could expect the VDE to increase when a third central atom is added. Therefore, we now move on to the discussion of the vertical electron detachment energies of the superhalogen anions containing three central atoms.

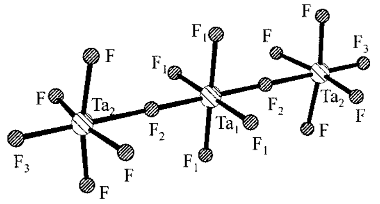
3.2. Trinuclear Superhalogen Anions

3.2.1. Equilibrium Geometries

Although our original intention was to determine the vertical electron binding energies for four trinuclear superhalogen anions $M_3F_{16}^-$ (where M = P, V, As, Ta), the VDEs of only two trinuclear species were determined. In the case of the two species $P_3F_{16}^-$ and $V_3F_{16}^-$, whose geometrical stability we initially assumed, it was not possible to find any structures corresponding to local minima on the potential energy surface. Instead, the geometry optimisations led to fragmentation of these two systems. Therefore, we concluded that neither $P_3F_{16}^-$ nor $V_3F_{16}^-$ was geometrically stable, and hence decided to focus on two trinuclear species, $As_3F_{16}^-$ and $Ta_3F_{16}^-$.



$As_3F_{16}^-$ (12.20 eV)



$Ta_3F_{16}^-$ (12.63 eV)

Figure 2. The SCF/6-311++G(d) equilibrium structures of the trinuclear superhalogen anions studied in this work. The corresponding OVGF/6-311++G(d) vertical electron detachment energies are given in parenthesis

The equilibrium structures of $As_3F_{16}^-$ and $Ta_3F_{16}^-$ are depicted in Figure 2 and the corresponding parameters defining these geometries are given in Table 5. Since the harmonic vibrational frequencies calculated for these structures are positive (see Table 6), we conclude that each of these trinuclear superhalogen anions is a true minimum on the potential energy surface. This indicates the geometrical stability of such a system.

In $As_3F_{16}^-$ and $Ta_3F_{16}^-$, the central atoms (M) are linked via fluorine atoms and the M−F−M bonds are linear (see Figure 2 and Table 5). The As−F bonds in the As−F−As−F−As linking fragment in $As_3F_{16}^-$ are longer (by ca. 0.1−0.3 Å) than those in which only two atoms (i.e. one As and one F atom) are involved. A similar situation can be observed in $Ta_3F_{16}^-$, where the Ta−F distances in the Ta−F−Ta−F−Ta linking fragment are longer (by ca. 0.1−0.3 Å) than those that involve only two atoms (see Table 5).

Both the $As_3F_{16}^-$ and $Ta_3F_{16}^-$ equilibrium structures possess relatively high symmetry (D_{4h}), and each of these

Table 5. The SCF geometrical parameters and the MP2 and OVGF estimates of the vertical electron detachment energies (VDE) for trinuclear superhalogen anions studied in this work [calculated with the 6-311++G(d) basis sets]. Bond lengths (R) in Å, valence angles (∠) in degrees, vertical electron detachment energies in eV

Species (symmetry)	VDE [eV] 6-311++G(d)	Geometry
$As_3F_{16}^-$ (D_{4h})	MP2 12.46 OVGF **12.20**	R(As1F1) = 1.686, R(As2F) = 1.689, ∠(FAs2F) = 89.38 R(As1F2) = 1.799, ∠(F1As1F2) = 90.0, ∠(FAs2F3) = 95.89 R(As2F2) = 2.029, ∠(F1As1F1) = 90.0, ∠(As2F2As1) = 180.0 R(As2F3) = 1.682 ∠(F2As2F) = 84.11
$Ta_3F_{16}^-$ (D_{4h})	MP2 10.45 OVGF **12.63**	R(Ta1F1) = 1.864, R(Ta2F) = 1.871, ∠(FTa2F) = 89.28 R(Ta1F2) = 1.983, ∠(F1Ta1F2) = 90.0, ∠(FTa2F3) = 96.44 R(Ta2F2) = 2.134, ∠(F1Ta1F1) = 90.0, ∠(Ta2F2Ta1) = 180.0 R(Ta2F3) = 1.842, ∠(F2Ta2F) = 83.55

Table 6. The SCF harmonic vibrational frequencies (in cm^{-1}) for trinuclear superhalogen anions

As_3F_{16}				Ta_3F_{16}			
ν_1 (a_{1u})	12	ν_{30} (b_{2g})	426	ν_1 (a_{1u})	9	ν_{29} (b_{2g})	313
$\nu_{2,3}$ (e_u)	14	ν_{31} (b_{1u})	430	$\nu_{2,}$(a_{2g})	16	ν_{30} (b_{1u})	314
ν_4 (a_{2g})	21	ν_{32} (b_{2g})	431	$\nu_{3,4}$ (e_u)	17	ν_{31} (b_{2g})	317
$\nu_{5,6}$ (e_g)	33	$\nu_{33,34}$ (e_u)	442	$\nu_{5,6}$ (e_g)	46	$\nu_{32,33}$ (e_u)	323
ν_7 (a_{1g})	95	ν_{35} (a_{2u})	448	ν_7 (b_{2u})	73	$\nu_{34,35}$ (e_g)	336
ν_8 (a_{2u})	130	ν_{36} (a_{1g})	556	$\nu_{8,9}$ (e_u)	85	ν_{36} (a_{2u})	565
$\nu_{9,10}$ (e_u)	138	ν_{37} (a_{2u})	594	ν_{10} (a_{1g})	90	ν_{37} (a_{1g})	597
$\nu_{11,12}$ (e_g)	184	ν_{38} (b_{1g})	647	ν_{11} (b_{1g})	107	ν_{38} (b_{1g})	649
ν_{13} (b_{2u})	193	ν_{39} (b_{2u})	648	ν_{12} (b_{2u})	108	ν_{39} (b_{2u})	649
ν_{14} (b_{1g})	194	ν_{40} (b_{1g})	657	ν_{13} (a_{2u})	130	$\nu_{40,41}$ (e_u)	656
ν_{15} (b_{2u})	215	ν_{41} (a_{1g})	742	$\nu_{14,15}$ (e_g)	139	ν_{42} (b_{1g})	670
$\nu_{16,17}$ (e_u)	281	ν_{42} (a_{2u})	744	ν_{16} (a_{2u})	188	$\nu_{43,44}$ (e_g)	681
$\nu_{18,19}$ (e_g)	316	$\nu_{43,44}$ (a_{1g})	762	$\nu_{17,18}$ (e_u)	192	$\nu_{45,46}$ (e_u)	692
ν_{20} (a_{2u})	320	ν_{45} (a_{2u})	781	$\nu_{19,20}$ (e_g)	217	ν_{47} (a_{2u})	710
$\nu_{21,22}$ (e_u)	342	$\nu_{46,47}$ (e_u)	812	$\nu_{21,22}$ (e_u)	218	ν_{48} (a_{1g})	711
ν_{23} (a_{1g})	358	$\nu_{48,49}$ (e_g)	817	ν_{23} (a_{1g})	237	ν_{49} (a_{1g})	770
$\nu_{24,25}$ (e_g)	386	$\nu_{50,51}$ (e_u)	832	ν_{24} (a_{2u})	255	ν_{50} (a_{2u})	773
$\nu_{26,27}$ (e_u)	410			$\nu_{25,26}$ (e_u)	259	ν_{51} (a_{1g})	776
$\nu_{28,29}$ (e_g)	425			$\nu_{27,28}$ (e_g)	259		

species can be viewed as three quasi-octahedral MF_6 systems (M = As, Ta) linked together by two bridging fluorine atoms.

3.2.2. Vertical Electron Detachment Energies

The vertical electron detachment energies for the two trinuclear superhalogen anions studied in this work [calculated at the OVGF and MP2 levels with the 6-311++G(d) basis sets] are presented in Table 5. As in the preceding Section (related to dinuclear species), we use the OVGF values whilst discussing the VDEs of $As_3F_{16}^-$ and $Ta_3F_{16}^-$.

We expected the VDEs of the $As_3F_{16}^-$ and $Ta_3F_{16}^-$ anions to be larger than the VDEs calculated for the corresponding dinuclear species (i.e. $As_2F_{11}^-$ and $Ta_2F_{11}^-$) because the excess negative charge can be delocalized over a larger number of electronegative ligands in the trinuclear superhalogen anions. Indeed, the VDE calculated for $As_3F_{16}^-$ (12.20 eV) is larger by 0.77 eV than the VDE of $As_2F_{11}^-$, and the VDE obtained for $Ta_3F_{16}^-$ (12.63 eV) is greater (by 0.79 eV) than that of $Ta_2F_{11}^-$ (see Tables 1 and 5). Hence, in both cases, the VDE of the superhalogen anion increases by ca. 0.8 eV when another central atom (of the same type) and the proper number of fluorine ligands is added to the parent structure.

We believe that our VDE values that exceed the 12 eV limit by 0.2−0.6 eV, found for the two negatively charged systems $As_3F_{16}^-$ and $Ta_3F_{16}^-$ may be approaching the largest possible VDE values because: (i) the largest known vertical electron detachment energies described in the literature thus far are those calculated by Boldyrev and Simons for TeF_7^- (11.9 eV),[14] and those obtained (also theoretically) by Schaefer's group for AsF_6^- (10.5 eV),[11] and (ii) the limit for the maximum possible excess electron binding energy is thought to be about 12 eV.[12,13] Although the extremely large VDE (12.63 eV) calculated by us for $Ta_3F_{16}^-$ seems to be the largest excess electron binding energy reported in the literature thus far, we believe the maximum possible VDE value has not yet been achieved. In addition, we conclude that the upper limit for the electron affinity characterising the neutral molecular system is in fact higher than 12 eV, and it seems likely it might be larger than 13 eV, as suggested by Gutsev and Boldyrev in the 80′s.[24] Therefore, we believe that the negatively charged system that has the maximum vertical electron detachment energy is yet to be found and we consider such species (i.e. those possessing extremely large VDEs) as systems of great importance in chemistry.

4. Summary

The vertical electron detachment energies of several polynuclear superhalogen anions were calculated at the OVGF/6-311++G(d) level. The largest vertical electron binding energy of 12.63 eV was found for $Ta_3F_{16}^-$, and it is recognised as the largest excess electron binding energy of a molecular system reported in the literature thus far. Since the VDE of 12.63 eV (found for $Ta_3F_{16}^-$) exceeds the upper VDE limit that was thought to be 12 eV, it is proposed that the largest possible excess electron binding energy of a molecular system be reconsidered. Several other anions were also found [at the OVGF/6-311++G(d) level] to have very large VDEs (i.e. $Al_2Br_7^-$: 7.08 eV, $Al_2Cl_7^-$: 7.75 eV, $Al_2F_7^-$: 11.16 eV, $P_2F_{11}^-$: 10.95 eV, $V_2F_{11}^-$: 10.98 eV, $As_2F_{11}^-$: 11.43 eV, $Ta_2F_{11}^-$: 11.84 eV, and $As_3F_{16}^-$: 12.20 eV).

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