Adiabatic electron affinities of small superhalogens: LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$

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Geometries and frequencies for the neutral MX_2 and ionic MX_2^- species (M=Li, Na, and X=F, Cl) are studied by several theoretical methods: density functional theory (Becke-3-Lee-Yang-Parr) [DFT(B3LYP)], second-order many-body perturbation theory [MBPT(2)], and coupled-cluster with singles and doubles (CCSD). The geometries optimized at the CCSD/6-311+G(d) level are used in CCSD(T) calculations with a large atomic natural orbital basis to compute adiabatic electron affinities (EA_{ad}), which are found for LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$ to be 5.45, 4.97, 5.12, and 4.69 eV, respectively. The highest EAs among all the atoms of the periodic table occur in the halogen atoms (fluorine, 3.40 eV; chlorine, 3.62 eV); therefore all four of these triatomic radicals are properly termed superhalogens. LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$ are thermodynamically stable, and their dissociation energies computed at the CCSD with the noniterative inclusion of triples [CCSD(T)] level are 20.5, 24.9, 19.3, and 25.2 kcal/mol, respectively. LiF_2^-, $LiCl_2^-$, NaF_2^-, and $NaCl_2^-$ are more stable than their neutral parents with CCSD(T) dissociation energies of 69.5, 58.7, 49.0, and 52.5 kcal/mol, respectively. The computed vertical electron detachment energies of LiF_2^-, $LiCl_2^-$, NaF_2^-, and $NaCl_2^-$ are 6.51, 5.88, 6.18, and 5.77 eV, respectively, which are in nice agreement with the values calculated by Scheller and Cederbaum by the Green–Function method. © *1997 American Institute of Physics.* [S0021-9606(97)01934-X]

I. INTRODUCTION

Systems with high electron affinities (EA) are especially important for the oxidation of counterpart particles with relatively high ionization potentials and allow the synthesis of unusual chemical compounds, many of which are highly energetic. The most famous example of an application of such a system is the synthesis of the chemically bound xenon in the $Xe^+[PtF_6^-]$ salt.[1] Such systems are widely used also in the production of organic metals and organic super-conductors.[2]

As is well known, halogen atoms possess the highest EA (3.0–3.6 eV) among the elements;[3] however, the EA of a polyatomic system may exceed the 3.6 eV atomic limit due to collective effects. Such systems are known as superhalogens[4,5] and the EA of many superhalogens have been estimated theoretically[4–33] and experimentally.[34–58] The superhalogens described by the general formula MX_{k+1} (where M is a main group or transition metal atom, X is a halogen atom, and k is the maximal formal valency of the central atom M) are especially important in chemistry. Their anions, such as BF_4^-, $AlCl_4^-$, ScF_4^-, $SiCl_5^-$, TaF_6^-, AsF_6^-, etc., are widely known as building blocks in solids and gas phase molecules.

Early discrete-variational X_a-method (DVM-Xα) calculations[4,5,8–12] led to somewhat underestimated values of the vertical electron detachment energies (VEDE) of many superhalogen anions, but nonetheless the VEDEs were found to be higher in energy than 3.6 eV. Recently, more accurate calculations with the Green's function technique provided higher VEDE values than those obtained in the DVM-Xα calculations, namely: 6.80 eV for LiF_2^-,[16,21,23] 5.73 eV for $LiCl_2^-$,[23] 6.54 eV for NaF_2^-,[23] 5.64 eV for $NaCl_2^-$,[23] 6.07 eV for KF_2^-,[23] 5.37 eV for KCl_2^-,[23] 7.86 eV for BeF_3^-,[16,19,26] 8.14 eV for MgF_3^-,[26] and 7.88 eV for CaF_3^-.[26]

The adiabatic electron affinity (EA_{ad}) of a superhalogen is a more important characteristic than the VEDE (or the vertical EA) of the corresponding anion, since it is related to the thermochemical stability of the latter. Theoretical estimates of the EA_{ad} of the MX_{k+1} superhalogens and dissociation energies are rather confusing. Kölmel *et al.*[23] found that the PF_6 radical is highly unstable (-76 kcal/mol at the O_h configuration) towards dissociation to PF_5+F using the Hartree–Fock (HF) approximation and the DZP basis augmented with some diffuse functions, while Gutsev[27] found the PF_6 radical to be stable towards this dissociation pathway by 40.5 kcal/mol at the local spin density approximation (LSDA) level and by 7.1 kcal/mol at the LSDA level with the inclusion of Becke's[28] nonlocal gradient corrections. Tschumper *et al.*[59] found that the optimized octahedral configuration of PF_6 provides doubly degenerate imaginary harmonic vibrational frequencies of $267i$ cm^{-1} at the DFT(B3LYP)/DZP level of theory; and that another stationary point of C_{2v} symmetry has one imaginary frequency of $692i$ cm^{-1}. Further optimizations of the latter configuration within C_s symmetry constraints led to a dissociative behavior when one fluorine atom leaves the trigonal bipyramidal PF_5

configuration. Another superhalogen, AlF_4, was found to be stable by 4.4 kcal/mol towards dissociation into AlF_3+F at the MBPT(4)/6-31+G(d)//UHF/6-31+G(d) level of theory.[31] The relatively large size of the neutral superhalogens studied makes it difficult to perform high-quality calculations, prohibiting definitive conclusions about the stability of these systems.

It is worth mentioning that Ortiz[24,25] has recently computed the VEDEs of BO_2^- and BS_2^- as well as the adiabatic electron affinities (EA_{ad}) of BO_2 and BS_2. These molecules are valent isoelectronic to the superhalogens considered in the present work, hence, they are expected to have high EA_{ad}s. Indeed, Ortiz found that both the VEDEs (4.75 and 3.68 eV in BO_2^- and BS_2^-, respectively) and the EA_{ad}s (4.65 and 3.63 eV in BO_2 and BS_2, respectively) are higher than the EAs of the halogen atoms. However, there is a difference between BO_2 and BS_2 and their isoelectronic LiF_2 and $LiCl_2$ counterparts. Whereas BO_2 and BS_2 are linear as well as their anions, LiF_2 and $LiCl_2$ are angular, while their anions are linear. This difference results in much smaller adiabatic corrections to the ionization potentials in BO_2^- and BS_2^- compared to those in LiF_2^- and $LiCl_2^-$.

Keeping in mind that the EA_{ad} values are important for thermochemical calculations for solids containing superhalogen groups, we report here results of ab initio calculations of the EA_{ad} only for the smallest superhalogens, namely, LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$, because high-quality calculations are certainly feasible for these systems. The neutral species are known to be thermodynamically stable and their Raman and ir spectra have been studied in inert matrices.[60,61]

For LiF_2^-, $LiCl_2^-$, NaF_2^-, and $NaCl_2^-$, the results of other ab initio calculations are available in the literature.[16,21,23] The HF calculations were performed for geometries and frequencies of the corresponding neutral species using the DZ+P[62,63] and 6-311+G(d)[64,65] basis sets. For LiF_2, potential energy surfaces (PES) $E(R_1,R_2)$ were calculated for six valence states of $^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$ symmetries at the MRSD-CI/6-311+G(d) level. It was found that the $^2B_2$ electronic state of C_{2v} symmetry which originates from the $^2\Pi_g$ electronic state of the linear XMX structure is the global minimum for the LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$ radicals and their charge distributions can be described as $M^+X_2^-$ (Refs. 64 and 65). Therefore we will limit our consideration to the (C_{2v}, $^2B_2$) electronic states of the neutral radicals and the ($D_{\infty h}$, $^1\Sigma_g^+$) electronic states of the anions.

II. COMPUTATIONAL DETAILS

Geometry optimizations and frequency calculations are performed at the density functional theory (DFT) level with the B3LYP exchange-correlation functional,[66,67] at the second-order many-body perturbation theory [MBPT(2)] level, and the infinite-order coupled-cluster method with all singles and doubles (CCSD) level[68] using the GAUSSIAN 94 suite of programs.[69] The basis set is moderate-sized 6-311+G(d).[70–73] Core electrons were kept frozen in all the optimizations except for MBPT(2), where all electrons are included in the correlated calculations.

TABLE I. Equilibrium geometries of LiF_2^-, $LiCl_2^-$, NaF_2^-, and $NaCl_2^-$ calculated at the DFT (B3LYP), MBPT(2), CCSD levels of theory with the 6-311+G(d) basis. Bond lengths are in Å and total energies (TE) are in Hartree.

Species	Level	R(M–X)	TE
LiF_2^-	DFT	1.699	$-207.469\ 695$
	MBPT(2)	1.706	$-207.049\ 796$
	CCSD	1.702	$-206.991\ 886$
$LiCl_2^-$	DFT	2.162	$-928.226\ 746$
	MBPT(2)	2.132	$-927.101\ 670$
	CCSD	2.140	$-927.012\ 990$
NaF_2^-	DFT	2.058	$-362.210\ 977$
	MBPT(2)	2.075	$-361.531\ 431$
	CCSD	2.122	$-361.351\ 894$
$NaCl_2^-$	DFT	2.509	$-1082.985\ 959$
	MBPT(2)	2.485	$-1081.596\ 374$
	CCSD	2.492	$-1081.390\ 037$

At the CCSD/6-311+G(d) optimized geometries, further calculations are performed with the ACES II suite of programs[74] and a large atomic natural orbital basis of Widmark–Malmquist–Roos (WMR)[75] comprising of $[14s9p4d3f/7s6p4d3f]$ for Li, $[14s9p4d3f/7s7p4d3f]$ for F, $[17s12p5d4f/7s7p5d4f]$ for Na, and $[17s12p5d4f/7s7p5d4f]$ for Cl. The coupled-cluster methods with the noniterative inclusion of triple excitations $[CCSD+T(CCSD)$ and $CCSD(T)]$[76,77] are applied. Dissociation energies of all species are computed at the CCSD(T)/WMR level using the CCSD(T)/WMR//CCSD/6-311+G(d) total energies of the triatomics optimized in the present work and the CCSD(T)/WMR results for all intermediate diatomics, atoms and anions obtained elsewhere.[78] The ZPE corrections to these dissociation energies are found to be small (about 0.1 kcal/mol) and are neglected.

The results of the geometry and frequency calculations are collected in Tables I–IV, the total energies, vertical electron detachment energies and vertical electron attachment energies, are presented in Table V, the bond dissociation energies for the neutral and anionic systems are shown in Table VI and the adiabatic electron affinities are presented in Table VII.

III. THE STRUCTURE OF THE MX_2^- ANIONS AND VERTICAL ELECTRON DETACHMENT ENERGIES

The MX_2^- anions are linear at the DFT, MBPT(2), and CCSD levels of theory and possess the valence $1\sigma_g^2 2\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 1\pi_g^4$ electronic configuration. The bond lengths optimized at these levels of theory agree with each other within 0.007 Å for LiF_2^-, 0.030 Å for $LiCl_2^-$, 0.047 Å for NaF_2^-, and 0.024 Å for $NaCl_2^-$. The somewhat larger difference in the bond lengths of NaF_2^- obtained at the MBPT(2) and CCSD levels is puzzling. The optimal bond lengths of these anions calculated by Scheller and Cederbaum[21,23] at the CISD level using the TZP basis augmented with diffuse sp functions [which is of similar size as the 6-311+G(d) basis] were found to be 1.679 Å in LiF_2^-,

TABLE II. Equilibrium geometries of LiF_2, $LiCl_2$, NaF_2, and $NaCl_2$ calculated at the DFT (B3LYP), MBPT(2), CCSD levels of theory with the 6-311+G(d) basis and the CCSD(T) level with the POL1 basis. Bond lengths are in Å, valence angles are in degrees, and total energies (TE) are in Hartree.

Species	Level	R(M–X)	R(X–X)	∠XMX	$\langle S^2 \rangle$	TE
LiF_2	DFT	1.715	2.037	78.9°	0.756	−207.282 250
	MBPT(2)	1.724	1.954	69.0°	0.783	−206.843 975
	CCSD	1.728	1.946	69.5°	0.784	−206.797 901
	CCSD(T)	1.702	1.947	69.8°	0.771	−206.820 384
$LiCl_2$	DFT	2.166	2.804	80.7°	0.753	−928.047 902
	MBPT(2)	2.144	2.696	77.9°	0.768	−926.922 023
	CCSD	2.153	2.725	78.5°	0.769	−926.835 513
	CCSD(T)	2.197	2.679	75.1°	0.771	−926.947 254
NaF_2	DFT	2.078	2.032	58.6°	0.755	−362.038 712
	MBPT(2)	2.093	1.947	55.4°	0.783	−361.342 529
	CCSD	2.250	1.973	52.0°	0.786	−361.171 489
	CCSD(T)	2.070	1.947	56.1°	0.771	−361.293 680
$NaCl_2$	DFT	2.534	2.803	67.2°	0.753	−1082.814 378
	MBPT(2)	2.514	2.688	64.6°	0.767	−1081.426 446
	CCSD	2.524	2.715	65.1°	0.768	−1081.222 270
	CCSD(T)	2.529	2.668	63.7°	0.762	−1081.431 457

2.152 Å in $LiCl_2^-$, 2.043 Å in NaF_2^-, and 2.601 Å in $NaCl_2^-$, which are in excellent agreement with our values, except for NaF_2^-. The bond lengths of NaF_2^- calculated at the CCSD/6-311+G(d) level are 0.079 Å longer than the values calculated by Scheller and Cederbaum. Such a difference is substantially larger than that to be expected for these methods and basis sets.

The vibrational frequencies calculated at the DFT, MBPT(2) and CCSD levels are rather similar and the largest deviations are 15 cm^{-1} for LiF_2^-, 60 cm^{-1} for $LiCl_2^-$, 28 cm^{-1} for NaF_2^-, and 27 cm^{-1} for $NaCl_2^-$, always for the $\nu_2(\sigma_u)$ antisymmetric stretch mode. The infrared intensities

TABLE III. Vibrational frequencies (in cm^{-1}), ir intensities [in brackets, km/mol], and zero-point energies (in eV) of LiF_2^-, $LiCl_2^-$, NaF_2^-, and $NaCl_2^-$ calculated at the DFT(B3LYP), MBPT(2), CCSD levels of theory with the 6-311+G(d) basis.

Species	Mode	DFT	MBPT(2)	CCSD
LiF_2^-	$\nu_1(\sigma_g)$	370[0]	359[0]	365
	$\nu_2(\sigma_u)$	867[198]	859[198]	880
	$\nu_3(\pi_u)$	252[118]	237[126]	238
	ZPE	0.108	0.105	0.107
$LiCl_2^-$	$\nu_1(\sigma_g)$	206[0]	222[0]	220
	$\nu_2(\sigma_u)$	634[214]	694[210]	688
	$\nu_3(\pi_u)$	182[118]	184[63]	177
	ZPE	0.075	0.068	0.078
NaF_2^-	$\nu_1(\sigma_g)$	312[0]	311[0]	339
	$\nu_2(\sigma_u)$	480[103]	478[106]	497
	$\nu_3(\pi_u)$	122[92]	119[98]	114
	ZPE	0.064	0.064	0.066
$NaCl_2^-$	$\nu_1(\sigma_g)$	181[0]	193[0]	192
	$\nu_2(\sigma_u)$	342[924]	369[90]	365
	$\nu_3(\pi_u)$	90[48]	92[50]	90
	ZPE	0.044	0.046	0.040

are available only at the DFT and MBPT(2) levels of theory, and they are in good mutual agreement for all four anions. We anticipate that our frequencies could be useful for identification of these anions in the gas phase or isolated in matrices.

The VEDEs of all four anions presented in Table V are calculated by a so-called indirect method, namely, as the differences between the total energies of the anions and the neutral precursors at the optimal geometries of the anions. The indirect method used in this work permits maximum orbital relaxation and CCSD(T) electron correlation contributions to the VEDE. Scheller and Cederbaum[23] have calculated the VEDEs using a direct method, where the electron correlation and electron relaxation corrections calculated with the ADC(3) technique are added to the orbital energy of the anion HOMO. Their VEDEs are 6.80 eV for LiF_2^-, 5.73 eV for $LiCl_2^-$, 6.54 eV for NaF_2^-, and 5.64 eV for $NaCl_2^-$. Agreement between our indirect and their direct results is rather satisfactory. The largest deviation of 0.36 eV was found for NaF_2^-.

The VEDEs calculated within Koopmans' approximation are overestimated by about 1.2 eV for alkali fluorides and by about 0.7 eV for alkali chlorides with respect to the CCSD(T)/WMR values presented in Table V. The main contribution to the Koopmans' VEDEs is due to the electron relaxation and this contribution is larger for alkali fluorides because of a smaller size of F^- with respect to Cl^-. The largest VEDE of 6.80 eV is found for the smallest LiF_2^- anion. The VEDEs decrease in the series: $LiF_2^- \rightarrow NaF_2^-$ (by 0.33 eV), $LiCl_2^- \rightarrow NaCl_2^-$ (by 0.11 eV), $LiF_2^- \rightarrow LiCl_2^-$ (by 0.63 eV), and $NaF_2^- \rightarrow NaCl_2^-$ (by 0.41 eV). However, all the VEDEs are substantially higher than 3.6 eV, the largest VEDE (or the EA, which is the same in this case) of the halogen atomic anions.

TABLE IV. Vibrational frequencies (in cm^{-1}), ir intensities [in km/mol], and zero-point energies (in eV) of LiF$_2$, LiCl$_2$, NaF$_2$, and NaCl$_2$ calculated at the DFT(B3LYP), MBPT(2), CCSD levels of theory with the 6-311+G(d) basis and the CCSD(T) level with the POL1 basis.

Species	Mode	DFT	MBPT(2)	CCSD	CCSD(T)	Exp. (Refs. 60, 61)
LiF$_2$	$\nu_1(a_1)$	721[129]	730[127]	722	734[113]	(708)[b]
	$\nu_2(a_1)$	338[12]	426[12]	408	431[14]	452
	$\nu_3(b_2)$	535[9]	(1804)[a]	604	479[0.03]	···
	ZPE	0.099	···	0.108	0.102	···
LiCl$_2$	$\nu_1(a_1)$	503[121]	543[125]	536	493[109]	518
	$\nu_2(a_1)$	179[5]	219[5]	211	232[5]	246
	$\nu_3(b_2)$	418[15]	513[797]	420	357[6]	···
	ZPE	0.068	0.079	0.072	0.067	···
NaF$_2$	$\nu_1(a_1)$	450[35]	489[15]	576	489[16]	475
	$\nu_2(a_1)$	311[23]	368[45]	402	369[42]	454
	$\nu_3(b_2)$	317[2]	(966)[a]	(1043)[a]	306[0.01]	···
	ZPE	0.064	···	···	0.072	···
NaCl$_2$	$\nu_1(a_1)$	295[43]	320[43]	315	313[33]	(270)[c]
	$\nu_2(a_1)$	171[9]	210[11]	203	220[15]	225
	$\nu_3(b_2)$	216[5]	255[156]	215	209[2.4]	···
	ZPE	0.042	0.049	0.045	0.046	···

[a]A symmetry broken problem.
[b]The frequency of the ^{6}LiF$_2$ isotopomer.
[c]An estimated frequency.

The reason why the VEDEs of the MX$_{k+1}$ superhalogen anions are substantially higher than the EAs has been discussed briefly based upon the results of the DVM-Xα calculations.[4,80] Three main factors are found to be responsible for the increase in the VEDE of LiF$_2^-$ with respect to that of F$^-$, namely: (i) the delocalization of an extra electron over two fluorine atoms instead of one; (ii) the nonbonding character of the LiF$_2$ HOMO (the central atom does not contribute any valence AOs to this MO, and the HOMO is composed from $p\pi$-AOs of the highly electronegative fluorine atoms); (iii) the coordination of the negatively charged ligands to the electropositive Li$^+$ ion.

TABLE V. Total energies (TE) of the radicals at the anions at the neutral (R_e) and anion (R_e^-) equilibrium geometries. Vertical electron affinities (EA$_{vert}$) of the radicals and the vertical electron detachment energy (VEDE) of the anions at different levels of theory calculated with the WMR basis set. Total energies are in a.u., EA$_{vert}$s and VEDEs are in eV.

Level	Neutral R_e			Anion R_e^-		
	LiF$_2$	LiF$_2^-$	EA$_{vert}$	LiF$_2$	LiF$_2^-$	VEDE
MBPT(2)	−207.063 626	−207.156 083	2.52	−207.021 147	−207.276 628	6.95
CCSD	−207.071 462	−207.148 278	2.09	−207.031 189	−207.271 026	6.53
CCSD+T	−207.092 926	−207.174 265	2.21	−207.054 888	−207.293 369	6.49
CCSD(T)	−207.091 400	−207.171 366	2.18	−207.052 589	−207.291 706	6.51
	LiCl$_2$	LiCl$_2^-$	EA$_{vert}$	LiCl$_2$	LiCl$_2^-$	VEDE
MBPT(2)	−927.322 106	−927.431 988	2.99	−927.287 191	−927.508 350	6.02
CCSD	−927.350 685	−927.454 352	2.82	−927.316 586	−927.534 106	5.92
CCSD+T	−927.375 926	−927.480 573	2.85	−927.342 761	−927.558 419	5.87
CCSD(T)	−927.375 604	−927.480 318	2.85	−927.342 319	−927.558 226	5.88
	NaF$_2$	NaF$_2^-$	EA$_{vert}$	NaF$_2$	NaF$_2^-$	VEDE
MBPT(2)	−361.560 130	−361.612 416	1.42	−361.519 671	−361.761 897	6.59
CCSD	−361.566 291	−361.600 307	0.93	−361.525 468	−361.753 499	6.20
CCSD+T	−361.590 905	−361.633 031	1.15	−361.552 931	−361.779 322	6.16
CCSD(T)	−361.588 820	−361.627 814	1.06	−361.550 033	−361.777 029	6.18
	NaCl$_2$	NaCl$_2^-$	EA$_{vert}$	NaCl$_2$	NaCl$_2^-$	VEDE
MBPT(2)	−1081.834 791	−1081.922 465	2.38	−1081.794 032	−1082.010 719	5.90
CCSD	−1081.861 832	−1081.942 827	2.20	−1081.820 884	−1082.034 956	5.83
CCSD+T	−1081.889 541	−1081.972 001	2.24	−1081.849 840	−1082.061 763	5.77
CCSD(T)	−1081.888 856	−1081.971 322	2.24	−1081.849 032	−1082.061 201	5.77

TABLE VI. Bond dissociation energies of the molecules and the anions calculated at the CCSD(T)/WMR level. The data for atoms and diatomics are taken from Ref. 78, for triatomics as calculated in the present work.

	Neutral triatomics			Anions		
Channel	D_e, eV	D_e, kcal/mol		Channel	D_e, eV	D_0, kcal/mol
$LiF_2 \rightarrow LiF + F$	0.889	20.51		$LiF_2^- \rightarrow LiF + F^-$	3.013	69.50
$LiCl_2 \rightarrow LiCl + Cl$	1.080	24.91		$LiCl_2^- \rightarrow LiCl + Cl^-$	2.544	58.68
$NaF_2 \rightarrow NaF + F$	0.838	19.33		$NaF_2^- \rightarrow NaF + F^-$	2.123	48.97
$NaCl_2 \rightarrow NaCl + Cl$	1.093	25.21		$NaCl_2^- \rightarrow NaCl + Cl^-$	2.277	52.52

One could assume that other factors such as the electron relaxation and the electron correlation should be taken into account as well. Let us compare different contributions to the VEDEs of F^- and LiF_2^-. The VEDE of F^- equals 4.92 eV at the Koopmans' approximation, 1.18 eV at the ΔSCF level and 3.33 eV at the CCSD(T)/WMR level compared to the experimental value of 3.40 eV.[3] The VEDE of LiF_2^- is 8.03 eV at Koopmans' approximation, 4.55 eV at the ΔSCF level, and 6.51 eV at the CCSD(T)/WMR level. One can see that the VEDE increases when going from F^- to LiF_2^- already at Koopmans' approximation as the result of the three factors mentioned above. However, the VEDE of LiF_2^- becomes somewhat larger, also, as the result of smaller orbital relaxation energy of LiF_2^- (-3.48 eV) than in F^- (-3.74 eV). The contribution from electron correlation equals about 2 eV and is nearly the same for both species. Therefore the decrease in the orbital relaxation contribution to the VEDE of the superhalogen anions with respect to that of halogen atomic anions is also a factor for increasing the VEDE of superhalogen anions with respect to the VEDE of the atomic halogen anions.

IV. THE STRUCTURE OF THE MX$_2$ NEUTRAL SUPERHALOGENS AND ADIABATIC ELECTRON AFFINITIES

A. Structure and thermodynamical stability

The (C_{2v}, $^2B_2$) electronic state with the valence configuration $1a_1^2 1b_2^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2 1a_2^2 3b_2^1$ was found to be the ground state for the MX$_2$ superhalogens in previous ab initio calculations.[62–65] The geometries optimized at three levels of theory are collected in Tables I and II. The bond length and valence angle of LiF_2 optimized at the MBPT(2) and CCSD levels are similar ($\Delta R < 0.01$ Å and $\Delta \angle FLiF < 0.5°$), but they are somewhat different at the DFT level ($\Delta R < 0.09$ Å

and $\Delta \angle FLiF < 9.4°$). The main reason for such a discrepancy is the failure of the DFT method in reproducing the $(F-F)^-$ bond length. Even for the isolated F_2^- anion, the DFT equilibrium bond length of 2.009 Å is substantially longer than the bond length obtained at the MBPT(2) (1.930 Å) and CCSD (1.948 Å) levels. The LiF_2 radical is found to be thermodynamically stable, and its CCSD(T)/WMR dissociation energy of 20.5 kcal/mol towards $LiF + F$ is somewhat larger than the previous estimates of 17.6 and 14.0 kcal/mol obtained at the MBPT(4)/6-311+G(d) and CISD/6-311+G(d) levels, respectively.[64]

The Li–Cl bond lengths and valence angle of $LiCl_2$ optimized at the MBPT(2) and CCSD levels are nearly the same ($\Delta R < 0.03$ Å and $\Delta \angle ClLiCl < 0.6°$), but they are somewhat different from those obtained at the DFT level ($\Delta R \approx 0.11$ Å and $\Delta \angle ClLiCl \approx 2.8°$). The reason for such a discrepancy is again due to the failure of the DFT method in reproducing the $(Cl-Cl)^-$ bond length. For an isolated Cl_2^- anion, the equilibrium bond length of 2.755 Å optimized at the DFT level is larger than obtained at the MBPT(2) (2.651 Å) and CCSD (2.675 Å) levels. The $LiCl_2$ is thermodynamically stable, and its CCSD(T)/WMR dissociation energy of 24.9 kcal/mol (into $LiCl + Cl$) is rather close to the previously computed values[64] of 21.7 [MBPT(4)/6-311+G(d)] and 24.1 [CISD/6-311+G(d)] kcal/mol.

The Na–F bond length and valence angle of NaF_2 optimized at all three levels of theory are rather different for this radical ($\Delta R \approx 0.17$ Å and $\Delta \angle FNaF \approx 6.6°$). Such large discrepancies between the bond lengths optimized at the MBPT(2) and CCSD levels are especially disturbing, and a similar pattern is found for the NaF_2^- anion as well. The NaF_2 radical is thermodynamically stable and possesses a dissociation energy of 19.3 kcal/mol (to $NaF + F$) computed at the CCSD(T)/WMR level, which is substantially higher

TABLE VII. Adiabatic electron affinities (in eV) of MX$_2$, MX, M, and X.

MX$_2$	MBPT(2)[a]	CCSD[a]	CCSD(T)[b]	MX	CCSD(T)[b]	Exp.[c]	A	CCSD(T)[b]	Exp.[d]
LiF$_2$	5.60	5.28	5.45	LiF	0.356	⋯	Li	0.617	0.6180(5)
LiCl$_2$	4.89	4.83	4.97	LiCl	0.577	0.593	Na	0.541	0.5479(25)
NaF$_2$	5.14	4.86	5.12	NaF	0.510	0.520	F	3.317	3.3999(3)
NaCl$_2$	4.62	4.56	4.69	NaCl	0.697	0.727	Cl	3.506	3.617(3)

[a]Basis is 6-31+G(d).
[b]Basis is WMR.
[c]See Ref. 82.
[d]See Ref. 3.

than the previously obtained[64] values of 9.0 [MBPT(4)/6-311+G(d)] and 6.5 [CISD/6-311+G(d)] kcal/mol.

Variations in the geometrical parameters of $NaCl_2$ obtained at all three levels of theory are similar to the variations found for the LiF_2 and $LiCl_2$ species. The Na–Cl bond length and valence angle optimized at the MBPT(2) and CCSD levels are close to each other ($\Delta R < 0.03$ Å and $\Delta \angle ClNaCl < 0.5°$), but they are rather different from those obtained at the DFT level ($\Delta R \approx 0.12$ Å and $\Delta \angle ClNaCl \approx 2.6°$). Such large deviations are again due to the failure of the DFT method in reproducing the $(Cl–Cl)^-$ bond length. The $NaCl_2$ radical is found to be thermodynamically stable and its CCSD(T)/WMR dissociation energy of 25.2 kcal/mol (to $NaCl+Cl$) can be compared to the values of 20.5 [MBPT(4)/6-311+G(d)] and 18.9 kcal/mol [CISD/6-311+G(d)].[64]

B. Vibrational frequencies

Let us first discuss the computed vibrational spectrum of LiF_2 (see Table III). While the $\nu_1(a_1)$ mode at 720 cm^{-1} is similar at all levels of theory, the second $\nu_2(a_1)$ mode varies from 338 cm^{-1} at the DFT level to 426 cm^{-1} at the MBPT(2) level, with an intermediate value of 408 cm^{-1} at the CCSD level. The first mode corresponds to the $Li^+–F_2^-$ interionic motion and the second corresponds to the intraionic $(F–F)^-$ motion. The interionic motion is described well at all levels of theory, while the intraionic motion is very sensitive to the method of calculations, which can be seen from the calculated vibrational frequencies in the isolated F_2^- ion: 365, 468, and 442 cm^{-1} at the DFT/6-311+G(d), MBPT(2)/6-311+G(d), and CCSD/6-311+G(d) levels of theory, respectively. For the third vibrational mode of LiF_2^-, the DFT and CCSD methods produce a discrepancy similar in range to those of the first mode, while the vibrational frequency obtained at the MBPT(2) level is different. This is an indication of a symmetry broken solution along this mode, which could be seen also from the UHF/6-311+G(d) calculations performed by Ju and Davidson,[64] where the $\nu_3(b_2)$ mode was found to be too high (979 cm^{-1}).

Howard and Andrews[60] have assigned the frequency of 452 cm^{-1} to the intraionic $(F–F)^-$ vibration for both $^6LiF_2$ and $^7LiF_2$ species and the mode with the frequency of 708 cm^{-1} to the $Li^+–F_2^-$ interionic motion. Our frequencies presented in Tables I and II correspond to the ^7Li isotope. For a correct comparison, we perform a frequency calculation for $^6LiF_2$ using the DFT force field. The corresponding frequencies are found to be: $\nu_1(a_1)=766$ cm^{-1}, $\nu_2(a_1)=340$ cm^{-1}, and $\nu_3(b_2)=565$ cm^{-1}. There is a substantial isotope shift of 45 cm^{-1} for $\nu_1(a_1)$ and of 30 cm^{-1} for $\nu_3(b_2)$. A small isotope shift of 2 cm^{-1} was found for $\nu_2(a_1)$ in agreement with the experimental findings.[60] According to the results of our calculations, the $\nu_1(a_1)$ vibration should be the most intense in the infrared spectra and the $\nu_2(a_1)$ mode should be the most intense in Raman spectra (Raman intensities are available only at the UHF/6-311+G(d) level of theory), in correspondence with

experimental observations of Howard and Andrews.[60] Therefore one could consider that there is good agreement between experimental and calculated spectra of LiF_2.

The frequencies of $LiCl_2$ computed at all three levels of theory are in better accord with each other than for LiF_2. (We will preserve in this paper the numeration of frequencies widely accepted in theoretical chemistry, namely: a higher frequency of a given symmetry has a higher number. Therefore our ν_1 and ν_2 frequencies correspond to the ν_2 and ν_1 frequencies in Howard and Andrews' articles.[60,61]) The $\nu_1(a_1)$ and $\nu_2(a_1)$ frequencies are similar at the CCSD (536 and 211 cm^{-1}, respectively) and MBPT(2) (543 and 211 cm^{-1}, respectively) levels of theory, but they are somewhat underestimated at the DFT level (503 and 179 cm^{-1}, respectively). The less accurate description at the DFT level seems to be due to the inability of the DFT(B3LYP) method to describe the vibrations in the isolated Cl_2^- ion: $\nu = 198$, 238, and 231 cm^{-1} at the DFT/6-311+G(d), MBPT(2)/6-311+G(d), and CCSD/6-311+G(d) levels, respectively. For the third $\nu_3(b_2)$ vibrational frequency of $LiCl_2$, the DFT and CCSD methods provide almost the same value, while this frequency is overestimated by 93 cm^{-1} with respect to the CCSD value at the MBPT(2) level. Ju and Davidson[64] found the same value of 513 cm^{-1} of the $\nu_3(b_2)$ vibrational frequency at the UHF/6-311+G(d) level, as we found at the MBPT(2)/6-311+G(d) level.

Howard and Andrews[61] have observed a well-resolved triplet at 540.4, 533.0, and 525.6±1.0 cm^{-1} and a very strong band at 243±0.7 cm^{-1} with weak features at 253.4 ±0.7 and 484.7±0.6 cm^{-1} in the Raman spectra of $^7Li^{35}Cl_2$ species. The $Ar–^{37}Cl_2$ (99.5% enriched) experiments with lithium have shown four bands in a Raman scan: a series at 241.4±0.5, 476±0.9, and 707.8±1.0 cm^{-1} and a single band at 522.1±0.5 cm^{-1}. We found from our calculations that the intraionic $(F–F)^-$ frequency $\nu_2(a_1)$ of 211 cm^{-1} has the highest Raman intensity (at the UHF/6-311+G(d) level) and the interionic $(Li^+–Cl_2^-)$ frequency $\nu_1(a_1)$ of 536 cm^{-1} has to be Raman intense in nice agreement with the experimental findings.

The calculated harmonic frequencies of NaF_2 reveal a strong dependence on the method used as well. The $\nu_3(b_2)$ values calculated with different methods are 538 cm^{-1} [UHF/6-311+G(d)],[64] 966 cm^{-1} [MBPT(2)/6-311+G(d)] and 1043 cm^{-1} [CCSD/6-311+G(d)], i.e., one sees unusually large differences. Even at the CCSD level, we have observed a symmetry broken problem for $\nu_3(b_2)$. The stability analysis revealed that this instability is of a ''UHF→UHF of broken symmetry'' type, which corresponds to lowering the symmetry to C_s. We performed additional calculations with ACES II at the CCSD(T)/POL1 level (POL1 is the basis[79] developed for describing polarizabilities), and have not found any instability at this level, see Table IV. The DFT method is found to be free from any symmetry-breaking problem as well.

Howard and Andrews[60] have assigned the frequency of 454 cm^{-1} to the $Na^+–F_2^-$ interionic vibration and the frequency of 475 cm^{-1} to the intraionic $(F–F)^-$ vibration of the NaF_2 radical. These values can be compared to the values of

369 cm^{-1} and 589 cm^{-1}, respectively, calculated at the CCSD(T) level.

Howard and Andrews stated[60] that the ν_1 and ν_2 modes should mix because these modes are of the same a_1 symmetry. They pointed out also a frequency crossover between the interionic and intraionic modes in LiF$_2$ and NaF$_2$, which is in agreement with our computational results. Indeed, we have found the higher frequencies in LiF$_2$, LiCl$_2$, and NaCl$_2$ to correspond to the intraionic mode and the lower frequencies to correspond to the interionic mode. The interionic mode has substantially higher ir intensity (see Table IV) according to the results of our calculations. However, the lower frequency has a higher ir intensity in NaCl$_2$, and the analysis of this mode reveals that it is mainly interionic, while both the ν_1 and ν_2 modes in NaF$_2$ are mixed substantially. Therefore the interionic and intraionic modes in NaF$_2$ have a crossover in correspondence with Howard and Andrews'[60] statement.

As concerns NaCl$_2$, two modes corresponding to the Na$^+$–Cl$_2^-$ interionic motion and to the intraionic (Cl–Cl)$^-$ motion are similar at all three levels of theory. As for the third vibrational mode, the DFT and CCSD methods provide nearly the same results, while the vibrational frequency obtained at the MBPT(2) level bears some attributes of a symmetry-broken solution, which could be anticipated from a rather high infrared intensity of the mode.

Howard and Andrews[61] found that in Ar matrices the most intense signal in the Raman spectra of Na–Cl$_2$ is located at 224.9±0.5 cm^{-1} and a moderately strong band is located at 274.0±1.0 cm^{-1}, while in Xe matrices they found a strong band at 219.1±0.8 cm^{-1} and weaker signals at 254.6±0.9 and 276.0±0.8 cm^{-1}. In the Kr matrices, the 273 cm^{-1} band was found to be five times stronger than the 225 cm^{-1} band. The same features at 225.5 and 272.0 cm^{-1} were found to be strong also in the infrared spectra of Na–Cl$_2$.[61]

According to the results of our calculations, the vibration $\nu_1(a_1)$ of 315 cm^{-1} should be the most intense in the infrared spectra of NaCl$_2$ and the vibration $\nu_2(a_1)$ of 203 cm^{-1} should be the most intense in the Raman spectra (the Raman intensity is available only at the UHF/6-311+G(d) level of theory). Once again, the Na$^+$–Cl$_2^-$ interionic $\nu_1(a_1)$ value is overestimated and the (Cl–Cl)$^-$ intraionic $\nu_2(a_1)$ value is underestimated, as was the value for LiF$_2$. However, we believe that there should be an overall good agreement between the experimental and calculated spectra of NaCl$_2$.

C. Electron affinities

The most accurate EA$_{ad}$ of LiF$_2$ calculated at the CCSD(T)/WMR level is 5.45 eV, which is much higher than the 3.6 eV superhalogen threshold. For comparison, the EA of the fluorine atom calculated at the same level of theory is 3.32 eV versus the experimental value of 3.3999(3) eV.[3] The EA$_{ad}$ equals the adiabatic electron detachment energy (AEDE) and is lower by 1.06 eV than the VEDE (compare entries of Table V and VII) of LiF$_2^-$. The vertical electron

attachment energy (EA$_{vert}$) for LiF$_2$ is the difference in the total energies of LiF$_2^-$ and LiF$_2$ at the equilibrium geometry of the neutral radical and equals 2.18 eV.

The CCSD(T)/WMR EA$_{ad}$ of LiCl$_2$ is 4.97 eV, which is also higher than 3.6 eV; therefore LiCl$_2$ is also a superhalogen. For comparison, the EA of the chlorine atom calculated at the same level of theory is 3.51 eV versus the experimental value of 3.617(3) eV.[3] The EA$_{ad}$ of LiCl$_2$ is lower than the VEDE of LiCl$_2^-$ by 0.91 eV, and the vertical electron attachment energy for LiCl$_2$ is 2.85 eV.

The EA$_{ad}$ of NaF$_2$ calculated at the CCSD(T)/WMR level is 5.12 eV, implying that NaF$_2$ is also a superhalogen. The EA$_{ad}$ of NaF$_2$ is lower by 1.06 eV than the VEDE of NaF$_2^-$, and the vertical electron attachment energy for NaF$_2$ was found to be only 1.06 eV.

The EA$_{ad}$ of NaCl$_2$ calculated at CCSD(T)/WMR level is 4.69 eV, being the lowest in the series considered. However, it is still higher than the superhalogen threshold of 3.6 eV. The EA$_{ad}$ of NaCl$_2$ is lower by 1.08 eV than the VEDE of NaCl$_2^-$, and the vertical electron attachment energy for NaCl$_2$ is found to be 2.24 eV.

V. OVERVIEW

All four systems, LiF$_2$, LiCl$_2$, NaF$_2$, and NaCl$_2$ considered in the present work possess high adiabatic electron affinities (EA$_{ad}$), which have been computed to be 5.45, 4.97, 5.12, and 4.69 eV, respectively, at the CCSD(T) level of theory with a large ANO basis set. While there is no experimental data on the EA$_{ad}$ of the MX$_2$ superhalogens, Miller and Lineberger[83] found that none of the F(NaF)$_n^-$ ions (including FNaF$^-$) can photodetach with 2.540 eV photons, which lends support to the high electron detachment energy of NaF$_2^-$ computed in this work. The EA$_{ad}$s of the diatomic MX molecules computed at the CCSD(T)/WMR level are in excellent agreement (within 0.03 eV) with the experimental data.[82] Even in the ''worst'' cases systems such as F and Cl (see Table VII) and the NH radical,[84] the CCSD(T)/WMR level is capable of reproducing the data obtained with the photodetachment spectroscopy within 0.1 eV. Similar or better accuracy should be anticipated for the EA$_{ad}$ of the MX$_2$ superhalogens.

The EA$_{ad}$s of the LiF$_2$, LiCl$_2$, NaF$_2$, and NaCl$_2$ radicals exceed the highest atomic EA [3.62 eV, Cl (Ref. 3)]; therefore, all these radicals are superhalogens. The radicals are found to be thermodynamically stable with dissociation energies of 20.5, 24.9, 19.3, and 25.2 kcal/mol, respectively. The computed vertical electron attachment energies are substantially lower than the EA$_{ad}$s, namely: 2.18 (LiF$_2$), 2.85 (LiCl$_2$), 1.06 (NaF$_2$), and 2.24 (NaCl$_2$) eV, respectively.

The vertical electron detachment energies (VEDE) for the corresponding LiF$_2^-$, LiCl$_2^-$, NaF$_2^-$, and NaCl$_2^-$ anions are calculated by a fully relaxed ΔCCSD(T) level of theory. The computed VEDEs are 6.51 (LiF$_2^-$), 5.88 (LiCl$_2^-$), 6.18 (NaF$_2^-$), and 5.77 (NaCl$_2^-$) eV, in nice agreement with the values calculated by the ADC(3) approximation of the Green function method.[23]

The dissociation energies of MX_2^- into $MX + X^-$ are found to be 69.5 (LiF_2^-), 58.7 ($LiCl_2^-$), 49.0 (NaF_2^-), and 52.5 ($NaCl_2^-$) kcal/mol, which are substantially higher than those for the neutral parents. This result does not fit the simple MO theory, because an extra electron is detaching from the nonbonding MO, which does not contain any valence contribution from the central atom; therefore, the detachment/attachment cannot be anticipated to seriously affect the stability. This question was addressed previously,[81] and the reason for the destabilization of the neutral parent was related to a strong electron relaxation of the neutral system.

The geometrical parameters of the anions and their neutral parents optimized at the DFT/6-311+G(d), MBPT(2)/6-311+G(d), and CCSD/6-311+G(d) levels are rather similar. However, the X–X bond lengths in the neutral species were found to be off by 0.1 Å at the DFT(B3LYP)/6-311+G(d) level, because of the failure of this method in reproducing the F–F and Cl–Cl bond lengths in the free F_2^- and Cl_2^- anions. There is no reasonable explanation for unexpectedly large Na–F bond lengths obtained at the CCSD/6-311+G(d) level of theory for both NaF_2^- and NaF_2 species.

The calculated frequencies of the anions are found to be in good agreement at all three levels of theory, but for neutral species a symmetry breaking affects the antisymmetric $\nu_3(b_2)$ frequencies at the MBPT(2) and even CCSD levels of theory. Surprisingly, the DFT calculation is free of the symmetry-broken problem.

Taking into account that M–X bond lengths are close to each other in the linear MX_2^- anions and in the corresponding triangular MX_{k+1} neutral parents, whereas the valence angles are changing dramatically from 180° to 69.5° (LiF_2), 78.5° ($LiCl_2$), 47.4° (NaF_2) and 65.1° ($NaCl_2$), one can expect a long progression in photoelectron detachment spectra of the MX_2^- anions with the deformation $\nu_2(a_1)$ mode dominating the spectra. Experimental photodetachment studies of the MX_2^- anions are certainly desirable.

ACKNOWLEDGMENTS

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