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Properties of Closed-Shell, Octahedral, Multiply-Charged Hexafluorometallates MF$_6^{3-}$, M = Sc, Y, La, ZrF$_6^{2-}$, and TaF$_6^-$

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Abstract: Properties of multiply-charged hexafluorometallates MF$_6^{3-}$, M = Sc, Y, La, ZrF$_6^{2-}$, and TaF$_6^-$, have been examined at the SCF, MP2, and Becke3LYP levels of theory using the SBKJ pseudopotentials and extended one-electron basis sets. For MF$_6^{3-}$, M = Sc, Y, La, our results suggest a different assignment of vibrational transitions than those quoted by Nakamoto[1] and recorded by von Becker et al.[2] For the series of isoelectronic complexes, we document that the discrepancy between the theoretical gas phase vibrational frequencies and those measured in condensed phase experiments increases as the Becke3LYP HOMO binding energies become more positive. The frequencies of stretching modes measured in condensed phase experiments are systematically higher than those calculated for the gas phase anions. We suggest that a partial charge transfer from the multiply-charged anions to countercations is responsible for the stiffening of vibrational modes in condensed phase environments. The vertical electron detachment energies were determined at the outer valence Green's function, MP2, and B3LYP levels. The binding energies of hexafluorometallates with respect to the energies of atomic ions were also calculated and only a small contribution of the electron correlation effects was found.

1. Introduction

Properties of triply-charged haxafluorometallates MF$_6^{3-}$, M = Sc, Y, La, reported in the literature[1] were inferred from the vibrational spectra of elpasolites Cs$_2$KMF$_6$.[2] The infrared and Raman spectra recorded by von Becker et al. included lattice vibrations in addition to those of the MF$_6^{3-}$ units.[2] The octahedral symmetry of the MF$_6^{3-}$ is probably not seriously altered by the crystalline environment as deduced from the small distortions of the peaks corresponding to degenerate vibrational modes,[2] as well as the bond lengths in crystalline phases.[3−5]

LaF$_6^{3-}$ has recently been recognized as a candidate for the triply-charged anion which may be electronically stable in the gas phase.[6] It possesses a closed-shell electronic structure and a O_h local minimum. Atomic charges determined from a fit to the electrostatic potential indicate that the complex is highly ionic and may be qualitatively interpreted as six F$^-$ ions coordinated to a La^{3+} cation. The vertical electron detachment (VED) energy for the LaF$_6^{3-}$ anion calculated using the third-order electron propagator method was found to be 0.78 eV. The complex is predicted to be thermodynamically unstable with respect to LaF$_5^{2-}$ + F$^-$, but the long-range Coulomb energy barrier along the decomposition path, which is typical for multiply-charged species,[7−10] may guarantee its kinetic stability.

Vibrational frequencies of LaF$_6^{3-}$ were calculated at the SCF level of theory.[6] The discrepancies between the theoretical and recommended experimental data[1] were quite significant and irregular. For instance, the calculated frequencies of two infrared active t$_{1u}$ modes were too high by 98 and 146 cm^{-1}, whereas the Raman active modes' frequencies were systematically too low (105 cm^{-1} for the a$_{1g}$ mode). These discrepancies were larger than usual errors resulting from the SCF harmonic approximation.

The discrepancies might be caused by any of four factors: (a) methodological deficiencies of the previous calculations (neglect of correlation effects, insufficient treatment of relativistic effects, and limited one-electron basis set used in ref 6); (b) marginal electronic stability of LaF$_6^{3-}$, which causes its properties to be strongly affected by the environment; (c) profound anharmonic effects; and (d) improper assignment of the experimentally observed vibrational transitions.

In this work we explore some of these possibilities. First, we extended our calculations beyond the SCF model. Electron correlation effects were included at the second-order Møller−Plesset (MP2) level of theory as well as using a variant of the density functional theory referred to as Becke3LYP (B3LYP).[11−15] Moreover, the quality of our one-electron basis set was improved. Second, we studied not only LaF$_6^{3-}$ but also YF$_6^{3-}$ and ScF$_6^{3-}$, which are expected to be less electronically stable or even unstable in the gas phase. We also calculated properties of the isoelectronic but electronically very stable anions ZrF$_6^{2-}$ and TaF$_6^-$, whose VED energies were recently found to be 5.0

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and 10.6 eV, respectively, at the third-order electron propagator theory level.[6] For this series of isoelectronic but differently charged molecular anions we monitored the extent to which the discrepancy between theoretical and experimental vibrational frequencies may be related to the electronic instability.

In this paper, we demonstrate that the above discrepancy for the t_{1u} modes of MF_6^{3-} (M = Sc, Y, La) can be reduced by a different assignment of the experimental peaks.[2] But even then, the frequencies of vibrational modes observed in the condensed phase experiments differ significantly from our MP2 and B3LYP gas phase results. Such discrepancies are not observed when we consider the electronically very stable TaF_6^- anion. We then speculate that the discrepancies observed for triply-charged anions are invariably related to the counterion environment which produces their stability.

A more general issue is how we should think about anions which are routinely considered as constituents of solids, melts, and solutions. Even for singly-charged anions there are many controversial issues, as for example polarizabilities of halides.[16−25] It was recognized long ago that accurate theoretical polarizabilities for free halides[16,17] differ by as much as 100% from the polarizability data for ionic crystals or from the solution polarizabilities of salts.[18−20] In theoretical studies for ionic clusters, it was demonstrated that the halide polarizabilities are dramatically supressed by the electrostatic crystal field[21−23] and by overlap effects with the neighboring ions.[22−24] It was concluded that the empirical model of in-crystal polarizabilities must incorporate the environmentally induced variations of anion polarizabilities.[25]

The issues become more convoluted as we consider multiply-charged anions,[7−10] the vast majority of which are electronically unstable in the gas phase.[26,27] However, the X-ray experiments clearly confirm their existence in the crystalline phase, at least in the structural sense.[3−5,28−31] Furthermore, a neutron[32] and X-ray diffraction study of MCl_3 (M = Y, La)[33] combined with the results of earlier Raman scattering experiments on yttrium−[34] and lanthanum chloride−alkali chloride mixtures,[35] has demonstrated that the trivalent metal atom in the melt is in a state of rather stable octahedral-type coordination by halide first neighbors.

A statistical mechanical modeling of such systems requires, among other factors, interaction potentials for the coordinated complexes and their binding energies *in vacuo* defined with respect to the energy of isolated atomic ions.[36−39] Of course, there is a formal issue to what extent the concept of the *in vacuo* complex is meaningful for such electronically unstable systems and whether its properties are adequate for the statistical mechanical simulations. Nevertheless, Erbölükbas et al. developed the charged-soft-sphere potential for isolated MCl_6^{3-} species supplemented by the polarization terms.[40] Akdeniz demonstrated the strong thermodynamic stability of the octahedral MCl_6^{3-} complexes in Y−alkali and La−alkali chloride solutions independent of the nature and concentration of the alkali counterions.[41]

In this work, we determine binding energies for the MF_6^{3-} (M = Sc, Y, La), ZrF_6^{2-}, and TaF_6^- complexes *in vacuo* at the SCF, MP2, and B3LYP levels. The work on analogous hexachlorometallates is underway in our group.

2. Computational Aspects

We used the relativistic, compact effective potentials of Stevens et al. together with their valence, energy-optimized, shared-exponent, contracted Gaussian basis sets.[42,43] We label this combination of pseudopotentials and basis sets SBKJ. For the M atoms (M = Ta, Zr, Sc, Y, La), and (n − 1)s, (n − 1)p, ns, np, and (n − 1)d orbitals are chemically active and take advantage of the double-ζ sp and triple-ζ d basis sets. For the F atom, only the valence 2s and 2p orbitals are chemically active, and they are described within a double-ζ quality basis set. Altogether, there are 56 chemically active electrons in the SBKJ calculations for these closed-shell anionic complexes.

Next, the SBKJ basis sets were *supplemented* with different sets of diffuse and polarization functions. For the F atom, we tested one- and two-term sets of diffuse s and p functions, as well as a polarization d function, whereas for the M atoms we allowed for one set of diffuse s, p, and d functions. The exponents of the one-term diffuse basis sets were taken to be equal to $^1/_3$ of the lowest exponent in the original basis. For the two-term diffuse sets, a geometrical progression was assumed with the progression constant equal to 2.4. The exponent of the polarization d function on F was 0.80.

Numerical tests described in the next section (see also refs 6,[6,44−47] suggested exploring the following *sequence* of one-electron basis sets: (a) the original SBKJ set (82 contracted Gaussian type orbitals (CGTO)); (b) the SBKJ set supplemented with the one-term of diffuse s and p functions on F, denoted SBKJ+d (106 CGTO's); (c) the SBKJ+d set supplemented with the one-term set of diffuse s, p, and d functions on M and one d polarization function on F, denoted SBKJ+ddp (152 CGTO's); and (d) the SBKJ+ddp set supplemented with the second set of diffuse s and p functions on F and denoted SBKJ+dddp (176 CGTO's).

The SCF equilibrium geometries and harmonic vibrational frequencies were refined at the MP2 level and the B3LYP hybrid method.[11−15] The accuracy of the MP2 optimized geometries and harmonic frequencies is well documented[48] whereas B3LYP is a density functional theory (DFT) method in which the exact (Hartree−Fock) exchange is combined with local and gradient-corrected exchange and correlation terms.[11]

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Preliminary indications are that the B3LYP functional is the best so far proposed, at least for estimating energetics of chemical processes[14] and vibrational frequencies.[15]

The diffuseness of the charge distribution for the systems studied here makes the DFT calculations more time consuming than in standard applications for neutral systems. We found that not only the "Coarse Grid" but even the "Fine Grid" with 75 radial shells and 302 angular points per atom is not sufficient. The G92/DFT code[49] encountered problems with spurious integrated densities and the SCF iterative procedure frequently failed to converge. In many cases, the more accurate grid of 99 radial shells and 302 angular points was found to be necessary. This, however, makes the B3LYP calculations more CPU demanding than the MP2 approach.

The complexes studied here may be viewed as consisting of ionic atoms.[6] Hence, the computational methods will be tested with respect to their ability to reproduce the electron affinity of F as well as the first few ionization potentials of the M atoms.

The vertical electron detachment energies for the octahedral closed-shell complexes were calculated directly, using the outer valence Green's function (OVGF) third-order method,[50-52] and indirectly, i.e., calculating the energy of the n-electron closed-shell anion and $(n - 1)$-electron open-shell species at the MP2 and B3LYP levels. While the third-order OVGF method is not very accurate for the isolated fluoride anion,[53] it may be reliable for fluorine-containing compounds.[51]

We calculated two quantities which characterize the electron charge distribution in octahedral complexes. First, the radial extent of the distribution is characterized by the mean value of R^2 ($\langle R^2 \rangle$). Second, the effective charges assigned to the M and F atoms were determined from a fit to the electrostatic potential at points selected according to the Merz−Singh−Kollman scheme.[54] For atomic radii, we used 1.60 (Sc), 1.80 (Y), 1.88 (La), 1.57 (Zr), 1.43 (Ta), and 1.36 (F^-) Å.[55] Effective atomic charges and values of $\langle R^2 \rangle$ have been calculated with electron densities and equilibrium geometries corresponding to the SCF, B3LYP, and MP2 levels of theory.

The dissociation energies of MX_6^{n-} into $6F^- + M^{(6-n)+}$ were also calculated. This dissociation limit is employed in statistical mechanical models of melts[37-39] in which the atomic ions are assumed to be building blocks. The attractive interaction within the complexes is expected to be dominated by the electrostatic interactions among the ions and slightly enhanced by the dispersion and induction terms. The dipole polarizabilities of atomic ions are also calculated to judge the quality of the latter interaction energy terms.

The counterpoise method of Boys and Bernardi was used to assure numerical consistency in calculations of the complex and the atomic ions' energies.[56] The standard function counterpoise method was used at the SCF and MP2 levels but it is not sufficient at the B3LYP level due to the numerical integrations involved. For such cases, Boys and Bernardi recommended performing numerical integrations with the same set of points and weights for the supermolecule and its isolated constituents to enforce a numerical consistency. The procedure was dubbed the point counterpoise method.[56] Our B3LYP binding energies were obtained in such function and point counterpoise calculations.

Due to the highly ionic character of the MX_6^{n-} species[6] and the isodesmic character of the decomposition process, the majority of the binding energy should be reproduced already at the SCF level of theory. The MP2 values of the binding energy are also calculated to evalute the importance of correlation effects such as the dispersion interaction and correlation corrections to the valence repulsion, induction, and electrostatic terms.[57]

Table 1. Basis Set Dependence of the LaF_6^{3-} Properties at the SCF and MP2 Levels of Theory[a]

method/basis set	R_{LaF}	ϵ_{HOMO}	$\langle R^2 \rangle$	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_3(t_{1u})$	$\nu_4(t_{1u})$
SCF/SBKJ	2.462	−1.23	1146	351	276	295	163
SCF/SBKJ+d	2.475	−1.69	1162	338	258	276	161
SCF/SBKJ+ddp	2.465	−1.56	1151	340	252	267	159
SCF/SBKJ+dddp	2.463	−1.57	1150	341	252	267	159
MP2/SBKJ+d	2.498	−1.75	1187	322	245	262	154
MP2/SBKJ+ddp	2.468	−1.58	1160	329	246	262	152

[a] R_{LaF} in Å, orbital energy of the highest occupied orbital (ϵ_{HOMO}) in eV, $\langle R^2 \rangle$ in au, vibrational frequencies in cm^{-1}.

Much less in known about the physical content of the B3LYP interaction energy. Only recently, Kristyán and Pulay demonstrated numerically that the counterpoise corrected DFT interaction energies fail to reproduce dispersion interactions in the van der Waals minimum region,[58] which is a serious deficiency that should be taken into account even for the highly ionic systems studied here.

Our calculations were performed primarily with the Gaussian 92/DFT[49] and Gamess[59] codes. The OVGF VED energies were obtained with the Gaussian 94 code.[60]

3. Results and Discussion

1. Basis Set Trends. The saturation of our results with respect to systematic extensions of the SBKJ basis set was tested for all hexafluorometallates but, for the sake of brevity, only the results for LaF_6^{3-} are presented in Table 1 at the SCF and MP2 levels of theory. Convergence for the t_{2g} and t_{2u} vibrational modes is not addressed in Table 1 since these frequencies were stable to 3 cm^{-1} for all basis sets.

The results presented in Table 1 indicate that the equilibrium distance R_{LaF} is affected by less than 0.005 Å for basis set extensions above SBKJ+ddp, at least at the SCF level of theory. The equilibrium R_{MF} distance is systematically longer at the MP2 level than at the SCF level, but the difference does not exceed 0.03 Å.

The values of $\langle R^2 \rangle$ reported in Table 1 are affected by both the diffuseness of the electron charge distribution and the equilibrium distance R_{LaF}. Their values indicate that even the SBKJ+d basis set is well suited to deal with the electron distribution in triply-charged anions.

The basis set extension from SBKJ+d to SBKJ+ddp affects vibrational frequencies by less than 10 and 8 cm^{-1} at the SCF and MP2 level, respectively, see Table 1. Further extension to the SBKJ+dddp basis set changes frequencies by not more than 1 cm^{-1} at the SCF level of theory. Therefore, we conclude that the SBKJ+ddp basis set is appropriate for further applications. Thus, to conserve space, only the SBKJ+ddp basis set results are presented in the later discussion.

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Table 2. The Basis and Method Dependence of the Vertical Electron Detachment Energy (eV) of F$^-$ (Experimental Result 3.399 eV[63])

	SBKJ+	6-311+	6-311+	aug-cc-pv			
method	ddp[a]	G*	G(2df)	DZ	TZ	TZ[b]	QZ
Koopmans	4.84	4.83	4.83	4.93	4.92	4.92	4.92
ΔPUHF	1.17	1.18	1.11	1.21	1.11	1.11	1.09
ΔPMP2	3.30	3.21	3.39	3.51	3.60	3.60	3.67
ΔPMP3	2.88	2.69	2.87	3.00	3.02	3.03	3.08
ΔPMP4	3.21	3.06	3.22	3.38	3.48	3.49	3.55
ΔMP5	2.87	2.82	2.97	3.04	3.12	3.12	3.18
ΔQCISD	3.06	2.89	3.02	3.18	3.20	3.20	3.25
ΔQCISD(T)	3.06	2.96	3.11	3.24	3.33	3.33	3.40
ΔQCISD(TQ)	2.99	2.92	3.07	3.18	3.26	3.26	3.32
OVGF[c]	4.97	4.27	4.39	5.05	5.00	5.00	5.02
ΔB3LYP	3.35	3.49	3.46	3.56	3.53	3.53	3.55

[a] Basis set used in this work for large systems. [b] All electrons were included in correlation calculations. [c] Method B from ref 51.

2. Atomic Properties. For the complexes studied in this paper, the HOMO and a few next occupied orbitals are dominated by the F's 2p atomic orbitals.[6] Hence, the lowest electron detachment energies correspond to the hole formation in the fluoride framework. Therefore, we calibrated accuracy of our computational approach on the isolated F$^-$ ion (see Table 2).

Accurate computation of the electron detachment energy for atomic and molecular anions requires large atomic basis sets and extended treatment of electron correlation.[61] F$^-$ is notoriously difficult and the Møller−Plesset series converges slowly with large oscillations between consecutive orders, see Table 2. The MP2 results are satisfactory, especially for smaller basis sets, but a significant deterioration occurs at the third-order. The fifth-order result obtained with the state-of-the-art aug-cc-pvQZ basis set[62] still differs by 0.22 eV from the experimental value of 3.40 eV.[63] The convergence is clearly accelerated and oscillation dampened at the QCI level.[64]

The third-order OVGF method systematically overshoots the experimental result, see also ref 53, and the discrepancy stabilizes at 1.6 eV for the largest basis sets. The OVGF results reported in Table 2 correspond to method B from ref 51, which is recommended in the Gaussian 94 code.[60] The results from methods A and C from ref 51, not reported in Table 2, are actually closer to the experimental result but still too large.

The B3LYP method performs very well and the discrepancy from the experimental result never exceeds 0.13 eV. In addition, saturation of the B3LYP results requires only s and p symmetry functions, whereas in the conventional many-body or CI approaches the high angular momentum basis functions are critical.[65−67]

The closed-shell $(n-1)s^2(n-1)p^6$ cations are considered as constituents of the hypothetical purely ionic complexes. Hence, the first few ionization potentials of the M atoms were calculated at the SCF, MP2, and B3LYP levels and compared with available experimental results.[68−72] To the best of our knowledge, for the Ta atom only the first ionization potential is experimentally known.[72] The spin−orbit coupling effects are not taken into account in our calculations. For the heaviest La and Ta atoms, the multiplet components of an atomic term may span the range of a few tenths of an electronvolt.[68]

Table 3. Dipole Polarizabilities and the Values of $\langle R^2 \rangle$ for Atomic Ions Calculated with the SBKJ+ddp Basis Set at the SCF, B3LYP, and MP2 Levels of Theory

method	F$^-$	Sc^{3+}	Y^{3+}	La^{3+}	Zr^{4+}	Ta^{5+}
			Dipole Polarizabilities in au			
SCF	5.02[a]	2.01	4.04	7.71	2.96	2.35
MP2	6.59[b,c]	1.97	3.99	7.62	2.91	2.32
B3LYP	6.81	2.05	4.08	7.72	2.98	2.37
ref 18	7.02	1.93	3.71	7.02	2.50	
			$\langle R^2 \rangle$ in au			
SCF	15.9	11.7	17.9	26.9	15.3	14.1
MP2	17.4	11.7	18.0	27.1	15.4	14.1
B3LYP	17.3	11.7	17.8	26.7	15.3	14.1

[a] SCF limit is 10.66.[74] [b] MP2 limit is 16.67.[74] [c] MP4 limit is 20.37.[74]

We have found that the B3LYP results are systematically closest to the experimental data. Overall, our B3LYP ionization potentials agree with the experimental results to 0.6 eV for the trivalent atoms and to 0.4 eV for the Zr atom.

For the neutral Ta atom, the B3LYP first ionization potential of 7.49 eV differs by 0.4 eV from the experimental data and the lowest energy term of the neutral atom (^{4}F) and the singly-charged cation (^{5}F) are consistent with the experimental findings.[68] The higher B3LYP ionization potentials of 15.32, 24.40, 36.42, and 48.70 eV, which correspond to the formation of the Ta^{2+}(^{4}F), Ta^{3+}(^{3}F), Ta^{4+}(^{2}D), and Ta^{5+}(^{1}S) cations, are probably accurate to 0.6 eV.

At the B3LYP level, formation of the closed-shell $(n-1)s^2(n-1)p^6$ cations from the neutral M atoms requires 45.1, 39.4, 36.0, 77.7, and 132.3 eV for Sc, Y, La, Zr, and Ta, respectively. The corresponding experimental data for the first four atoms are very close to our findings and amount to 44.2, 39.4, 36.2, and 79.8 eV.[72] For the Ta atom, an extrapolated result is 132.0 eV.[73]

Our theoretical dipole polarizabilities (α) of atomic ions are compared in Table 3 to the semiempirical[18] and other theoretical results.[74] The MP2 and B3LYP results for F$^-$ are in satisfactory agreement with the semiempirical data.[18] However, when compared with the exact theoretical results of Diercksen and Sadlej,[74] the SBKJ+ddp α is underestimated by 50% at the SCF level of theory, and the error increases at the correlated level. Therefore, the induction and dispersion components of the binding energy will be underestimated in our SBKJ+ddp calculations. For the closed−shell metal cations, the correlation corrections to the SCF α's are quite small (see Table 3), and our theoretical results are probably quite accurate, see also ref 75.

3. Physical Properties of Complexes. For triply-charged anions, the shortest R_{MF} is obtained for the B3LYP method, the largest for the MP2 method, with the magnitude of the discrepancy decreasing from 0.011 Å for ScF$_6^{3-}$ to 0.004 Å

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Table 4. Properties of the Octahedral, Closed-Shell MF_6 Anions Calculated with the SBKJ+ddp Basis Set at the SCF, B3LYP, and MP2 Levels of Theory[a]

system	method	R_{MF}	ϵ_{HOMO}	$\langle R^2 \rangle$	$\langle Q_F \rangle$	D_e
ScF_6^{3-}	SCF	2.112	−0.44	857	−0.916	1132
	B3LYP	2.106	+4.84	859	−0.941	1156
	MP2	2.117	−0.46	867	−0.927	1120
YF_6^{3-}	SCF	2.276	−1.03	989	−0.916	1048
	B3LYP	2.274	+4.25	991	−0.924	1056
	MP2	2.282	−1.03	998	−0.920	1035
LaF_6^{3-}	SCF	2.465	−1.55	1151	−0.937	969
	B3LYP	2.464	+3.67	1155	−0.936	975
	MP2	2.468	−1.58	1160	−0.941	959
ZrF_6^{2-}	SCF	2.052	−6.04	805	−0.726	2087
	B3LYP	2.061	−0.49	812	−0.712	2127
	MP2	2.067	−6.10	818	−0.720	2077
TaF_6^{-}	SCF	1.901	−11.95	690	−0.533	3335
	B3LYP	1.922	−6.18	701	−0.481	3416
	MP2	1.923	−11.97	704	−0.489	3331

[a] R_{MF} in Å, orbital energy of the highest occupied orbital (ϵ_{HOMO}) in eV, $\langle R^2 \rangle$ in au, effective atomic charge on F (Q_F) in au, counterpoise-corrected binding energies (D_e) in kcal/mol.

Table 5. The OVGF,[a] MP2, and B3LYP Vertical Electron Detachment Energies (in eV) Calculated with the SBKJ+ddp Basis Sets at the MP2/SBKJ+ddp Geometries

system	method	final state[b]	VED
ScF_6^{3-}	OVGF	$^2T_{1g}$	−0.17
	OVGF	$^2T_{1u}$	0.12
	OVGF	$^2T_{2u}$	0.20
	MP2	$^2T_{1g}$	−1.78
	B3LYP	$^2T_{1g}$	−2.82
YF_6^{3-}	OVGF	$^2T_{1g}$	0.48
	OVGF	$^2T_{1u}$	0.70
	OVGF	$^2T_{2u}$	0.75
	MP2	$^2T_{1g}$	−1.17
	B3LYP	$^2T_{1g}$	−2.27
LaF_6^{3-}	OVGF	$^2T_{1g}$	1.08
	OVGF	$^2T_{1u}$	1.07
	OVGF	$^2T_{2u}$	1.26
	MP2	$^2T_{1g}$	−0.66
	B3LYP	$^2T_{1g}$	−1.79
ZrF_6^{2-}	OVGF	$^2T_{1g}$	5.11
	OVGF	$^2T_{1u}$	5.39
	OVGF	$^2T_{2u}$	5.51
	MP2	$^2T_{1g}$	3.58
	B3LYP	$^2T_{1g}$	2.69
TaF_6^{-}	OVGF	$^2T_{1g}$	10.62
	OVGF	$^2T_{1u}$	10.98
	OVGF	$^2T_{2u}$	11.14
	MP2	$^2T_{1g}$	9.14
	B3LYP	$^2T_{1g}$	8.54

[a] Method B from ref 41. [b] $^2T_{1g}$, $^2T_{1u}$, and $^2T_{2u}$ are the electronic open-shell doublet states resulting from the electron removal from HOMO, HOMO-1, and HOMO-2, respectively.

for LaF_6^{3-}, see Table 4. For ZrF_6^{2-} and TaF_6^{-}, the MP2 values of R_{MF} remain the largest, but the B3LYP results follow closely and the magnitude of the SCF-MP2 discrepancy slightly increases to 0.015 (ZrF_6^{2-}) and 0.022 Å (TaF_6^{-}).

The SCF values of ϵ_{HOMO}, reported in Table 4, offer the zero-order estimation of the VED energy. For the systems studied here, the sum of the electron correlation and relaxation terms lowers the Koopmans' theorem (KT) prediction of the VED energy. The third-order OVGF results presented in Table 5 for the first three IP's of every closed-shell octahedral anion demonstrate that the correlation/relaxation effect amounts to about a half an electronvolt for the triply-charged anions. At the OVGF level, LaF_6^{3-} and YF_6^{3-} are electronically stable by 1.08 and 0.48 eV, respectively. The ScF_6^{3-} anion is, however, electronically unstable.

The correlation and relaxation corrections to the KT prediction of the detachment energy are even more destabilizing for the doubly- and singly-charged anions and amount to 0.98 and 1.36 eV for ZrF_6^{2-} and TaF_6^{-}, respectively. Both anions are electronically very stable at the OVGF level with the VED energies of 5.1 and 10.6 eV, respectively, hence in good agreement with earlier predictions.[6] The pole strength in the OVGF calculations reported in Table 5 never dropped below 0.93.

The electronic stability of the complexes may be easily overestimated at the OVGF level, as suggested by the results for the isolated F^- reported in Table 2. In fact, the MP2 VED energies for the complexes are smaller by ca. 1.5 eV than the OVGF results (see Table 5). The B3LYP VED energies are even smaller and differ by ca. 1 eV from the MP2 results. Clearly, the resolution of the electronic stability of the triply-charged anions requires methodologies more advanced than OVGF or MP2.

The Koopmans' theorem interpretation of orbital energies does not apply to the density functional formalism. There, $\epsilon_j = \partial E_{DFT}/\partial n_j$, where E_{DFT} is the total energy and ϵ_j and n_j are the orbital energy and the orbital occupation number, respectively.[76] The B3LYP ϵ_{HOMO} values reported in Table 4 are positive for the triply-charged anions, which indicates that for these complexes a decrease of the HOMO occupation would decrease the total B3LYP energy (stabilize the complex). A positive value of ϵ_{HOMO} does not mean that the anion is electronically unstable. For instance, the B3LYP/SBKJ+ddp ϵ_{HOMO} value for F^- is +0.13 eV, but the VED energy is 3.35 eV, in satisfactory agreement with the experimental result 3.40 eV.[63] Only for the ZrF_6^{2-} and TaF_6^{-} anions are the B3LYP orbital energies negative, hence supporting an unusual electronic stability of these anions.

The values of $\langle R^2 \rangle$ presented in Table 4 remain quite stable for every anion, irrespective of the computational method used. The MP2 values are systematically the largest and the SCF values the smallest, but the extraction of the correlation effect on $\langle R^2 \rangle$ requires the same value of R_{MF} in the SCF and MP2 calculations. Such results (not presented in Table 4) demonstrate that the correlation correction actually increases the value of $\langle R^2 \rangle$ and is essentially constant for all triply-charged anions at ca. 6 au. For ZrF_6^{2-} and TaF_6^{-} the correction is smaller and amounts to 2.8 and 0.8 au, respectively.

The fluctuations among the SCF, B3LYP, and MP2 values of the atomic charges Q_F do not exceed 0.05 au, see Table 4. For all triply-charged anions, the values of the fluorine atomic charge remain above 0.9 au in magnitude. This confirms the highly ionic character of these species. The ionicity decreases for the doubly- and singly-charged anions to the extent that the Q_F value for TaF_6^{-} drops below 0.5 au. This trend is a consequence of the large ionization potentials accompanying the formation of Zr^{4+} and Ta^{5+}.

The counterpoise-corrected values of D_e are reported in the last column of Table 4. We reiterate that these binding energies are defined with respect to the energy of isolated atomic ions. Typical values of the counterpoise corrections are 3 and 20 kcal/mol at the SCF and MP2 level, respectively. At the B3LYP level and the integration grid of 99 radial and 302 angular points per atom, the value of the cunterpoise correction is 20 kcal/mol for TaF_6^{-} and ca. 5 kcal/mol for other complexes.

It is instructive to compare the D_e values from Table 4 with the binding energies calculated in the ionic limit model (every atom is considered as a point charge: −1 (F), +3 (Sc, Y, La),

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Table 6. Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol, in parentheses) for the Octahedral Closed-Shell MF_6^{3-} Anions Calculated with the SBKJ+ddp Basis Set at the SCF, B3LYP, and MP2 Levels of Theory

system	method	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_3(t_{1u})$	$\nu_4(t_{1u})$	$\nu_5(t_{2g})$	$\nu_6(t_{2u})$
ScF_6^{3-}	SCF	405	281	400 (418.7)	245 (1.4)	216	125 [153][a]
	B3LYP	392	260	362 (460.7)	218 (1.3)	199	111 [140][a]
	MP2	394	276	386 (415.3)	235 (0.3)	210	125 [148][a]
Nakamoto[1]	IR/raman	498	390	176	90	230	[163][a]
Becker[2]	IR/raman	498	390	482	265	230	[163][a]
Turrell[82]	IR/raman	495	375	458	257	235	[166][a]
YF_6^{3-}	SCF	375	276	317 (331.4)	200 (23.6)	186	102 [132][a]
	B3LYP	364	262	296 (355.5)	182 (11.3)	173	90 [122][a]
	MP2	363	270	305 (329.1)	190 (17.4)	178	96 [126][a]
Nakamoto[1]	IR/raman	476	382	160	74	194	[137][a]
Becker[2]	IR/raman	476	382	419	200	194	[137][a]
LaF_6^{3-}	SCF	340	252	267 (313.6)	159 (38.6)	160	82 [113][a]
	B3LYP	329	240	253 (335.0)	141 (23.6)	148	66 [105][a]
	MP2	329	246	262 (315.7)	152 (31.5)	153	77 [108][a]
Nakamoto[1]	IR/raman	443	334	130	63	171	[121][a]
Becker[2]	IR/raman	443	334	362	170−130	171	[121][a]
ZrF_6^{2-}	SCF	551	444	488 (403.3)	234 (45.6)	230	117 [163][a]
	B3LYP	522	420	464 (404.7)	208 (30.2)	214	98 [151][a]
	MP2	527	425	464 (401.7)	217 (35.4)	222	108 [157][a]
Nakamoto[1]	IR/raman	589	416	522, 537	192, 241	244, 258	[172, 182][a]
Lane[84]	IR/raman	579−588	450−452	496−530	196−236	236−255	[167−180][a]
TaF_6^{-}	SCF	718	596	594 (352.0)	242 (63.5)	292	135 [206][a]
	B3LYP	659	557	567 (316.4)	211 (44.3)	267	107 [189][a]
	MP2	670	560	561 (342.8)	219 (48.4)	274	123 [193][a]
Nakamoto[1]	IR/raman	692	581	560	240	272	[192][a]
Gantar[85]	IR/raman	692−702	581−583	560−582	232	272−300	[192−212][a]

[a] Estimated from the relation $\nu_6 = \nu_5/\sqrt{2}$.

+4 (Zr), +5 (Ta), and only the Coulomb interactions are considered). At the MP2 equilibrium geometries, the ionic limit binding energies are as follows: 1257 kcal/mol for ScF_6^{3-}; 1166 kcal/mol for YF_6^{3-}; 1078 kcal/mol for LaF_6^{3-}; 2252 kcal/mol for ZrF_6^{2-}; and 3456 kcal/mol for TaF_6^{-}. These energies are quite close to the corresponding numbers in Table 4. The qualitative agreement is understandable for the highly ionic triply-charged anions and the discrepancy of ca. 100 kcal/mol may be attributed to the valence repulsion energy, which is neglected in the ionic model. For ZrF_6^{2-} and TaF_6^{-}, the minimum develops before the MF distance is small enough that the complete charge transfer is energetically favorable. It is then surprising that the ionic model binding energies are larger than the ab initio predictions.

The differences among the SCF, B3LYP, and MP2 values of D_e are also unexpected, in particular for the highly ionic triply-charged anions, which may be considered as six fluoride ions interacting with the M^{3+} cation. The electron correlation effects increase the polarizability of F^-, see Table 3, thus increasing the attractive induction interaction at the MP2 and B3LYP levels of theory. In addition, for the MP2 method, the attractive dispersion interaction is taken into account. Despite such arguments, the total computed binding energy is systematically the smallest at the MP2 level and the largest at the B3LYP level.

There are at least two reasons for the unexpected values of the theoretical interaction energies. First, our recent results indicate that non-pairwise interactions constitute a significant fraction of the interaction energy for hexafluorometallates.[77] Second, the electron correlation effects increase not only the dipole polarizability of F^- but also the spatial extent of its electron distribution, as indicated by the values of $\langle R^2 \rangle$ reported in Table 3. In consequence, the valence repulsion for the $M^{3+}-F^-$ and $F^- - F^-$ pairs might increase substantially. Such an effect has been observed for the interaction of F^- with noble gases,[74,78,79,80] where the correlation contribution to the interaction energy curve is also surprisingly small.

4. Vibrational Frequencies. The harmonic vibrational frequencies for the hexafluorometallates calculated at the SCF, MP2, and B3LYP levels of theory are reported in Table 6 and compared with the experimental condensed phase data.

For every complex and each vibrational mode, the SCF frequencies are the largest and the B3LYP frequencies are usually the smallest, indicating that correlation effects systematically lower the computed vibrational frequencies, although the correlation effects rarely exceed 40 cm^{-1}, in agreement with common experience.[48] More specifically, the difference between the SCF and B3LYP frequencies does not exceed 59, 39, 38, 31, 25, and 28 cm^{-1} for the a_{1g}, e_g, t_{1u} (stretching), t_{1u} (bending), t_{2g}, and t_{2u} mode, respectively.

The discrepancies between the MP2 and B3LYP results serve as an indication how far the results may be from the "exact" harmonic frequencies. These differences are small and do not exceed 11, 16, 24, 17, 11, and 16 cm^{-1} for the a_{1g}, e_g, t_{1u} (stretching), t_{1u} (bending), t_{2g}, and t_{2u} mode, respectively.

As far as the two IR active t_{1u} modes are concerned, the computed transition intensity is always larger by one or even two orders of magnitude for the higher frequency stretching mode than for the lower frequency bending mode.

Our theoretical results are in satisfactory agreement with the experimental data for the TaF_6^{-} complex. However, for ZrF_6^{2-} the discrepancies reach 60 cm^{-1} (the stretching a_{1g} and t_{1u} modes), and for the triply-charged complexes discrepancies above 110 cm^{-1} are found for the a_{1g}, e_g, and t_{1u} modes.

There are at least two likely sources for these discrepancies. First, as we argue below, the t_{1u} vibrational frequencies of the triply-charged anions reported in the Nakamoto tables[1] may not correspond to the frequencies of the MF_6^{3-} moieties but to lattice modes. In fact, a different assignment of the experimental peaks

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recorded by von Becker et al.[2] offers more consistent t_{1u} vibrational frequencies. Second, as we also suggest below, the larger values of the vibrational frequencies observed in condensed phase experiments may result from partial electron charge transfer from the anion to neighboring countercations.

In the IR spectra recorded by von Becker et al. for elpasolites Cs_2KMF_6, M = Sc, Y, La, the highest frequency peak (345−500 cm^{-1}) is significantly more intensive than the second peak, which is in the range of 130−265 cm^{-1}. Neither of these peaks was assigned by Nakamoto to the MF_6^{3-} moieties; rather he chose two peaks with much lower frequencies and quite similar intensities to assign to MF_6^{3-}.[1]

Our results indicate, however, that the higher frequency t_{1u} peak of MF_6^{3-} should be much more intensive than the second t_{1u} peak. Moreover, judging from the theoretical and experimental frequencies for TaF_6^- and ZrF_6^{2-}, we would not expect such low t_{1u} vibrational frequencies for triply-charged anions as those quoted in ref 1. We therefore suggest that the two higher frequency IR peaks from ref 2 be assigned as those corresponding to MF_6^{3-}. Such an assignment is proposed in Table 6 in the rows labeled "Becker". In support of this assignment, we point out the more recent IR and Raman spectra recorded by Turrell et al. for solid M_3ScF_6, M = Na, K, Rb, Cs, Tl.[81,82] After analysis of force constants, these authors assigned the high-frequency IR transitions to the ScF_6^{3-} moieties (the row labeled "Turrell" in Table 6) and transitions below 200 cm^{-1} to translatory lattice modes.

Even accepting the new assignment of the t_{1u} frequencies, our theoretical gas phase frequencies are systematically lower than the condensed phase data, in particular for the stretching a_{1g}, e_g, and t_{1u} modes. We recall that the B3LYP HOMO energies of triply-charged anions are positive (see Table 4), indicating that the total energy of the complex would decrease if the HOMO occupation were to decrease. If such an anion is placed in a condensed phase environment, there can be a spontaneous partial charge transfer from the anion to the neighboring countercations, for which the B3LYP LUMO orbital energies are negative. This may then rationalize the systematic deviation among gas and condensed phase data.

For triply-charged anions, the B3LYP value of ϵ_{HOMO} are positive and large, clearly indicating a preference to reduce the excess electronic charge. In these species, the discrepancies between our computed and measured condensed phase frequencies are large, frequently above 100 cm^{-1}. It is encouraging that these disrepancies are larger than the variations in experimental frequencies observed for the same complex but in different solids or melts (these variations usually do not exceed 30 cm^{-1}.[2,34,35,81,82] This indicates that properties of a complex are, to a large extent, transferable from one environment to another, although quite different from the properties of the gas phase complex, and justifies the unique parametrization of the interaction potential for the MX_6^{3-} species used in the statistical mechanical modeling.[37−41]

The negative value −0.49 eV of the B3LYP HOMO energy in the ZrF_6^{2-} complex indicates a tendency to retain the excess electronic charge. The complex, however, must compete for "its" electron density in a condensed phase environment, because the values of the typical countercations B3LYP LUMO energies are −6.95, −7.09, and −6.39 eV for Li^+, Na^+, and NH_4^+, respectively (the 6-311+G** results). A partial loss of electronic charge is then unavoidable, and may be reflected by the discrepancy of 60 cm^{-1} between the theoretical and experimental a_{1g} and t_{1u} vibrational frequencies.

Finally, the TaF_6^- anion with the HOMO B3LYP energy of −6.18 eV can easily withstand the countercation's preference to acquire an extra electronic charge, as a result of which the experimental and theoretical vibrational frequencies are nearly identical for this complex.

The t_{2u} vibrational mode is neither Raman nor IR active and experimental data for the hexafluorometallates studied here are not available. The general valence force field (GVFF) method implies a relation $\nu_{t_{2u}} = \nu_{t_{2g}}/\sqrt{2}$.[83] A deviation from this relation may serve as an indication of the magnitude of the bond-angle interaction constant.[84] Our values of $\nu_{t_{2u}}$ are systematically smaller than those predicted from the GVFF relation, see Table 6. Since t_{2u} is a bending mode, we expect our theoretical MP2 and B3LYP values of its frequency are meaningful in condensed phases as well.

4. Summary and Conclusions

We have studied five hexafluorometallate complexes MF_6^{3-}, M = Sc, Y, La, ZrF_6^{2-}, and TaF_6^-, at the SCF and second-order Møller−Plesset theory levels as well as using a variant of the density functional method dubbed B3LYP. We used the SBKJ pseudopotentials throughout this study.

The SBKJ basis sets were supplemented with diffuse and polarization functions and the convergence of the complexes' properties with the basis set extensions was determined. The flexibility of the final SBKJ+ddp basis set was also tested on the polarizabilities of F^- and the metal closed-shell $(n-1)s^2(n-1)p^6$ cations, as well as on the electron affinity of F. For each metal atom, the sum of ionization potentials necessary to produce the corresponding closed-shell cations was also calculated. All of these results were found to be in satisfactory agreement with the available experimental data.

The complexes ZrF_6^{2-} and TaF_6^- were confirmed to be electronically very stable with VED energies of 5.1 and 10.6 eV, respectively, at the third-order OVGF level of theory. The ScF_6^{3-} complex was found to be electronically unstable and the electronic stabilities of LaF_6^{3-} and YF_6^{3-} are disputable in view of contradictory results at different theoretical levels. For the two latter complexes, the largest electronic stability was found at the third-order OVGF level, with VED energies of 1.08 and 0.48 eV, respectively. However, the triply-charged anions are electronically unstable at the MP2 and B3LYP levels.

All triply-charged anions were found to be very ionic as the partial charge on F exceeds 0.9 au, irrespective of the computational scheme used to estimate it. The ionicity decreases for ZrF_6^{2-} and TaF_6^-, as expected from the values of ionization potentials required to form M^{3+} (M = Sc, Y, La), Zr^{4+}, and Ta^{5+}.

The binding energies of the complexes with respect to the energies of isolated atomic ions were also calculated at the SCF, MP2, and B3LYP levels of theory. The ab initio binding energies were found to be counterintuitive and further analysis of the interaction energy in haxafluorometallates is underway.[77]

The correlation corrections to the SCF harmonic vibrational frequencies were found to be similar at the MP2 and B3LYP levels. Good agreement was found between the theoretical and condensed phase experimental frequencies for TaF_6^-.[1] For other complexes, in particular for triply-charged anions, the discrep-

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ancies between the condensed phase and theoretical frequencies are larger than those commonly found in ab initio correlated calculations. Perusal of the experimental data suggested a partial reconciliation: a new assignment of experimental peaks was thus proposed for the triply-charged anions.[1,2] The new assignment, dictated by the intensity of experimental peaks and frequencies of peaks in the isoelectronic ZrF_6^{2-} and TaF_6^{-} anions, is also supported by the more recent IR and Raman spectra of the alkali metal salts of ScF_6^{3-}.[81,82]

After the new assignment, the discrepancies remain for the stretching modes only, for which the condensed phase frequencies are systematically larger by as much as 100 cm^{-1}. We suggest that the remaining discrepancies are a manifestation of partial electron transfer which takes place when a multiply-charged anion is placed in a condensed phase environment. As countercations acquire a fraction of the anion electron density, the anion vibrations become "stiffer" which is reflected in the experimental vibrational frequencies. Orbital energies obtained in the density functional calculations, such as Becke3LYP, may be used to quantify this chemically straightforward interpretation. Such partial charge transfer also may be responsible for the serious discrepancies between the theoretical gas phase and experimental condensed phase polarizabilities of anions.[16−20]

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