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Structures of RgF_n ($\text{Rg} = \text{Xe}, \text{Rn}$, and Element 118. $n = 2, 4$) Calculated by Two-component Spin–Orbit Methods. A Spin–Orbit Induced Isomer of $(118)\text{F}_4$

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Ab initio calculations of RgF_n ($\text{Rg} = \text{Xe}, \text{Rn}$, and Element 118; $n = 2, 4$) were performed using relativistic effective core potentials and two-component HF, MP2, CCSD, and CCSD(T) methods. Geometries were optimized at the HF level with and without effective spin–orbit operators. The D_{4h} structures of all tetrafluorides and the linear difluorides are local minima with and without spin–orbit interactions. Spin–orbit contributions makes the T_d form of $(118)\text{F}_4$ another local minimum with the energy comparable to that of the D_{4h} one. The spin–orbit interactions stabilize the (118) fluorides by a significant margin (~ 2.0 eV) and the Rn fluorides by 40–60% ($0.2 \sim 0.4$ eV) of the stabilization energy obtained at the corresponding scalar relativistic level. For $(118)\text{F}_4$, the vibrational frequency of the B_{2u} mode of the D_{4h} form decreases from 143 to 20 cm^{-1} upon inclusion of the spin–orbit interactions, and a doubly degenerate mode of the T_d structure, which is stable only with the inclusion of spin–orbit interactions, has the frequency of 34 cm^{-1} , indicating that the $(118)\text{F}_4$ molecule is very flexible due to spin–orbit effects.

1. Introduction

Despite the difficulty that electron correlations and the relativity must necessarily be taken into account to obtain reliable results, ab initio calculations for molecules have been progressing rapidly in the field of superheavy element chemistry. Four-component Dirac–Hartree–Fock(DHF) calculations were performed for several diatomic molecules, such as $(111)\text{H}^1$ and $(117)\text{H}^2$ and for many polyatomic molecules such as RfCl_4 and SgCl_6 .³ Correlated relativistic calculations based on the all-electron DHF method for the polyatomic molecules containing superheavy elements, however, have not been attempted. Instead, high-level correlated calculations were performed including proper relativistic effects by using relativistic effective core potentials(RECP). The growing list of molecules calculated by RECP methods includes DbO ,⁴ $(111)\text{H}$,¹ $(112)\text{H}^+$, $(112)\text{F}_n$ ($n = 2, 4$),⁵ $(111)\text{F}_n^-$ ($n = 2, 4, 6$),⁶ $(113)\text{X}_n$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$; $n = 1, 3, 5$),⁷ and $(114)\text{X}_n$ ($\text{X} = \text{H}, \text{F}, \text{Cl}$; $n = 2, 4$),^{7,8} as can be seen in a recent review on superheavy element chemistry by Schwerdtfeger et al.⁹

Among the molecules studied by RECP methods, the RgF_4 ($\text{Rg} = \text{Xe}, \text{Rn}$, and (118)) molecules were studied by Nash and Bursten (NB) at the spin-averaged RECP/spin–orbit configuration interaction(AREP–SOC) level of theory.¹⁰ NB showed that all tetrafluorides have the D_{4h} form as the most stable form and no T_d forms as local minima in potential energy surfaces (PESSs) at the AREP–CI level of theory, but the spin–orbit interactions make the T_d form slightly more stable than the D_{4h} form for $(118)\text{F}_4$. NB concluded that relativistic shell and spin–orbit effects conspire to change the valency of (118) relative to other members of their chemical families and that the valence shell electron pair repulsion (VSEPR) theory becomes inadequate to describe the geometry of the $(118)\text{F}_4$. Styszyński et al. reported nonrelativistic (NR) HF and DHF results for XeF_n ($n = 2, 4, 6$)¹¹ and Møller–Plesset second-order perturbation theory(MP2) results using NRHF molecular orbitals for XeF_2 ¹²

and XeF_4 .¹³ Dolg et al. calculated RnF_n ($n = 2, 4, 6, 8$) at the HF and MP2 levels of theory using NR effective core potentials (ECPs) and scalar relativistic energy-adjusted ECPs without considering spin–orbit interactions.¹⁴ To our knowledge, NB's work is unique for providing spin–orbit effects on the rare-gas fluoride systems. In this work, we hope to shed more light on the spin–orbit effects for those molecules by employing two-component spin–orbit methods, which treat spin–orbit interactions at all levels of theory including the HF level.

In the RECP methods, scalar relativistic effects such as mass velocity and Darwin effects are included using AREPs, while spin–orbit contributions are obtained by effective one-electron spin–orbit operators. In a conventional approach treating both the electron correlations and relativity, spin–orbit electron correlation effects are simultaneously accounted for by including the spin–orbit operators in the Hamiltonian for the CI calculations based on scalar relativistic molecular orbitals, which is called the AREP–SOC method.¹⁵

A common procedure of studying a polyatomic molecule is to perform HF geometry optimizations followed by high-level correlation calculations at HF geometries. HF geometries are usually investigated by normal-mode analysis to ensure that obtained geometries are minima.^{16,17} Recently, we have implemented two-component geometry optimization method using analytic gradient¹⁸ and then added normal-mode analysis methods. Therefore, we can follow the above common procedure of studying polyatomic molecules explicitly considering spin–orbit interactions. In the present work, we study the RgF_2 and RgF_4 ($\text{Rg} = \text{Xe}, \text{Rn}$, and (118)) molecules following the above procedure with and without spin–orbit interactions. Electron correlation is treated at the MP2, CCSD, and CCSD(T) levels of theory. Spin–orbit effects on the molecular structures, vibrational frequencies, and stabilities are discussed.

2. Methods and Computational Details

There can be many variations in the form of RECPs and the present RECP(REP) is expressed by the following form,¹⁹

$$U^{\text{REP}} = U_{\text{LJ}}^{\text{REP}}(r) + \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} \sum_{m=-j}^j [U_{lj}^{\text{REP}}(r) - U_{\text{LJ}}^{\text{REP}}(r)] |ljm\rangle \langle ljm| \quad (1)$$

where $|ljm\rangle \langle ljm|$ represents a two-component projection operator. Molecular spinors which are one-electron eigenfunctions of the Hamiltonian containing the above REP have two components. The U^{REP} which is referred to as REP here can be expressed as the sum of the AREP, U^{AREP} , and the effective one-electron spin-orbit (ESO) operator¹⁹ U^{SO} as

$$U^{\text{REP}} = U^{\text{AREP}} + U^{\text{SO}} \quad (2)$$

We have developed a two-component Kramers restricted Hartree-Fock (KRHF) method^{20,21} which includes spin-orbit interactions at the HF level of theory using the REPs. The KRHF program utilizes the REPs with effective one-electron spin-orbit operators at the HF level and produces molecular spinors obeying double-group symmetry. The KRHF method can be a starting point for many single-reference correlated methods of treating spin-orbit interactions. We have implemented MP2, CI, and CC methods on the basis of the KRHF molecular spinors and designated them as KRMP2,²² KRCI,²³ and KRCC^{24,25} methods, respectively. The KRHF, KRMP2, KRCI and KRCC calculations try to mimic all-electron calculations DHF, DHF-MP2, DHF-CI, and DHF-CC, respectively, for valence states. In our two-component calculations, any RECPs that are in the form of eq 1 or eq 2 can be employed, provided that radial parts of AREP and ESO are expanded in terms of Gaussian functions. We usually employ shape-consistent REPs²⁶ generated by Christiansen, Ernler, and their co-workers,²⁷ who published REPs for most elements including superheavy elements. The present study is also based upon their REPs.¹⁰

The 26 valence electrons (VE) shape-consistent RECPs including one-electron spin-orbit operators and corresponding (6p6sd1f)/[5p5sd1f] valence basis sets were used for Xe, Rn, and (118) atoms.¹⁰ An all-electron basis set (9s5p1d)/[4s2p1d] was used for fluorine.²⁹ The HF geometry optimization, HF normal-mode analysis, and single-point electron correlation calculations at the HF-optimized geometries were performed using the AREPs and REPs. The REP normal-mode analysis calculations were performed with a modified GAMESS suite of programs,³⁰ using the force constants obtained by numerically differentiating the analytic gradient at the KRHF level of theory. To the best of our knowledge, there has been no previous attempt to perform normal-mode analysis using analytic gradients in the presence of spin-orbit interactions. The AREP calculations were carried out with the GAUSSIAN94³¹ and the REP calculations with the two-component packages on the CRAY C90 at ETRI. All occupied and virtual orbitals except fluorine-1s core orbitals were included at all correlated levels of theory employed here.

3. Results and Discussion

The AREP- and REP-optimized geometries at the HF level of theory are listed in Table 1. The REP bond lengths of XeF₂ and XeF₄ are 1.975 and 1.939 Å, respectively, which are shorter than the DHF values, 2.004 and 1.969 Å, by about 0.03 Å, but are in good agreement with the experimental data^{32–34} of 1.977

TABLE 1: AREP-HF and REP-KRHF Optimized Bond Lengths of RgF₂ and RgF₄ (Rg = Xe, Rn, and (118)) which Have $D_{\infty h}$ and D_{4h} Molecular Symmetry, Respectively. Units in angstroms

molecule	AREP	REP	SO ^a
XeF ₂	1.973	1.975	+0.002
RnF ₂	2.075	2.095	+0.020
(118)F ₂	2.169	2.228	+0.059
XeF ₄	1.938	1.939	+0.001
RnF ₄	2.029	2.045	+0.016
(118)F ₄ ^b	2.114	2.164	+0.050

^a The spin-orbit(SO) value is defined by REP bond length – AREP bond length. ^b The REP-optimized bond length for T_d structure of (118)F₄ is 2.187 Å.

TABLE 2: Optimized Bond Lengths of RgF₂ (Rg = Xe, Rn, and (118)) at the HF, MP2, CCSD, and CCSD(T) Levels of Theory Using AREPs. Molecular Symmetry Is $D_{\infty h}$. Units in angstroms

molecule	HF	MP2	CCSD	CCSD(T)
XeF ₂	1.973	2.038	2.025	2.041
RnF ₂	2.075	2.129	2.119	2.135
(118)F ₂	2.169	2.211	2.204	2.217

and 1.95 Å. The bond lengths using scalar relativistic ECPs by Dolg et al. are 2.067 and 2.025 Å for RnF₂ and RnF₄,¹⁴ respectively, which are in very good agreement with the present AREP values, although they used large-core 8VE-ECPs.

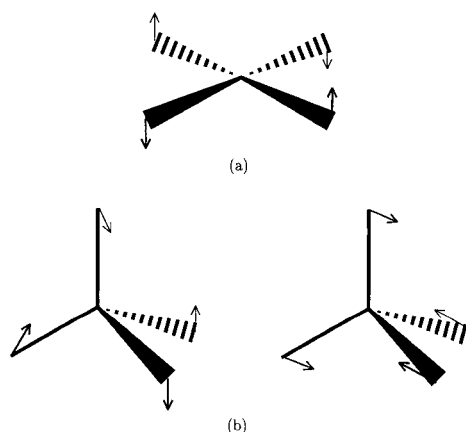
The structural changes due to spin-orbit interactions for Xe fluorides are negligible and those for Rn and (118) fluorides are modest. The spin-orbit coupling elongates the Rn-F bond lengths by about 0.02 Å and the (118)-F ones by about 0.05 Å (Table 1). The bond length changes of 0.05–0.06 Å due to spin-orbit effects are common in superheavy element chemistry. Spin-orbit interactions contract the bond length of a 7p_{1/2} valence molecule (113)H by 0.21 Å and elongate that of a 7p_{3/2} valence molecule (117)H by 0.20 Å at the CCSD(T) level of theory.³⁵ The bond elongation for the p_{3/2} valence molecules can be explained by the expansion of the p_{3/2} spinor due to spin-orbit splitting of 7p. NB showed that the contribution of the p_{3/2} spin-orbit components of the p shell to bonding increases dramatically from Xe to (118). There is a 0.91 bohr difference in the radial expectation values and a 0.44 hartree difference in the eigenvalues of the 7p spin-orbit components for (118).^{10,36} The bond elongation phenomenon for p_{3/2} valence molecules also appears in the molecules containing sixth-row elements with open-shell p electrons such as Bi, Po, and At.^{18,37} The REP bond length for the T_d structure of (118)F₄ molecule is 2.187 Å, which is slightly longer than the D_{4h} bond length of 2.164 Å. The geometric changes due to spin-orbit coupling are discussed at the HF level only. To estimate electron correlation effects on the geometries, we optimized the RgF₂ (Rg = Xe, Rn, and (118)) molecules at the MP2, CCSD, and CCSD(T) levels of theory using AREPs. Electron correlations elongate the bond lengths by about 0.05–0.07 Å (Table 2). Malli et al.¹² reported that electron correlation effects lead to an increase of 0.053 Å for the bond lengths in XeF₂ at the NRHF-MP2 level of theory. The MP2 method seems to yield quite reasonable geometries for the rare gas fluorides. The correlation effects on the geometries decrease somewhat from Xe to (118).

Normal-mode analyses were performed at the HF-optimized geometries using AREPs and REPs. All the optimized geometries are local minima as can be seen from all the positive frequencies in Table 3. Stretching modes are vibrational modes with frequencies larger than 500 cm^{−1} in Table 3. Spin-orbit effects decrease the harmonic frequencies in all cases in Table

TABLE 3: AREP–HF and REP–KRHF Harmonic Vibrational Frequencies in cm^{-1}

mode	XeF ₂			RnF ₂			(118)F ₂		
	AREP	REP	SO ^a	AREP	REP	SO ^a	AREP	REP	SO ^a
symmetry	598	593	−5	572	551	−21	568	520	−48
asymmetry	599	593	−6	548	542	−6	529	515	−14
bending	238	235	−3	200	186	−14	159	120	−39

	XeF ₄			RnF ₄			(118)F ₄ ^b		
	AREP	REP	SO ^a	AREP	REP	SO ^a	AREP	REP	SO ^a
E _u (b) ^c	162	162	0	142	143	+1	131	145	+14
B _{2u} (b)	196	194	−2	172	152	−20	143	20	−123
B _{2g} (b)	238	236	−2	220	208	−12	212	191	−21
A _{2u} (b)	321	318	−3	260	235	−25	197	134	−63
B _{1g} (s)	594	591	−3	583	563	−20	600	551	−49
E _u (s)	624	623	−1	583	581	−2	579	575	−4
A _{1g} (s)	638	636	−2	613	597	−16	615	587	−28

^a The SO value is defined by REP frequency − AREP frequency.^b The KRHF harmonic frequencies are for the T_d form of (118)F₄ are 34(E), 89(T₂), 548(T₂), and 588(A₁) cm^{-1} . ^c b: bending, s: stretching.**Figure 1.** (a) The B_{2u} mode of the D_{4h} structure for the RgF₄ (Rg = Xe, Rn, and (118)). (b) The E mode of the T_d structure for the RgF₄ (Rg = (118)).

3 except for the E_u mode of RnF₄ and (118)F₄. The spin–orbit induced reduction of harmonic frequencies increases from Xe to (118), as expected. This reduction is larger for bending and symmetric stretching vibrational modes of difluorides than for the asymmetric stretching mode. For the bending modes, the spin–orbit changes of the harmonic frequencies are 1%, 7%, and 25% for Xe, Rn, and (118) difluorides, respectively, in Table 3. For the tetrafluorides, the changes due to spin–orbit effects are more mode specific than the difluorides. As a result, spin–orbit effects change the ordering of vibrational frequencies for (118)F₄. The most dramatic decreases, by 1% for Xe, 12% for Rn, and 86% for (118) tetrafluorides, appear in the out-of-plane B_{2u} modes. As depicted in Figure 1a, two opposite fluorines move up and the other two fluorines down in the B_{2u} mode. The T_d form of (118)F₄ is also confirmed to be a local minimum with the lowest frequencies of 34 cm^{-1} for a doubly degenerate mode (Table 3). In these modes, four fluorines move in such directions that lead to a planar geometry as shown in Figure 1b. Low-frequency modes of two forms correspond to the transformation between the D_{4h} and T_d structures, implying that the PES connecting the two forms is very flat. In light of these harmonic frequency calculations, (118)F₄ would have to be considered stereochemically nonrigid. From the results for (118)F₄, one may expect that a C_{2v} structure of (118)F₂ will be competitive with the linear($D_{\infty h}$) structure. However, we could not find any local minimum for the nonlinear form of (118)F₂.

TABLE 4: AREP and REP Reaction Energies (eV) for the Reaction $\text{Rg} + \text{F}_2 \rightarrow \text{RgF}_2$ and $\text{RgF}_2 + \text{F}_2 \rightarrow \text{RgF}_4$

	XeF ₂	XeF ₄	RnF ₂	RnF ₄	(118)F ₂	(118)F ₄ ^a
AREP						
HF	+0.18	+0.96	−0.17	+0.43	−0.76	−0.38
MP2	−0.46	−0.41	−0.86	−0.94	−1.50	−1.66
CCSD	−0.20	+0.17	−0.58	−0.35	−1.21	−1.13
CCSD(T)	−0.31	−0.04	−0.68	−0.54	−1.30	−1.30
REP						
HF	+0.12	+0.95	−0.66	+0.21	−3.30	−2.80(−2.69)
MP2	−0.52	−0.43	−1.29	−1.17	−3.42	−3.48(−3.29)
CCSD	−0.26	+0.16	−1.03	−0.57	−3.30	−3.15(−2.98)
CCSD(T)	−0.37	−0.06	−1.11	−0.77	−3.30	−3.24(−3.07)
SO ^b						
HF	−0.06	−0.01	−0.49	−0.22	−2.54	−2.42
MP2	−0.06	−0.02	−0.43	−0.23	−1.92	−1.82
CCSD	−0.06	−0.01	−0.45	−0.22	−2.09	−2.02
CCSD(T)	−0.06	−0.02	−0.43	−0.23	−2.00	−1.94

^a The REP reaction energies for the T_d form of (118)F₄ are in parentheses. ^b The SO value is defined by REP reaction energy − AREP reaction energy.

The AREP and REP reaction energies calculated at the HF, MP2, CCSD and CCSD(T) levels of theory are summarized in Table 4. Since the reactions are defined by $\text{Rg} + \text{F}_2 \rightarrow \text{RgF}_2$ and $\text{RgF}_2 + \text{F}_2 \rightarrow \text{RgF}_4$, a negative value means the stable RgF₂ and RgF₄, respectively. The MP2 method widely used for these systems seems to overestimate the stability of the product molecules by about 0.3–0.4 eV in comparison with the more sophisticated CCSD(T) method. The stability increases from Xe to (118), which is a consequence of increasing polarizability of the central atom. The reaction energies in the absence of spin–orbit interactions at the AREP–CCSD(T) level of theory are −0.31, −0.68, and −1.30 eV for Xe, Rn, and (118) difluorides, respectively, and −0.04, −0.54, and −1.30 eV for Xe, Rn, and (118) tetrafluorides, respectively. Spin–orbit interactions always stabilize the product molecule and the stabilization is largest for (118). The REP–CCSD(T) reaction energies are −0.37, −1.11, and −3.30 eV for difluorides and −0.06, −0.77, and −3.24 eV for Xe, Rn, and (118) tetrafluorides, respectively. The spin–orbit interactions stabilize the (118) fluorides by a significant margin, about 2.0 eV, and even the Rn fluorides by 40–60% of the corresponding AREP energy. The enormous stabilization caused by spin–orbit effects can be explained mainly by the radial expansion and energetic destabilization of the 7p_{3/2} (REP) spinors compared with the 7p (AREP) orbitals. The larger 7p_{3/2} may allow better overlap with atomic orbitals or spinors of the F atom resulting in a stronger bond. The local (118) atom in (118)F₂ and (118)F₄ will lose electron densities due to highly electronegative fluorines and become an open-shell ion. The HF natural population charges for (118) of (118)F₂ and (118)F₄ are 1.44 and 2.79, respectively. The spin–orbit effects may be more significant for open-shell cationic (118) than for the closed-shell neutral one. The energy lowerings due to the inclusion of the spin–orbit operators are −35.52 and −37.88 eV for (118) and (118)⁺, respectively, at the HF level. Spin–orbit effects are in the opposite direction for molecules of a p_{1/2} valence atom like (113).³⁵ The (113) atom in the (113)F molecule can be reasonably described as a locally closed-shell configuration due to highly electronegative fluorine. The HF natural population charge is 0.90 for the (113) atom in (113)F. The spin–orbit coupling contracts the bond length by 0.04 Å and increases the harmonic frequency by 12 cm^{-1} for (113)F at the HF level of theory. The energy lowerings due to the inclusion of the spin–orbit operators are −24.40 and −21.97 eV for (113) and (113)⁺, respectively, at the HF level, which

is mainly responsible for the spin-orbit destabilization of D_e by 2 eV for $(113)\text{F}_2$.³⁵

All tetrafluorides have the D_{4h} structure as a most stable form with and without spin-orbit interactions in the present calculations. The T_d energy is slightly higher than the D_{4h} energy at all levels of theory even for $(118)\text{F}_4$. Although our energy ordering for $(118)\text{F}_4$ differs from that of NB, the energy differences are still fairly small in both works, and the different energy ordering little affects the conclusions of both works. In the present work, the differences in energy between the D_{4h} and the T_d geometries of $(118)\text{F}_4$ are 0.11, 0.19, 0.17, 0.17 eV at the HF, MP2, CCSD, and CCSD(T) levels of theory, respectively. The stable T_d structure can also be explained by the enormous splitting of the 7p shell of (118), as well as the stabilization and contraction of 7p_{1/2} spinor and the destabilization and expansion of the 7p_{3/2}, in conjunction with the filling of the 7p_{1/2} shell which generates a stereochemically inactive pair of electrons. Besides, 7s electrons may be also regarded as stereochemically inactive due to relativistic shell stabilization. The net effect is to remove two electron pairs, 7s and 7p_{1/2}, from the valence to produce an atom which must be considered tetravalent, as was pointed out by NB.¹⁰ This spin-orbit modification of VSEPR theory for the (118) atom, however, should be applied with caution since we have not been able to locate any nonlinear $(118)\text{F}_2$ as a minimum on PES at the HF level of theory.

Since any truncated CI method is not size extensive, reaction energies should be treated very carefully in the AREP-SOCI scheme. Although one may suggest CCSD(T) calculations corrected with spin-orbit energies from AREP-SOCI calculations as an alternative, the procedure may still require a large SOCI to successfully overcome inherent size-extensivity errors in the evaluation of the spin-orbit energies and the nonadditivity between electron correlations and spin-orbit contributions for systems exhibiting large spin-orbit effects. Two-component methods used in our work do not suffer these problems as long as the size-extensive methods, such as MP2 and CC methods, are employed. The spin-orbit effects on the reaction energies (Table 4) at the HF level are in good agreement with highly correlated results although there is some nonadditivity between correlation and spin-orbit effects for the (118) fluorides.¹⁰ It appears that the single reference scheme is quite reasonable for the present molecules. Furthermore, this implies that the KRHF itself could be a useful tool for studying spin-orbit effects for similar systems containing heavy and superheavy elements. We are trying to study more complex molecules containing the superheavy element Sg such as SgH_6 and SgO_2Cl_2 . In the present study of reaction energies, zero-point energies are not considered. HF frequencies in Table 3 suggest that these corrections will, in general, raise the reaction energies by about 0.1 eV and change the magnitude of spin-orbit effects by about 0.01 eV, implying that zero-point energies can be ignored for the present discussion. Reaction energies are usually sensitive to the basis set truncation errors and the current basis sets contain some of those errors. The reaction energies in Table 4 are expected to decrease by the addition of polarization and diffuse basis functions, but we believe that major conclusions of the present work, especially those on spin-orbit effects, will be affected only slightly by the enlarged basis set.

4. Conclusions

We optimized geometries of RgF_n ($\text{Rg} = \text{Xe}, \text{Rn}, (118)$ and $n = 2, 4$) molecules using AREPs and REPs at the HF level. The HF normal-mode analysis and MP2, CCSD, and CCSD-

(T) single-point correlation calculations with and without spin-orbit interactions were performed at the optimized geometries. Two-component results for the polyatomic rare gas fluoride molecules indicate that spin-orbit interactions elongate the bond lengths. The D_{4h} structures of all tetrafluorides are local minima with or without spin-orbit interactions. Spin-orbit effects make the T_d form of $(118)\text{F}_4$ another local minimum at the HF level. Due to the spin-orbit coupling, the unstable T_d structure of $(118)\text{F}_4$ changed into a stable structure with the energy comparable to that of the D_{4h} one. The spin-orbit interactions stabilize the (118) fluorides by a significant margin (~ 2.0 eV), and even stabilize the Rn fluorides by 40–60% of their AREP reaction energy. Spin-orbit contributions are more dominant than the electron correlations for reaction energies of (118) fluorides. In cases such as this, the advantage of having KRHF method is significant.

The two-component approaches seem to be very promising for studying molecular structures, vibrational frequencies, and stabilities for polyatomic molecules containing heavy and superheavy elements when the spin-orbit interactions are substantial. The present approaches can be easily applied to the molecules with many geometrical parameters and the work in this direction is under way.

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