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Structures and Stabilities for Halides and Oxides of Transactinide Elements Rf, Db, and Sg Calculated by Relativistic Effective Core Potential Methods

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The ground states of the halides and oxides containing transactinide elements Rf (element 104), Db (element 105), and Sg (element 106) were calculated at the HF, MP2, QCISD, CCSD, and CCSD(T) levels of theory using one- and two-component relativistic effective core potentials. Spin−orbit effects are rather small for geometries, harmonic vibrational frequencies, charge distributions, overlap populations, and dipole moments, but considerable for atomization energies. Electron correlations are necessary for any accurate determination of the molecular properties, in particular for the evaluation of atomization energies. The bond lengths of Sg compounds are consistently longer than those of the corresponding W compounds by 0.04−0.06 Å. The atomization energies for Sg compounds are slightly smaller than those for the corresponding W compounds due to spin−orbit and correlation effects. The differences tend to increase with the number of oxygen atoms in the compounds. Metal charges and dipole moments are larger for the Sg compounds than for the W compounds, implying that Sg is more ionic than W. The D_{3h} structures are calculated to be more stable by about 2 kcal/mol than the C_{4v} ones for $TaCl_5$, $TaBr_5$, $DbCl_5$, and $DbBr_5$.

I. Introduction

Quantum mechanical calculations for molecules have been progressing rapidly in the field of transactinide element ($Z > 103$) chemistry. Chemical studies of these elements have been limited to the elements with atomic numbers up to 106[1] because experiments at one-atom-at-a-time scale requires half-lives at least in the order of the second range. Therefore, reliable information on chemical properties from theoretical studies could be valuable even in deciding what molecules to look for experimentally.

Most studies for the molecules containing the elements Rf, Db, and Sg have been performed with the Dirac−Slater discrete variational (DS-DV) method.[2] Malli and Styszyński,[3,4] however, reported geometries, Mulliken population analysis (MPA)[5] charges, and atomization energies for the molecules calculated by the four-component Dirac−Fock−Breit (DFB) Hartree−Fock (HF) method. The approaches using the DFB Hamiltonian could yield reliable data for those compounds when electron correlation effects are properly treated with accurate basis sets. The electron correlations were not considered in the above study. Pershina, Fricke, and co-workers[6] have been studying those molecules using another four-component approach, the four-component DS-DV method. A review on the application of the DS-DV method applied in transactinide element chemistry has been given by Pershina.[2] The DS-DV approach can treat both electron correlation and relativistic effects including spin−orbit interactions at relatively low cost, but had some disadvantages due to insufficient accuracy for the total energy in obtaining optimized geometries and dissociation energies for polyatomic molecules. Hence, the authors estimated geometries and dissociation enthalpies (ΔH_{diss}) from experimental data for lighter homologues and their calculated parameters from the DS-DV method. The DFB-HF and DS-DV calculations often provided qualitatively different results for the same molecular properties,

in particular for dissociation energies and charge distributions. In a previous paper,[6] Pershina et al. reported bond lengths and atomization energies for some molecules using the DS-DV method with the improved estimate for the total energy, but there still remain discrepancies.

Transactinide compounds can be easily treated with relativistic effective core potentials (RECPs). Since f electrons can be effectively removed from the valence space using core potentials, the RECP approaches can be much simpler for the transactinide compounds than the actinide ones. We applied two-component RECPs to study (113)H, (113)F, and (117)H molecules and showed that the two-component results using the RECPs are in good agreement with available Dirac−Hartree−Fock (DHF) ones at various levels of theory.[7] The methods were tested for Hartree−Fock (HF), Møller−Plesset second-order perturbation theory(MP2), coupled-cluster singles and doubles (CCSD), and CCSD with triple contributions in a perturbative way (CCSD(T)) calculations. It was also shown that the potential averaging is a useful scheme for obtaining the scalar relativistic ECPs even for the transactinide elements.

Only a few RECP calculations for molecules containing Rf, Db, and Sg have been reported. Dolg et al.[8] calculated the DbO molecule using energy-adjusted RECPs at the averaged coupled-pair functional (ACPF) and multireference configuration interaction (CI) levels of theory. The spin−orbit effects were evaluated by a spin−orbit CI method. Nash et al.[9] calculated $Sg(CO)_6$ compounds using shape-consistent RECPs at the HF, MP2, CCSD, and CCSD(T) levels of theory but the spin−orbit effects were neglected.

In the present work, we study the ground states of $RfCl_4$, $DbCl_5$, $DbBr_5$, $SgCl_6$, $SgOCl_4$, SgO_2Cl_2, and SgO_3 employing various correlated levels of theory with the hope that our RECP calculations may shed some light to resolve the discrepancies among results of the DFB-HF and DS-DV calculations. We calculated geometries, atomization energies, MPA gross atomic charges, MPA overlap populations, natural population analysis

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(NPA)[10] charges, dipole moments, harmonic vibrational frequencies, and relative energies between isomers. The NPA charge calculations are aimed at assessing the reliability of the MPA charges widely used in the DHF and the DS-DV approaches. Spin−orbit interactions are accounted for by effective one-electron spin−orbit operators within the two-component formalism.[11]

In section II details of the calculations are given. Results and discussion are presented in section III.

II. Calculational Details

Nash, Bursten, and Ermler[12] generated the shape-consistent one- and two-component RECPs starting from all-electron DHF calculations for the elements 104−118. The approach uses, as reference data, the shape of the valence spinors in the spatial valence region and their corresponding one-particle energies.

The present RECP(REP) is expressed by the following form[11]

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

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 also be expressed as the sum of the spin-averaged relativistic effective core potential (AREP), U^{AREP}, and the effective one-electron spin−orbit(ESO) operator,[11] U^{SO}, as

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

We developed a two-component Kramers' restricted Hartree−Fock (KRHF) method[13,14] which includes spin−orbit interactions at the HF level of theory using the REP. The KRHF program,[13] which produces two-component molecular spinors obeying the double group symmetry, is a starting point for the single reference correlated methods of treating spin−orbit interactions. We have implemented MP2 and CC methods on the basis of the KRHF molecular spinors and denoted them as KRMP2[15] and KRCC.[16] KRHF, KRMP2, and KRCC calculations are intended to mimic DHF, DHF-MP2, and DHF-CC calculations, respectively, for the properties of valence states when REP is used. We estimated spin−orbit effects by comparing results of REP calculations with those of AREP ones at each level of theory. AREP calculations can be performed with the two-component programs, but the same results are obtained more efficiently and reliably from the conventional molecular programs. All the molecules were calculated with AREPs at various levels of theory to obtain the desired molecular properties. Two-component REP calculations were carried out for selected cases to estimate spin−orbit corrections. Since we can perform the two-component geometry optimization[17] and the normal-mode analysis using analytic gradients at the KRHF level of theory, spin−orbit effects on geometries and vibrational frequencies were calculated, too.

The 13 valence electrons (VEs) and 14 VEs shape-consistent RECPs and corresponding 5s5p4d basis sets were used for Ta and W, respectively.[18] The 12 valence electrons, 13 VEs, and 14 VEs shape-consistent RECPs and corresponding (5p6sd)/[5p5sd] basis sets were used for Rf, Db, and Sg, respectively.[12] A 5p6sd basis set refers to the basis set in which all s basis functions are represented as a component of d basis functions. The 6 VEs and 7 VEs shape-consistent RECPs and correspond-

TABLE 1: Optimized Bond Lengths (Å) of RfCl$_4$ at the HF, MP2, CCSD, and CCSD(T) Levels of Theory

	HF	MP2	CCSD	CCSD(T)
AREP	2.390	2.374	2.382	2.384
REP	2.386	2.370	2.378	2.380
SO[a]	−0.004	−0.004	−0.004	−0.004
AREP[b]	2.379	2.348	2.359	2.361
DHF[c]	2.385			

[a] (REP bond length) − (AREP bond length). [b] All basis sets were used as uncontracted forms and one f function was added to Rf. [c] Reference 4.

TABLE 2: Atomization Energies (eV) of RfCl$_4$ at the HF, MP2, CCSD, and CCSD(T) Levels of Theory

	HF	MP2	CCSD	CCSD(T)
AREP	17.2	20.4	19.4	19.7
REP	16.9	19.7	18.6	18.8
SO[a]	−0.3	−0.7	−0.8	−0.9
AREP[b]	17.5	20.4		
DFB-HF[c]	15.5			

[a] (REP atomization energy) − (AREP atomization energy). [b] All basis sets were used as uncontracted forms and one f function was added to Rf. [c] Reference 4.

TABLE 3: Spinor Energies (eV) of the Valence Relativistic Molecular Spinors of RfCl$_4$

spinor[a]	REP	DHF[a]	difference
26u	−13.033	−13.231	+0.198
17e$_1$	−13.068	−13.268	+0.200
25u	−13.630	−13.730	+0.100
17e$_2$	−13.959	−13.970	+0.011
24u	−14.174	−14.231	+0.057
23u	−14.470	−14.463	−0.007
16e$_2$	−14.992	−14.779	−0.213
16e$_1$	−15.911	−15.799	−0.112

[a] Notations for the spinors are from ref 4.

ing (4s4p1d)/[3s3p1d] basis sets were used for O and Cl,[19] respectively. In an effort to estimate the basis set effect, we calculated some molecules with uncontracted basis sets augmented with one f polarization function on the metal atom (ζ_f(W) = 0.86, ζ_f(Rf) = 0.58, and ζ_f(Sg) = 0.64). Two-component geometry optimization code was employed for the calculations of SgO$_2$Cl$_2$ and DbCl$_5$. Harmonic vibrational frequencies were evaluated for the SgO$_2$Cl$_2$ with and without spin−orbit interactions. The AREP calculations were carried out with the GAUSSIAN94[20] and MOLPRO98[21−23] and the REP calculations with two-component packages on the CRAY C90 at ETRI. All occupied and virtual orbitals (or spinors) were included at all correlated levels of theory employed here.

III. Results and Discussion

The optimized geometries and atomization energies for RfCl$_4$ at the HF, MP2, CCSD, and CCSD(T) levels of theory are listed in Tables 1 and 2, respectively. Our REP-KRHF bond length 2.386 Å is in good agreement with DHF bond length 2.385 Å of Malli et al.[4] Spin−orbit coupling contracts the bond lengths by 0.004 Å at all the levels of theory considered. The spinor energies of the valence relativistic molecular spinors for RfCl$_4$ are in good agreement with the DHF spinor energies, which are summarized in Table 3. The atomization energy at the REP-KRHF level of theory is 16.9 eV in Table 2, which is somewhat larger than the DFB-HF value 15.5 eV. In the DFB-HF calculations, there were no d polarization functions on the Cl atoms. In the AREP-HF calculations, excluding the d polarization functions on the Cl atoms decreases atomization

TABLE 4: Optimized Geometries of WO₂Cl₂ and SgO₂Cl₂ at the HF, MP2, CCSD, and CCSD(T) Levels of Theory (Bond Lengths in Å and Angles in deg)

	HF	HF[a]	MP2	MP2[a]	CCSD	CCSD(T)	exp[b]
WO₂Cl₂							
r(W=O)	1.657	1.648	1.732	1.719	1.691	1.708	1.710
r(W−Cl)	2.282	2.271	2.282	2.262	2.279	2.281	2.270
∠(O−W−Cl)	109.4	109.4	108.8	108.8	109.2	109.1	104(107 ± 2)
∠(Cl−W−Cl)	111.9	111.4	116.2	116.1	112.8	113.2	112
SgO₂Cl₂[c]							
r(Sg=O)	1.714(1.709)	1.716	1.769	1.768	1.744	1.756	
r(Sg−Cl)	2.337(2.334)	2.318	2.337	2.308	2.337	2.339	
∠(O−Sg−Cl)	108.9(108.7)	108.9	107.9	108.0	108.5	108.4	
∠(Cl−Sg−Cl)	114.7(115.7)	113.5	120.0	119.2	116.4	117.2	

[a] All basis sets were used as uncontracted forms and one f function was added to the central metal atoms. [b] Electron diffraction experimental data. Reference 26. The values in parentheses refer to the infrared spectroscopic data for ∠(O−W−Cl). Reference 27. [c] The REP-KRHF optimized geometries of SgO₂Cl₂ are included in parentheses.

energy by 1.4 eV, which exactly corresponds to the energy difference between REP-KRHF and DFB-HF atomization energies. Uncontracting and adding one f polarization function to the basis set shortens the bond lengths by 0.01−0.02 Å at various levels of theory, but do not change the atomization energies. Spin−orbit coupling decreases the atomization energies by 0.7−0.9 eV at the correlated levels of theory, but the decrease at the HF level is merely 0.3 eV. Our best estimate of atomization energy for RfCl₄ is 18.8 eV obtained at the CCSD(T) level.

The optimized geometries for WO₂Cl₂ and SgO₂Cl₂ at the HF, MP2, CCSD, and CCSD(T) levels of theory are listed in Table 4 along with available experimental data from electron diffraction[26] and infrared spectroscopies[27] for WO₂Cl₂. There has been no experimental report for the geometry of SgO₂Cl₂ molecule. For the SgO₂Cl₂ molecule, REP optimized geometries were also calculated at the HF level of theory. Spin−orbit coupling slightly contracts the bond lengths and increases Cl−Sg−Cl angle by 1°. Effects of enlarging the basis set and increasing electron correlations are found to be more significant than the spin−orbit effects for bond lengths and angles. Adding one f polarization function on central metal atoms and uncontracting the basis set somewhat shortens bond lengths. Electron correlations elongate double bonds between metal and oxygen, and change the Cl−M−Cl angle by as much as 6°, as shown in Table 4. After all, the bond lengths of SgO₂Cl₂ are longer than the corresponding ones of WO₂Cl₂ by 0.05−0.06 Å at the CCSD(T) level, which are close to the bond length difference (0.061 Å) between WH₆ and SgH₆ calculated with the DHF one-center expansion method by Pyykkö et al.[28] The Cl−Sg−Cl angle is larger than the Cl−W−Cl angle by 5° when spin−orbit effects are also considered. The CCSD(T) geometries are in good agreement with the electron diffraction parameters except for the O−W−Cl angle 109.1° which is closer to the infrared spectroscopic data. Harmonic vibrational frequencies for WO₂Cl₂ and SgO₂Cl₂ at the HF level are all positive, as shown in Table 5, and the spin−orbit effects on them for SgO₂Cl₂ are negligibly small (<3 cm⁻¹). As one may expect, the HF frequencies are somewhat larger than the observed experimental values.[27]

The atomization energies for WO₂Cl₂ and SgO₂Cl₂ evaluated at the HF, MP2, CCSD, and CCSD(T) levels of theory are summarized in Table 6. The atomization energies calculated using higher levels of theory, i.e., MP2, CCSD, and CCSD(T) methods, at the HF optimized geometries differ by less than 0.3 eV from those obtained at the optimized geometries of the respective levels of theory. For SgO₂Cl₂, REP calculations were also carried out. The DFB-HF results[27] and available experimental data[29] may be compared with our HF and CCSD(T)

TABLE 5: Harmonic Vibrational Frequencies (cm⁻¹) for WO₂Cl₂ and SgO₂Cl₂ at the HF Level of Theory

	W		Sg	
sym	AREP	exp[a]	AREP	REP
A1	121		111	110
B1	183		165	162
A2	233		227	229
B2	249		233	231
A1	373	340	361	364
B2	431	425	423	423
A1	440		424	423
B1	1082	974	1066	1066
A1	1163	1014	1163	1160

[a] Reference 27.

TABLE 6: Atomization Energies (eV) of WO₂Cl₂ and SgO₂Cl₂ Employing the HF, MP2, CCSD, and CCSD(T) Methods at the HF-Optimized Geometries, and the Atomization Energies at the Corresponding Level of Optimized Geometries (in Parentheses)

	HF	MP2	CCSD	CCSD(T)	exp[a]
WO₂Cl₂					
AREP	11.7	24.4(24.7)	20.9(21.0)	22.1(22.2)	23.5
DFB-HF[b]	16.3				
SgO₂Cl₂					
AREP	14.6	24.8(25.0)	21.6(21.7)	22.5(22.6)	
REP	14.2	23.5	20.2	20.9	
SO[c]	−0.4	−1.3	−1.4	−1.6	
DFB-HF[b]	9.7				

[a] Experimental ΔH_{diss} values obtained from Born−Haber cycle. Reference 29. [b] Reference 3. [c] (REP atomization energy) − (AREP atomization energy).

results, respectively. A decrease due to spin−orbit interactions amounts to 1.6 eV at the CCSD(T) level. The larger spin−orbit effects on atomization energies for SgO₂Cl₂ than those for RfCl₄ are mainly explained by the increasing d₃/₂−d₅/₂ splittings and the occupation of four d₃/₂ spinors in Sg. Due to the spin−orbit interactions, the atomization energy for SgO₂Cl₂ becomes smaller than that for WO₂Cl₂ by 1.2 eV. Unfortunately, there are no direct experimental results for these systems, which makes it difficult to assess the reliability of our CCSD(T) calculations for the dissociation energies. We calculated the dissociation energies of NbO and TaO molecules, for which the experimental dissociation energies are known. At the AREP-CCSD(T) level of theory, the D_e values are 7.51 and 8.45 eV for NbO and TaO, respectively, which are in good agreement with the experimental data 7.8 and 8.2 eV, respectively.[30] The spin−orbit effect on the D_e value of TaO evaluated at the spin−orbit CI level by Dolg et al.[8] is −0.22 eV, which makes our D_e value closer to the experimental data. The D_e values at the

TABLE 7: Atomization Energies (eV) of MCl_6, $MOCl_4$, MO_2Cl_2, and MO_3 (M = W and Sg) at the HF and CCSD(T) Levels of Theory

molecule	HF	DFB-HF[a]	CCSD(T)[b]	exp[c]	DS-DV[d]	ΔE_{corr}[e]
WCl_6	10.9	14.4	19.9	21.7	22.2	9.0
$SgCl_6$	15.0	16.8	19.9	20.1	20.1	4.9
$WOCl_4$	12.0	21.8	21.5	23.0		9.5
$SgOCl_4$	15.2	14.2	21.0	21.2		5.8
WO_2Cl_2	11.7	16.3	22.2	23.5		10.5
SgO_2Cl_2	14.2	9.7	21.0	21.8		6.8
WO_3	7.2		18.9			11.7
SgO_3	9.3		17.8			8.5

[a] Reference 3. [b] The CCSD(T) energies were evaluated at the QCISD optimized geometries. [c] Experimental values obtained from Born–Haber cycle for the W systems and estimated values for the Sg systems by Pershina et al. References 29, 31, and 32. [d] Reference 6. [e] ΔE_{corr} = (CCSD(T) atomization energy) − (HF atomization energy).

CASSCF+ACPF level reported by Dolg et al.[8] are 6.91 and 7.67 eV for NbO and TaO, respectively. For the heavier homologue DbO, the D_e values are 8.92 and 8.35 eV at the CCSD(T) level using the AREP and REP, respectively. The difference in dissociation energies between TaO and DbO is merely 0.12 eV, somewhat smaller than 0.5 eV calculated by Dolg et al. However, spin–orbit effects on the D_e value (−0.63 eV) for DbO at the spin–orbit CI level is in good agreement with that at the CCSD(T) level of theory. From the spin–orbit effects on the TaO and DbO, one may estimate for the W compounds that the decrease of atomization energy due to spin–orbit coupling is about 0.5 eV at the correlated levels of theory. Large spin–orbit effects on the atomization energies for $RfCl_4$ and SgO_2Cl_2 compared with those for DbO may partly originate from molecular spin–orbit quenching effects. Four highly electronegative ligands such as oxygen and chlorine remove d electrons from the metal atom which can also contribute to molecular spin–orbit effects, leading to relatively large spin–orbit effects on the atomization energies for $RfCl_4$ and SgO_2Cl_2. A large decrease of dissociation energy (−1.85 eV) due to spin–orbit effects was also observed for (113)F where the highly electronegative F atom depletes a significant portion of the electron density of valence p electrons of (113).[7]

We evaluated the atomization energies for various closed-shell molecules MCl_6, $MOCl_4$, MO_2Cl_2, and MO_3 (M = W and Sg) at the HF and CCSD(T) levels of theory and summarized them in Table 7. The CCSD(T) energies were evaluated at the quadratic CI singles and doubles (QCISD) optimized geometries as shown in Table 8, since the QCISD-optimized geometries for WO_2Cl_2 and SgO_2Cl_2 are very similar to the CCSD(T) ones in Table 4. The optimized MCl_6, $MOCl_4$, MO_2Cl_2, and MO_3 (M = W and Sg) molecules have O_h, C_{4v}, C_{2v}, and C_{3v} point group symmetries, respectively. For WCl_6,[24] $WOCl_4$,[25] and WO_2Cl_2,[26] the geometries obtained from the electron diffraction experiments are also included in Table 4. The bond lengths of the Sg compounds are consistently longer than corresponding ones of the W compounds by 0.04–0.06 Å for the systems considered here. Assuming that differential spin–orbit effects for the Sg compounds are very small, the atomization energies for the Sg compounds were corrected by spin–orbit effects estimated for SgO_2Cl_2. As predicted by Pershina et al.,[2] oxychlorides have higher thermodynamic stability than pure chlorides even for the Sg compounds. It should be noted that the thermodynamic stabilities of $SgOCl_4$ and SgO_2Cl_2 are nearly same although the higher-order electron correlations may raise the stability of the dioxychloride slightly more than that of the monochloride. The CCSD(T) atomization energies for the W compounds are smaller than the experimental ΔH_{diss} values[29,31,32]

TABLE 8: Optimized Geometries of MCl_6, $MOCl_4$, MO_2Cl_2, and MO_3 (M = W and Sg) at the QCISD Level of Theory (Bond Lengths in Å and Angles in deg)

	W[a]	Sg
MCl_6		
r(M−Cl)	2.319(2.26)	2.359
DS-DV[b]	2.36	2.45
DHF[c]	2.31	2.38
$MOCl_4$		
r(M=O)	1.670(1.685)	1.720
r(M−Cl)	2.317(2.280)	2.364
∠(MOCl)	103.9(102.4)	103.2
MO_2Cl_2		
r(M=O)	1.700(1.710)	1.749
r(M−Cl)	2.282(2.270)	2.339
∠(O−M−Cl)	109.2(104)	108.4
∠(Cl−M−Cl)	113.2(112)	117.1
MO_3		
r(M=O)	1.735	1.777
∠(O−M−O)	109.0	105.5

[a] Electron diffraction parameters are in parentheses. References 24–26. [b] Reference 6. [c] Reference 3.

TABLE 9: Mulliken Population Analysis (MPA) Charges, Natural Population Analysis (NPA) Charges, MPA Overlap Populations (OP), and Dipole Moments of WO_2Cl_2 and SgO_2Cl_2 at the HF, MP2, and QCISD Levels of Theory

	HF	MP2	QCISD	DS-DV[a]
WO_2Cl_2				
Q_{MPA}(W)	2.18	1.46	1.71	1.08
Q_{NPA}(W)	2.21	1.60	1.85	
OP(total)	2.14	2.07	2.03	2.23
dipole moment	1.70	0.92	1.51	1.35
SgO_2Cl_2[b]				
Q_{MPA}(Sg)	1.94(1.91)	1.32	1.52	0.97
Q_{NPA}(Sg)	2.60	2.00	2.23	
OP(total)	2.72(2.69)	2.53	2.55	2.34
dipole moment	2.64(2.65)	1.90	2.39	1.83

[a] Reference 29. [b] The values in parentheses refer to the REP-KRHF results for MPA charges, overlap populations, and dipole moments.

by 1.3–1.8 eV. For the Sg compounds, our CCSD(T) atomization energies are very close to the ΔH_{diss} values estimated by Pershina et al. using experimental data for lighter homologues and calculated parameters. The agreement is reassuring for both values although part of the agreement must be attributed to the cancellation of error. The atomization energies from the direct DS-DV results[6] for WCl_6 and $SgCl_6$ also justified the procedure to estimate ΔH_{diss} values. Electron correlation effects (ΔE_{corr}) on the atomization energies at the CCSD(T) level are larger in the W compounds than in the Sg compounds, and become more significant as the number of oxygen atoms increases. Such variation of correlation effects implies that the HF level of calculation does not provide qualitatively correct atomization energies for these compounds. At the HF level of theory, atomization energies for the Sg compounds are always larger than those for the W analogues, and the differences decrease with the increasing number of oxygen atoms. On the contrary, the CCSD(T) results indicate that atomization energies for the Sg compounds are always smaller than those for the corresponding W compounds, and the differences are usually larger for the compounds with more oxygen atoms. The REP-KRHF atomization energies differ substantially from the DFB-HF values[3] except for $SgCl_6$ and $SgOCl_4$. The DFB-HF atomization energies are qualitatively different from our REP-KRHF ones partly because, we think, the geometries in DFB-HF calculations are not fully optimized.

Table 9 shows MPA charges, NPA charges, MPA overlap populations, and dipole moments for WO_2Cl_2 and SgO_2Cl_2 at the

TABLE 10: Mulliken Population Analysis (MPA) Charges, Natural Population Analysis (NPA) Charges, MPA Overlap Populations (OP), and Dipole Moments of MCl_6, $MOCl_4$, MO_2Cl_2, and MO_3 (M = W and Sg) at the HF and QCISD Levels of Theory[a]

	HF			QCISD			DS-DV[b]	
	W	Sg	Sg*	W	Sg	Sg*	W	Sg
MCl_6								
$Q_{MPA}(M)$	1.53	1.41	1.90	1.08	1.02	1.43	0.74	0.59
$Q_{MPA}(Cl)$	−0.25	−0.23	−0.32	−0.18	−0.17	−0.24		
$Q_{NPA}(M)$	1.01	1.48	1.39	0.69	1.14	1.04		
$Q_{NPA}(Cl)$	−0.17	−0.25	−0.23	−0.12	−0.19	−0.17		
OP(total)	2.91	3.02	3.03	2.49	2.66	2.62	2.75	2.72
$MOCl_4$								
$Q_{MPA}(M)$	1.86	1.75	2.07	1.40	1.35	1.61	1.04	0.90
$Q_{MPA}(Cl)$	−0.31	−0.32	−0.34	−0.23	−0.25	−0.26	−0.18	−0.15
$Q_{MPA}(O)$	−0.62	−0.45	−0.73	−0.47	−0.33	−0.56	−0.32	−0.31
$Q_{NPA}(M)$	1.80	2.25	2.18	1.44	1.88	1.80		
$Q_{NPA}(Cl)$	−0.30	−0.36	−0.34	−0.24	−0.30	−0.28		
$Q_{NPA}(O)$	−0.60	−0.81	−0.81	−0.48	−0.67	−0.66		
OP(M−4Cl)	2.17	2.26	2.26	2.03	2.12	2.13	1.69	1.71
OP(M=O)	0.44	0.80	0.55	0.34	0.72	0.43	0.70	0.77
OP(total)	2.61	3.06	2.81	2.37	2.84	2.56	2.35	2.40
dipole moment	0.26	0.90	1.01	0.24	0.77	0.83	0.49	1.03
MO_2Cl_2								
$Q_{MPA}(M)$	2.18	1.94	2.32	1.71	1.52	1.83	1.08	0.97
$Q_{MPA}(Cl)$	−0.37	−0.36	−0.35	−0.29	−0.29	−0.28	−0.19	−0.13
$Q_{MPA}(O)$	−0.72	−0.61	−0.81	−0.57	−0.47	−0.64	−0.37	−0.35
$Q_{NPA}(M)$	2.21	2.61	2.59	1.85	2.23	2.19		
$Q_{NPA}(Cl)$	−0.38	−0.43	−0.41	−0.33	−0.37	−0.35		
$Q_{NPA}(O)$	−0.72	−0.88	−0.89	−0.60	−0.74	−0.75		
OP(M−2Cl)	1.13	1.20	1.19	1.11	1.16	1.16	0.86	0.85
OP(M=2O)	1.01	1.52	1.21	0.92	1.39	1.06	1.38	1.48
OP(total)	2.14	2.72	2.40	2.03	2.55	2.22	2.23	2.34
dipole moment	1.70	2.64	2.80	1.51	2.39	2.51	1.35	1.83
MO_3								
$Q_{MPA}(M)$	2.36	2.03	2.48	1.83	1.57	1.93		
$Q_{MPA}(O)$	−0.79	−0.68	−0.83	−0.61	−0.52	−0.64		
$Q_{NPA}(M)$	2.55	2.81	2.79	2.07	2.28	2.28		
$Q_{NPA}(O)$	−0.85	−0.94	−0.93	−0.69	−0.76	−0.76		
OP(total)	1.53	2.21	1.85	1.50	2.00	1.59		
dipole moment	5.64	6.86	7.30	5.50	6.15	6.19		

[a] The MPA charges for metal atoms at the DHF level are −1.21, −1.16, 0.65, and 1.64 for WCl_6, $SgCl_6$, $SgOCl_4$, and SgO_2Cl_2, respectively. Reference 3. [b] References 29, 31, and 32.

the HF, MP2, and QCISD levels of theory. For the SgO_2Cl_2, REP-KRHF calculations were also performed. Spin−orbit coupling has negligible effects on MPA charges, overlap populations, and dipole moments, implying that such analyses in AREP calculations need not be corrected for spin−orbit effects for these systems. The MPA charges, overlap populations, and dipole moments from DS-DV method and the MPA charges at the DHF level are also included for comparison. Pershina et al.[32] subdivided the experimental ΔH_{diss} values evaluated by the Born−Haber cycle into ionic and covalent contributions using their calculated MPA charges. They evaluated the ionic contributions by a simple formula involving MPA atomic charges and regarded ΔH_{diss} − (ionic term) as the covalent contributions. For the Sg compounds, whose ΔH_{diss} value could not be determined by experiments, they evaluated the ΔH_{diss} values by the sum of calculated ionic contribution from a simple formula involving the MPA charges and estimated covalent contributions using their overlap populations on the basis of the empirical correlation between overlap populations and covalent contributions. They have also tried to explain trends of the experimental volatility using the MPA charges, overlap populations, and dipole moments obtained from the DS-DV calculations.[6] From W to Sg, MPA charges of the central metal decrease, while overlap populations and dipole moments increase, which is consistent with the DS-DV results of Pershina et al. However, NPA charges, which are usually considered more reasonable than MPA charges, are qualitatively different from

MPA charges. Larger positive metal charges were obtained for SgO_2Cl_2 than WO_2Cl_2 at all the levels of theory considered.

In Table 10, MPA charges, NPA charges, overlap populations, and dipole moments for MCl_6, $MOCl_4$, MO_2Cl_2, and MO_3 (M = W and Sg) at the HF and QCISD levels of theory are summarized. The analyses for those properties of the molecules are expected to reveal the contributions of M−O and M−Cl bonds explicitly. We assume that spin−orbit effects on the properties are small enough to warrant the reliability of such analyses using only AREP. In line with the results in Table 9, MPA and NPA provide qualitatively different trends for the charge distributions of all the systems considered. To check whether the discrepancies are caused by the differences in the pattern between the W and Sg basis sets or not, we also calculated the Sg compounds using a 5s5p4d basis set for Sg[9] which has the same pattern as the basis set for W. The results are listed in the Sg* column in Table 10. In this case, both MPA and NPA predict that the positive charges of Sg are larger than those of W for all the systems. The change of basis set increases MPA charges of the metals by a significant margin, but little affects the NPA charges. In fact, it is known that MPA charge distributions are very much dependent on the size of the basis set. Overlap populations decrease as the number of oxygen atoms increases when the 5s5p4d basis set is used for Sg, but it is not the case when using the original [6sd5p]/(5sd5p) basis set of Sg. The MPA charges and overlap populations evaluated using the original Sg basis set appear to be spurious,

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TABLE 11: Optimized Geometries of MCl$_5$ and MBr$_5$ (M = Ta and Db) at the HF and MP2 Levels of Theory (Bond Lengths in Å and Angles in deg)

	Ta		Db	
	HF	MP2^a	HF^b	MP2
MCl$_5$				
D_{3h}				
r(M−Cl$_{ax}$)	2.340	2.323(2.369)	2.394(2.393)	2.380
r(M−Cl$_{eq}$)	2.287	2.276(2.227)	2.356(2.354)	2.344
C_{4v}				
r(M−Cl$_{ax}$)	2.247	2.237	2.325(2.321)	2.313
r(M−Cl$_{eq}$)	2.325	2.311	2.385(2.384)	2.372
∠(Cl$_{ax}$−M−Cl$_{eq}$)	104.2	103.8	104.0(104.1)	103.4
MBr$_5$				
D_{3h}				
r(M−Br$_{ax}$)	2.500	2.481(2.473)	2.551	2.536
r(M−Br$_{eq}$)	2.442	2.435(2.412)	2.508	2.499
C_{4v}				
r(M−Br$_{ax}$)	2.394	2.388	2.467	2.460
r(M−Br$_{eq}$)	2.484	2.472	2.541	2.530
∠(Br$_{ax}$−M−Br$_{eq}$)	104.0	103.5	103.6	103.1

^{a} The values in parentheses refer to the bond lengths from electron diffraction experiments. References 33 and 35. ^{b} The values in parentheses refer to the REP-KRHF geometries.

and those values should be interpreted in a cautious way. However, we confirmed that changing the basis set for Sg insignificantly modifies the results for the atomization energies.

The RECP calculated charges on Sg are always larger than those on W for all the cases, which disagree with the MPA results of the DS-DV method. The origin of the discrepancies is not clear, since the DS-DV calculations were performed with near-minimal basis sets which are not likely to be affected by spurious MPA results typical of extended basis sets. The smaller ionic term due to smaller charge separation in the DS-DV method seems to produce ΔH_{diss} values close to our CCSD(T) atomization energies for the Sg compounds, whereas their ΔH_{diss} values for the W compounds are somewhat larger than ours by 1.3−1.8 eV. Nevertheless, overlap populations and dipole moments for Sg compounds are larger than those for W compounds, which are in good accord with the DS-DV results, as shown in Table 10. We expect to reach the same conclusion as Pershina et al. for the molecular volatility of transactinide compounds, which can be estimated on the basis of the overlap populations and dipole moments. The MPA charges obtained at the DFB-HF level[3] significantly differ from our MPA charges at the HF level. In particular, the metal atoms in the WCl$_6$ and SgCl$_6$ have negative charges −1.21 and −1.16, respectively, in the DFB-HF results. Since six highly electronegative chlorines are attached to the metal atom, our charges appear more reasonable than DHF ones.

Optimized geometries for the D_{3h} and C_{4v} isomers of TaCl$_5$, TaBr$_5$, DbCl$_5$, and DbBr$_5$ at the HF and MP2 levels of theory using AREP and REPs are listed in Table 11. An electron diffraction study[33] has shown that the TaCl$_5$ monomer has the geometrical structure of a trigonal bipyramid possessing D_{3h} symmetry. Pershina et al.[34] could not determine the ground states for those molecules due to the insufficient accuracy in the total energy calculated by the DS-DV method. In the present calculations, the D_{3h} structures are found to be more stable than the C_{4v} ones for all the systems considered. Furthermore, the C_{4v} forms are not local minima on the potential energy surfaces since they contain one imaginary frequency in the normal-mode analysis. The difference in the calculated bond lengths between the axial bonds and the equatorial bonds (0.047 Å) for the D_{3h} form of TaCl$_5$ is considerably smaller than that from the electron diffraction experiment (0.142 Å). In the later electron diffraction

TABLE 12: Energy Differences ($E_{C_{4v}} - E_{D_{3h}}$) between D_{3h} and C_{4v} Isomers of TaCl$_5$, DbCl$_5$, TaBr$_5$, and DbBr$_5$ at the HF-Optimized Geometries (in kcal/mol)

	TaCl$_5$	DbCl$_5$^{a}	TaBr$_5$	DbBr$_5$
HF	2.13	2.28(2.26)	2.04	2.21
MP2	1.71	2.24	1.46	1.94
CCSD	1.84	2.27	1.65	2.01
CCSD(T)	1.80	2.26	1.62	1.98

^{a} The value in parentheses is the energy difference using the REP.

work,[35] it was shown that the axial bonds in TaBr$_5$ are longer than the equatorial bonds merely by 0.061 (10) Å, which is in good agreement with the small difference (0.046 Å) in our calculations. The changes of geometries due to spin−orbit coupling are negligible, but show a definite trend of the bond length contraction. The energy differences between D_{3h} and C_{4v} forms of the molecules at the HF, MP2, CCSD, and CCSD(T) methods using the HF optimized geometries are listed in Table 12. The energy differences between D_{3h} and C_{4v} structures are approximately 2 kcal/mol for these molecules. Both spin−orbit and electron correlation effects are unimportant for the determination of relative energies between isomers.

IV. Conclusions

We have performed the HF, MP2, QCISD, CCSD, and CCSD(T) calculations for the ground states of the halides and oxides containing transactinide elements Rf, Db, and Sg using one- and two-component shape-consistent RECPs. Spin−orbit interactions contract the bond lengths for all the calculated molecules but the amounts of geometrical changes are very small. Electron correlation effects on geometries are significant. Spin−orbit effects on atomization energies are considerable at the correlated levels of theory. The CCSD(T) atomization energies for WCl$_6$, WOCl$_4$, and WO$_2$Cl$_2$ are in good accord with, but somewhat smaller (by 1.3−1.8) than the experimental ΔH_{diss} values obtained from the Born−Haber cycle. The CCSD(T) atomization energies for SgCl$_6$, SgOCl$_4$, and SgO$_2$Cl$_2$ are also in good agreement with the values estimated by Pershina et al. from experimental data for lighter homologues and their DS-DV parameters. Electron correlation effects, which are crucial for determining accurate atomization energies, strongly depend on the types of metal and ligands. In conclusion, the HF level of calculations do not provide qualitatively correct trends of atomization energies for these systems. Both electron correlation and spin−orbit contributions are necessary to make atomization energies of the W compounds larger than those of the Sg compounds. The DFB-HF results reported by Malli for the W and Sg compounds qualitatively differ from our REP-KRHF results, our correlated results, and the ΔH_{diss} values estimated by Pershina et al., although the DFB-HF results for RfCl$_4$ are in good agreement with our REP-KRHF ones.

MPA charges and overlap populations strongly depend on the basis set, but NPA charges appear more consistent. Calculated NPA charges indicate that Sg is more ionic than W. Overlap populations of MPA and dipole moments increase from W to Sg. Although the trends of the charges do not agree with those of DS-DV, the trends of the overlap populations and the dipole moments are in agreement with the DS-DV results. Spin−orbit effects at the HF level are negligibly small for MPA charges, overlap populations, dipole moments, harmonic vibrational frequencies, and relative energies between isomers.

RECP approaches afford a balanced treatment of the relativity and electron correlations for the transactinide compounds with

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relatively low cost. Spin−orbit effects are rather small but electron correlations are necessary for any accurate determination of molecular properties. We conclude that coupled-cluster calculations using scalar relativistic ECP, i.e., AREP, will be reasonable enough for most purposes to study ground states of the d-block transactinide compounds.

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