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Evaluation of Two Computational Models Based on Different Effective Core Potentials for Use in Organocesium Chemistry

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Abstract: The performance of two computational models was evaluated in describing some aggregated structures, the bond lengths and dimerization energies of cesium halides, aquation energies of the cesium cation, and protonation energies of a range of organocesium compounds. One model used the Hay–Wadt (HW) effective core potential (ECP) and a double- ζ valence basis set on Cs; the other used the Ross ECP with two polarization functions on Cs. In both models, the standard 6-31+G** basis was used for the other atoms. At the Hartree–Fock (HF) level, the Ross ECP was found to give geometries and energies in good agreement with experimental results. Second-order Møller–Plesset calculations with this model gave only modestly improved results compared to HF; the B3LYP level gave variable results with unsatisfactory energies. Although the HW model is generally less satisfactory, it often shows comparable trends to those of the Ross model.

Introduction

Over the course of a number of years, we have contributed a number of quantitative data on organocesium chemistry, particularly in cesium ion-pair carbon acidity,¹ the aggregation of cesium enolates,^{2–8} and kinetic acidities with cesium cyclohexylamide.⁹ If these results could be modeled effectively with *ab initio* computations at some reasonable theory level, then they could presumably be extrapolated to other compounds and further extend their usefulness. We are currently engaged in such modeling. To this end, it is important to have an appropriate effective core potential (ECP)¹⁰ for cesium. The use of ECPs reduces the number of electrons to be treated explicitly in electronic structure calculations and, perhaps more importantly, can account for relativistic effects essential in treating the cores of heavy elements. The traditional and most widely used set of ECPs is that developed by Hay and Wadt (HW)¹¹ for most of the elements in the periodic table. Several other ECPs have been developed in recent years, of which that developed by Ross et al. (Ross)¹² has also been widely used. Both ECPs are calibrated for relativistic effects, but the Ross potential

includes spin–orbit effects. The HW ECP has been used, for example, in studies of Cs⁺ complexed to ethers,^{13,14} liquid cesium,¹⁵ cesium boranes,¹⁶ ¹⁹F NMR spectra of Cs salts,¹⁷ and the effect of pressure on cesium sulfide.¹⁸ Similarly, the Ross ECP has been used in studies of diatomic cesium,¹⁹ crown ethers complexed to Cs⁺,²⁰ and the excitation of CsI.²¹

Several years ago, we began calculations to model our ion-pair acidity studies of organocesium compounds. For this purpose, we used Hartree–Fock (HF) calculations using the HW ECP for Cs plus a double- ζ basis set for the Cs valence shell and the standard 6-31+G** basis for the other atoms. Results from this model were not satisfactory, and we repeated the calculations using the larger Ross ECP. This ECP includes a polarization d function with four primitives. We introduced greater flexibility by spitting this d function in two by liberating the penultimate primitive as a separate function. The result was a significant improvement over the HW model. In the present paper, we compare results from both of these computational models symbolized as HW and Ross.

Except for a limited study of arylcesiums,²² we are not aware of any comparisons of these basis sets for organocesium chemistry.

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Table 1. Comparison of ECPs with the Experimental Bond Lengths (Å) for Cesium Diatomics (CsX)

X	HW				Ross			Ross HF – d ^a
	HF	MP2	B3LYP	exptl	HF	MP2	B3LYP	
H	2.762	2.770	2.710	2.494	2.597	2.553	2.527	2.716
F	2.657	2.703	2.664	2.345	2.445	2.434	2.414	2.575
Cl	3.241	3.252	3.214	2.906	3.053	3.007	2.981	3.182
Br	3.377	3.381	3.340	3.072	3.210	3.156	3.136	3.315

^a Ross ECP with d functions deleted from the ECP basis.

Computational Methods

Calculations were done using various editions of the Gaussian series of programs up to Gaussian 03.²³ Geometries at all theory levels used were optimized using the 6-31+G** basis set on all atoms except cesium, for which the modified HW and Ross ECPs were used. The HW ECP included the double- ζ valence basis set as supplied in Gaussian with the LANL2DZ keyword. The basis set provided by the Ross ECP was split into s 4/4/1, p 3/1/1, and d 3/1 and provides greater flexibility than the HW set. We are not concerned here with spin–orbit effects, and this part of the Ross ECP was not used. The complete sets used are tabulated in Table S1 (Supporting Information).

The study involved HF, second-order Møller–Plesset (MP2), and B3LYP computations. In each case, all structures were fully optimized and shown to be local minima on the potential energy surface by frequency calculations (zero imaginary frequencies). The structure coordinates and energies for all computations are summarized in Table S2 (Supporting Information).

Results and Discussion

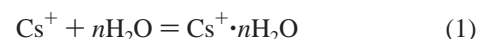
A simple study of some cesium diatomics shows immediately that the two computational models give quite different results (Table 1). At the HF level, as well as with MP2 and the popular hybrid density functional theory method, B3LYP, the HW model gives computed bond distances much larger than experimental results. The Ross model does much better and with the incorporation of correlation at the MP2 level gives bond distances that average only 0.08 Å greater than experimental results. The ability of MP2 to give good bond lengths was shown previously for CsH using a different ECP.²⁴ Computations of the cesium halides with the Ross ECP and a somewhat smaller basis set for the halides at MP2 have been published previously.²⁵ B3LYP computations with the Ross ECP give good bond distances for the cesium halides, but we'll see below that this promise is not sustained in computations of reaction energies.

Much of the improvement with the Ross ECP appears to be related to the inclusion of d functions. When these are deleted from the ECP, the CsX bond distances are significantly longer and start to resemble the HW results (Table 1). A much larger ECP has recently been proposed that adds both f and g functions to the outermost nine electrons of Cs.²⁶ We have not compared this new ECP.

Some energy quantities are available for a further comparison. Gas-phase aquation energies, eq 1, are known for cesium cations with up to four waters.²⁷ Feller et al.,²⁸ and an earlier paper of Glendening and Feller,²⁹ have provided

an extensive study of water clusters with alkali cations up to eight waters. They compared several theory levels and basis sets but for Cs used the Hay–Wadt ECP augmented with polarization functions. The resulting ECP is thus actually closer to our Ross model. They also showed that the 6-31+G* basis set with the other elements can give satisfactory results. These studies described a number of types of structures including those with hydrogen bonds among waters, particularly for higher numbers of coordinated waters. In our present study, to compare the two Cs ECPs, we have focused on Cs⁺ with up to four waters of coordination sufficiently separated so that hydrogen bonding is not involved.

The comparisons in Table 2 show that the Ross ECP gives better quantitative results. The Ross aquation energies are lower than experimental values by only 1 kcal mol^{−1} per water. The MP2 results are only slightly better. With increasing waters, the Cs–O bond distance increases and the aquation energy per water decreases as expected. The HW Cs–O bond distances are systematically larger, and the computed aquation energies correspondingly are lower but only by about another 1–2 kcal mol^{−1}. The MP2 results differ only slightly from those of Ross HF. In all cases, the bonding increases with a shorter Cs–O distance; these are shortest with Ross MP2 and longest with HW. The Ross B3LYP results show aquation energies that are significantly lower.



Of particular interest are some of the structures. Cs⁺·2H₂O with the Ross ECP is bent with an O–Cs–O angle of 113.5°. The same result was found by Kaupp and Schleyer³⁰ using larger basis sets. Similar bent structures were found at several theory levels by Feller et al.^{28,29} Such bent structures are normally attributed to polarization of the central cation. In this connection, it is interesting that, with the HW ECP, without additional polarization functions, the minimum structure of Cs⁺·2H₂O is *D*_{2d} with O–Cs–O = 180°. Similarly, Cs⁺·3H₂O with the Ross ECP is pyramidal with O–Cs–O = 103.7°, as found by others,^{28–30} whereas the minimum structure with HW is *D*₃ with oxygens and cesium in the same plane. These results would seem to confirm the role of polarization in cesium structures and the importance of including polarization functions.

Dimerization energies of the cesium halides provide a further opportunity for ECP comparison and are a more complex function of bond distances since the Cs–X distances are different in monomers and dimers. These monomers and dimers have been treated frequently in the past, especially with various ionic models.³¹ Thermodynamic measurements are almost all several decades old and were tabulated in 1974 by Kondrat'ev.³² We know of only one measurement (for CsBr³³) since then. The available results are compared to computed values at several levels of theory in Table 3. It is difficult to compare the experimental results to theory since results from different laboratories vary by several kilocalories per mole. Moreover, the experiments were all done at high temperatures, although some were extrapolated to lower

Table 2. Enthalpies of Reaction of Cesium Cation with 1–4 Molecules of Water; Energies in kcal mol^{−1}

compound	−ΔE _{aq} exptl ^a	Ross −ΔE ^b	r(CsO), Å	HW −ΔE ^b	r(CsO), Å	Ross, MP2 −ΔE ^c	r(CsO), Å	Ross, B3LYP −ΔE ^d	r(CsO), Å
Cs ⁺ ·H ₂ O	13.7	12.91	3.058	11.96	3.154	13.22	2.985	12.67	2.996
Cs ⁺ ·2H ₂ O	26.2	24.29	3.096	22.86	3.190	24.87	3.014	23.85	3.032
Cs ⁺ ·3H ₂ O	37.4	34.35	3.132	32.59	3.211	35.09	3.040	33.62	3.072
Cs ⁺ ·4H ₂ O	48.0	43.20	3.166	41.19	3.238	44.35	3.074	41.98	3.103

^a ref 27. ^b ΔE = E(Cs⁺·nH₂O) − E(Cs⁺) − nE(H₂O) including unscaled ZPE; HF 6-31+g(d,p) + Cs ECP. ^c ΔE = E(Cs⁺·nH₂O) − E(Cs⁺) − nE(H₂O) including unscaled ZPE; MP2 6-31+g(d,p) + Cs ECP. ^d ΔE = E(Cs⁺·nH₂O) − E(Cs⁺) − nE(H₂O) including unscaled ZPE; B3LYP 6-31+g(d,p) + Cs ECP.

Table 3. Dissociation Energies (kcal mol^{−1}) of Cesium Halide Dimers to Monomers, Experimental and Theoretical

com- pound	ΔH _d ^o exptl	ΔE _d calcd ^a	ΔE _d HW ^b	ΔE _d Ross ^b	ΔE _d Ross- MP2 ^b	ΔE _d Ross- B3LYP ^b
Cs ₂ F ₂	37.8 ± 1.3 (863 K) ^c 42.3 (298 K) ^d 38.8 ± 2 (298 K) 38.9 (0 K) ^e	43.4	46.35	40.04	39.92	35.56
Cs ₂ Cl ₂	38.9 (815 K) ^f 34.7 ± 1.1 (1300 K) ^g 40.1 (1300 K) ^h 36.2 ± 1.0 (298 K) 36.7 (0 K) ^c	42.2	40.60	36.76	36.58	30.55
Cs ₂ Br ₂	40.4 (1300 K) ^h 39.4 (1600 K) ^h 38.8 ± 2.4 (298 K) ⁱ 34.5 ± 1.0 (298 K) 34.7 (0 K) ^e	39.3	39.84	38.53	38.23	34.67

^a 6-31G* + ECP(Cs, Cl, Br) + MP2; ref 25. ^b This work. HF, MP2, or B3LYP, 6-31+G(d) + unscaled ZPE. ^c Ref 39. ^d Ref 40. ^e Ref 35. ^f Ref 41. ^g Ref 42. ^h Ref 34. ⁱ Ref 33.

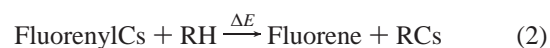
temperatures using thermodynamic functions. The theoretical results all pertain to 0 K. We could try to discern trends from the results of two compounds in the same laboratory. The Romanian group³⁴ reports almost equal values for CsCl and CsBr. Kondrat'ev³² reports values for all of the cesium halides given in a dissertation³⁵ but without details. These results show a monotonic decrease in dissociation energies from Cs₂F₂ to Cs₂I₂. The theoretical results of Hilpert et al.³³ also show such a monotonic decrease, but these results are known to contain a basis set superposition error (BSSE) of several kilocalories per mole. Our use of diffuse functions should minimize the importance of BSSE.^{28,36} The Ross MP2 results summarized in Table 3 are probably the most reliable values currently available for these energies; they show a nonmonotonic change along the halide series with a dip in ΔE_{diss} at Cs₂Cl₂. The Ross HF values show the same trend and indeed vary from the MP2 results by only 0.1–0.3 kcal mol^{−1}. The HW ECP, however, gives results substantially different and also gives a monotonic series. The Ross B3LYP energies show a nonmonotonic trend but are several kilocalories per mole lower than the other results.

Structure determinations could also provide suitable tests for the two ECPs. Most crystal structures of cesium compounds show extended networks not suitable for modeling with computations of isolated single molecules. A few structures are available, however, that have well-isolated units. An example is the dimer, **1**, of cesium hexamethyldisilazide.³⁷ This compound crystallized with a molecule of toluene. The cesium salt units show an inversion center with two Cs–N bond lengths of 3.074 and 3.149 Å. The HF/Ross results are reasonably consistent with the Cs–N bond

lengths being slightly longer, 3.145 and 3.254 Å, as expected from the cesium halide results above. The calculated N–Cs–N angle of 94.7° is also a little larger than the crystal structure's 90.7°. The bonds to cesium in the HW structure are substantially longer: Cs–N = 3.308 and 3.390 Å and N–Cs–N = 95.8°. The bonds not involving cesium are closer with both ECPs to those measured. The N–Si bond lengths are 1.673 and 1.679 Å (experimental), 1.683 and 1.684 Å (Ross), and 1.676 and 1.677 Å (HW). Similarly, the methyl groups form sets of six with Si–C = 1.872–1.890 Å (experimental), 1.904–1.917 Å (Ross), and 1.905–1.919 Å (HW). The agreement between the crystal structure and the Ross ECP results are clearly satisfactory and only a little less so for the HW ECP.

Unfortunately, this agreement does not extend to the structure of the tetramer, **2**, of cesium (trimethylsilyl)amide, (CsNHSiMe₃)₄.³⁸ The reported crystal structure is cubanelike but with a “remarkably short” Si–N bond length of 1.59 Å, as well as a rather short Cs–N bond length of 2.915 Å. The computational model was that of the tetramer of cesium silylamide, (CsNHSiH₃)₄, because of the size of the trimethylsilyl moiety. The computed structure with both ECPs is that of a distorted cube with two Cs–N bond lengths (Ross, 3.231 Å; HW, 3.345 Å) differing from the third (Ross, 3.167 Å; HW, 3.320 Å). Both sets of distances are comparable to those found with **1**. The N–Si bond length is also normal (Ross, 1.691 Å; HW, 1.686 Å) and also comparable to Si–N computed for **1**. The reported unusual structure for **2** finds no support in the computations with either ECP, and we suspect that there is some problem with the crystal structure.

Finally, we compare the HW and Ross protonation energies for a test group of cesium compounds including the Cs salts of both delocalized and localized carbanions as well as compounds with Cs–O, Cs–N, and Cs–S bonds; Cs–H; and some cesium halides. For the present, we compare the two sets of ECP results. Comparison with experimental relative acidities is beyond the scope of the present study and will be discussed in a separate paper. For convenience, the results are considered relative to fluorene in terms of the proton and cesium exchange in eq 2.



The data are summarized in Table 4 and plotted in Figure 1. Since we are comparing electronic energy calculations with two ECPs, these data do not include the zero-point energy (ZPE). These energies are, in any event, quite similar to the

Table 4. Ross and HW ΔE Values (eq 2, kcal mol⁻¹) for Various RCs Compounds

RH	RCs	$\Delta E(\text{Ross})$	$\Delta E(\text{HW})$
Delocalized C–Cs			
cyclopentadiene	CpCs	-15.073	-11.759
indene	IndCs	-7.473	-6.314
fluorene	FICs	0.000	0.000
benzo[b]fluorene	Benzo[b]FICs	3.362	2.856
benzo[def]fluorene	Benzo[def]FICs	1.716	1.096
toluene	BnCs	24.338	25.101
<i>p</i> -methylbiphenyl	<i>p</i> -PhBnCs	23.421	23.312
diphenylmethane	Ph ₂ CHCs	16.224	15.850
triphenylmethane	Ph ₃ CCs	16.033	15.407
propylene	AllylCs	23.872	27.040
1,3-pentadiene	PentadienylCs	14.259	15.707
1,3-diphenylpropene	1,3-DiPhAllylCs	11.367	10.752
Localized C–Cs			
methane	MeCs	44.351	48.009
ethane	EtCs	49.175	53.198
ethylene	VinylCs	34.187	38.085
benzene	PhCs	35.074	37.568
<i>m</i> -fluorobenzene	<i>m</i> -FPhCs	31.050	32.971
<i>p</i> -fluorobenzene	<i>p</i> -FPhCs	33.052	35.227
2,6-difluorobenzene	2,6-DiFPhCs	11.684	12.037
acetylene	EthynylCs	2.775	4.444
dimethyl sulfide	CH ₃ SCH ₂ Cs	28.388	30.618
dimethyl sulfoxide	CH ₃ SOCH ₂ Cs	3.881	5.825
dimethyl sulfone	CH ₃ SO ₂ CH ₂ Cs	-4.024	-4.235
PhSCH ₃	PhSCH ₂ Cs	25.278	26.823
PhSOCH ₃	PhSOCH ₂ Cs	3.811	5.270
PhSO ₂ CH ₃	PhSO ₂ CH ₂ Cs	-2.367	-2.738
dithiane	DithianylCs	14.272	15.778
phenyldithiane	PhDithianylCs	10.351	10.126
methyldithiane	MeDithianylCs	18.693	20.267
O–Cs			
water	CsOH	-1.845	4.582
methanol	CsOMe	-2.008	3.792
phenol	Cs phenoxide	-17.254	-15.341
ethanol	Cs vinyloxide	-16.700	-14.137
2-propenol	Cs α -MeVinyl oxide	-16.135	-15.364
2-methyl-1-propenol	Cs $\beta\beta$ -DiMeVinyl oxide	-13.010	-10.123
1-phenylethanol	Cs 1-PhVinyl oxide	-17.730	-16.092
α -tetralone enol	Cs tetralone-enolate	-16.068	-14.102
isobutyrophenone enol	CsIBP	-14.631	-12.889
N–Cs			
ammonia	CsNH ₂	20.666	26.704
CH ₃ NH ₂	Cs MeAmide	23.598	29.707
Me ₂ NH	Cs DiMeAmide	23.468	29.036
PhNH ₂	Cs anilide	5.656	7.404
Ph ₂ NH	Cs diphamide	-1.906	-2.016
carbazole	Cs carbazolid	-10.371	-11.126
S–Cs			
H ₂ S	CsSH	-21.653	-20.820
CH ₃ SH	CsSMe	-15.428	-14.078
PhSH	CsSPh	-25.933	-25.713
Miscellaneous			
H ₂	CsH	20.339	26.560
HF	CsF	-22.623	-16.036
HCl	CsCl	-46.644	-44.898
HBr	CsBr	-55.608	-53.103

two ECPs, and the overall results are not dependent on this treatment. For carbonyl compounds, the comparison was made for the corresponding enols. In this way, all of the Cs–O results reflect the change RO–H \rightarrow RO–Cs.

Despite the generally longer bond lengths with the HW ECP, the two calculation models give results that correlate quite closely. When all of the data in Figure 1 is used, the plot of $\Delta E(\text{HW})$ versus $\Delta E(\text{Ross})$ gives an intercept of 1.82 kcal mol⁻¹ and a slope close to unity. An alternative approach is to focus on the cesium salts of delocalized carbanions since these are expected to have generally longer bonds to cesium and polarization of the cesium cation, a significant difference between the two ECPs, might be less important. This correlation is quite similar but with a smaller intercept of 0.54 kcal mol⁻¹ and a slope just slightly less than unity. Both

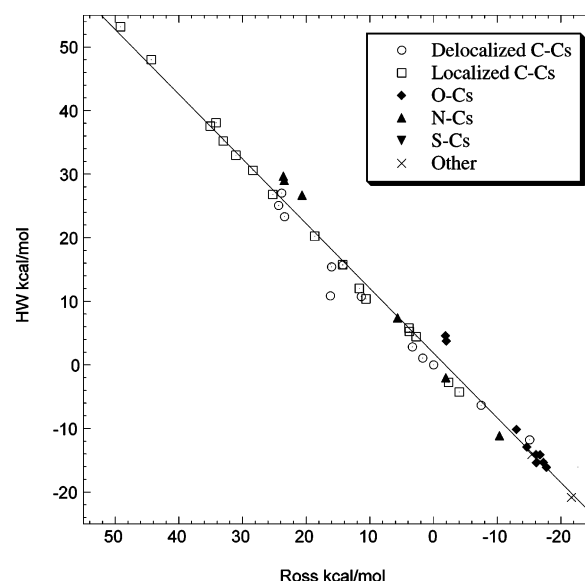


Figure 1. Plot of $\Delta E(\text{HW})$ vs $\Delta E(\text{Ross})$ for eq 2 (kcal mol⁻¹). The line shown is the regression line through all of the points: $\Delta E(\text{HW}) = 1.82 \pm 0.31 + (1.017 \pm 0.015)\Delta E(\text{Ross})$, $R^2 = 0.990$. A similar regression line for the delocalized C–Cs compounds gives $\Delta E(\text{HW}) = 0.54 \pm 0.82 + (0.960 \pm 0.054)\Delta E(\text{Ross})$, $R^2 = 0.970$.

correlations have high R^2 values. Although the general correlation is good, some compounds deviate substantially but in only a few systematic ways. The exception that the delocalized carbanion salts fall generally below the correlation given by the other more localized cesium salts does suggest that polarization functions on cesium are somewhat less important for those carbanions with effectively longer distances between positive and negative charge.

Conclusions

A computational model using the HW ECP without d functions on Cs gives bond lengths to cesium that are generally too long and corresponding bond strengths that are significantly too small. An alternative model based on the Ross ECP with d functions on Cs gives results that are generally more satisfactory. Nevertheless, for some qualitative work, the smaller HW basis set can give satisfactory results. For more quantitative work, however, the larger Ross ECP is to be preferred. B3LYP with the Ross ECP gives bond energies that are too low and should only be used after further calibration.

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Supporting Information Available: Tables of basis sets, energies, and structural coordinates. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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