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Atomic and Molecular Properties of Elements 112, 114, and 118

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The results of calculations outlining aspects of the chemistry of element 112, element 114, and element 118 are compared to those for their 6th row analogues Hg, Pb, and Rn, respectively. Element 112 and element 114 are found to be relatively inert as compared to Hg and Pb, while element 118 is much more active than radon. Spin−orbit coupling plays a dominant role in this behavior.

Introduction

In 1975, K. Pitzer made a bold and unconventional suggestion: despite their positions in the periodic table and in marked contrast to their 6th row analogues, Hg and Pb, element 112 and element 114, are likely to be inert gases under standard conditions.[1] This prediction was based on an analysis of extreme valence-shell relativistic effects expected for these transactinides. Since then, numerous theoretical and a few experimental studies reveal a chemistry for transactinides that in some cases is indeed significantly different from elements of lower periods.[2] The disparities seem to be more acute for the 7p block (element 113−element 118) than for 6d transition elements (Lr-element 112) and for the former result principally from dramatic shell structure effects induced by spin−orbit coupling. In the 7th row of the periodic table, a $7p_{1/2}$ "spinor shell" ($j = l + s = {}^1/_2$) is completed at element 114 ($7s^27p_{1/2}{}^2$ valence electron configuration), while the entire 7p shell, including both $7p_{1/2}$ and $j = {}^3/_2$ $7p_{3/2}$ spinor components, is fully filled at element 118 ($7s^27p_{1/2}{}^27p_{3/2}{}^4$ valence electron configuration). A question then arises about the degree to which the completion of the $7p_{1/2}$ spinor mirrors in its chemical consequences a valence shell or subshell closing. Put another way, does spin−orbit splitting in the 7p shell of transactinide atoms lead to a secondary periodicity wherein two different atoms in the same period resemble completed valence electron shells?

From this perspective, mercury and element 112, which complete the 5d and 6d blocks, respectively, can also in some sense each be seen as "honorary" closed valence-shell atoms (ns^2np^0). Elements 112 and 118, and to a lesser extent element 114, might therefore all be expected to exhibit behavior dominated by their closed-shell character. This is certainly true of the 6th row analogues of element 112 and element 118, Hg and Rn, respectively, a relatively noble metal and classic noble gas. On the other hand, as an analogue of element 114, lead, though not an active metal, is certainly not noble. This work will extend previous theoretical investigations into the prospective chemistry of "closed-shell" p-block superheavy elements (including element 112) and attempt to put into context aspects of it that differ from expected periodic behavior.[3]

Pitzer's 1975 proposition followed Desclaux's publication of relativistic atomic orbital eigenvalues for H-element 120,[1,4] and for most of the intervening years, it has remained an interesting although largely untestable hypothesis. However, recent years have seen the synthesis of transactinide elements through $Z = 116$, and advances in "atom at a time" analytical techniques have led to reports detailing chemical investigation for elements as heavy as element 112.[5,6] It now seems possible to experimentally address Pitzer's hypothesis, but it will be helpful to have reasonably accurate predictions for ionization potentials and other properties for these elements. It is in that context I make this submission. That relativistic effects dominate the electronic structure of the superheavy transactinide elements has been well established, and the particular chemical consequences of these effects, hypothetical "nonrelativistic" elements, will not be dealt with here.[7] Rather, to flesh out a rough draft outline for their behavior, I shall examine various properties of elements 112, 114, and 118 and compare their predicted behavior with the known or imputed chemistry of Hg, Pb, and Rn, respectively.

This work will focus on particular properties of these elements that are taken as proxies for higher-order chemical behavior. Atomic polarizability and proton affinity are analyzed in terms of their relationship to the relative basicities of the elements in question. Properties related to these are bond length, bond dissociation energy, ionization potential, and σ-bonding capacity (the only bonding mode available to H). In addition, there is perhaps no more fundamental information about an element than its capacity to bond with other atoms of the same type, even if it is extraordinarily unlikely that any experiment would find two atoms of any transactinide element within bonding distance of one another. For this reason, I have elected to examine the cohesive properties of these superheavy elements, and their lighter periodic analogues, through the spectroscopic constants of the homonuclear diatomic molecules.

One point bears elaboration: It is well known that spin−orbit coupling mixes the σ and π character of atomic valence orbitals. For example, the $\boldsymbol{\omega} = {}^1/_2$ projection along a bond axis of a $p_{1/2}$ atomic valence spinor has a ${}^1/_3\sigma$ character and a ${}^2/_3\pi$ character, while the $\boldsymbol{\omega} = {}^1/_2$ projection of a $p_{3/2}$ spinor is comprised of ${}^2/_3\sigma$ and ${}^1/_3\pi$. The $\boldsymbol{\omega} = {}^3/_2$ projection of $p_{3/2}$ is entirely π-like. For atoms in which spin−orbit coupling is modest or negligible, pure σ or π character is recovered through hybridization or admixtures of $p_{1/2}$ and $p_{3/2}$ spinors. As the magnitude of spin−orbit coupling increases, the extent of spinor mixing decreases and the strict distinction between bonding orbitals of σ and π character is lost. At the extreme of spin−orbit coupling represented by the 7p elements, such mixtures

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TABLE 1: "Chemical" Polarizabilities α (au) for 6p and 7p Block Elements Calculated As Described in the Text

α_c (au)	Hg	(112)	Pb	(114)	Rn	(118)
ccsd(t)	28.48	28.68	50.95	34.35	28.61	52.43
ccsd	28.82	28.61	51.22	34.08	28.61	52.50
mp2	27.13	27.67	49.94	34.42	28.48	49.47
hf	32.46	30.30	55.47	33.74	29.22	54.46
			Other Experimental/Theoretical Results			
	33.91[a]	25.82*c*	45.89[a]	33.5[d]	35.77[a]	
	31.24[b]	29.8[d]			33.83[e]	

[a] Reference 12. [b] Reference 36. [c] Reference 15 (without spin−orbit coupling). [d] Reference 26 (DFT results). [e] Reference 16.

TABLE 2: Calculated and Experimental Ionization Potentials (eV) of 6p and 7p Block Elements[a]

ionization potential (eV)	Hg	(112)	Pb	(114)	Rn	(118)
ccsd(t)	10.394	11.675	7.156	8.529	10.482	8.642
	(10.59)	(10.88)	(7.30)	(8.68)	(10.45)	(8.51)
ccsd	10.243	11.547	7.074	8.499	10.436	8.568
	(11.11)	(12.67)	(7.78)	(8.91)	(10.94)	(9.33)
mp2	10.584	11.961	7.005	8.478	10.587	8.773
	(11.73)	(12.83)	(9.21)	(9.65)	(11.52)	(10.37)
hf	8.582	10.316	6.399	8.043	9.806	10.769
	(12.34)	(13.38)	(10.64)	(11.67)	(12.46)	(11.74)
expt[b]	10.4375		7.4167		10.7485	

[a] Data in parentheses are calculated using a Morse fit to the calculated potential energy surface as described in the text [b] Reference 12.

of $7p_{1/2}$ and $7p_{3/2}$ spinors are energetically unfavorable and σ/π separability in molecular orbitals is completely absent. So in part, the σ-donating capacity of an element is not only indicative of the polarizability of an atom's electron cloud but also is a measure of the degree to which rehybridization among the $p_{1/2}$ and $p_{3/2}$ spinors of an atomic valence shell has occurred.

Computational Methods

As the computational methods used in the present study are standard and well established, I include only a brief synopsis here. All atomic and molecular calculations were performed under *jj*-coupling using the MOLFDIR program package.[8] Two-component, shape-consistent relativistic effective core potentials have been deployed to replace the inner 92 electrons of elements 112, 114, and 118 and the inner 60 electrons of Hg, Pb, and Rn.[9,10] This procedure leaves the $(n-1)$s, p, and d orbitals to be treated explicitly as an outer core space along with the valence *n*s and *n*p orbitals. For all of the heavy elements examined, an uncontracted Cartesian 6sd6p2pf1g basis set was used, and for compounds involving hydrogen a 6-31G** basis set chosen.[11] All properties were calculated at the HF, MP2, CCSD, and CCSD(T) levels.

In all correlated dimer calculations, computational limitations dictated that the virtual space be truncated to exclude high-lying virtual orbitals. No such restrictions were enforced for atomic or hydride calculations in which all orbitals were used. Polarizabilities were determined by calculating the difference between the energy of the isolated atom and the energy in the field of a unit test charge ($-e$). The distance between the subject atom and the test charge was varied from 2.6 to 12.6 bohr, and α was taken as the second derivative of the resulting curve at the zero-field limit. Polarizabilities calculated in this manner are closely related but not directly comparable to atomic dipole polarizabilities calculated by, for example, the finite-field method and therefore might be expected to vary somewhat from those values. In fact, I do find that values for α calculated this way tend to differ by about 20% as compared to accepted experimental or finite-field polarizabilities.[12] I elected to use this unconventional method because it more closely represents the close-contact "chemical" interaction of a (negatively) charged particle with the atom in question. Differences between my calculated values of α and those of other methods result in large part from the particulars of the method itself. The monopole field of one electron placed relatively near the atom in question is not particularly uniform in contrast to the very uniform dipole field experienced by an atomic electron cloud in a traditional finite-field calculation. Also, no attempt was made to include the effect of core polarization in my calculations, and therefore my α values reflect only valence (and near valence) shell polarization. In any case, I am primarily interested in the relative polarizabilities of the elements I have studied and am confident that the results are internally consistent.

In addition to calculating it directly as the energy difference between the ground-state atomic energy and that of the ground-state monocation, I have also adopted an indirect strategy to calculate ionization potentials for the atoms under consideration. The difference between the IP of hydrogen and that of the target atom M (where M = Hg, (112), Pb, (114), Rn, (118)) is taken as the sum of the proton affinity of M ($M + H^+ \rightarrow MH^+$) and the MH^+ bond dissociation energy (D_e; $MH^+ \rightarrow M^+ + H$). The proton affinity, uncorrected for zero-point energy, is calculated directly as the difference between the energy of the isolated atom M and the equilibrium energy of MH^+. The MH^+ dissociation energy, D_e, is calculated both directly and indirectly by fitting data points on the molecular ion potential energy surface to a Morse function.[13] This procedure seems to lead to results that compare well to available experimental data and to the directly calculated results save a possible exception for element 112.

Results

Element 112 versus Hg. In many respects, the properties of element 112 closely resemble those of mercury. Their calculated polarizabilites, listed in Table 1, are virtually identical at all levels of theory. However, as indicated in Table 2, the first ionization potential of element 112 is approximately 1.3 eV higher than that of Hg, which at 10.394 eV is in good agreement with the experimental value of 10.437 eV.[12] Eliav et al., using a Fock-space coupled cluster method, report a somewhat higher value of 11.97 eV for the IP of element 112, which is close to

TABLE 3: Proton Affinities (eV) of 6p and 7p Block Elements[a]

PA (eV)	Hg	(112)	Pb	(114)	Rn	(118)
ccsd(t)	5.846(5.844)	5.429(5.382)	7.942(7.922)	6.092(6.030)	5.593(5.587)	6.564(6.567)
ccsd	5.899(5.892)	5.470(5.475)	7.973(7.990)	6.043(6.046)	5.572(5.572)	6.552(6.564)
mp2	5.534(5.538)	5.128(5.126)	7.847(7.858)	5.932(5.941)	5.422(5.431)	6.262(6.274)
hf	6.299(6.292)	5.679(5.674)	7.937(7.965)	5.702(5.698)	5.340(5.333)	6.411(6.431)

[a] The values in parentheses are obtained from a fit of the data to a Morse potential.

TABLE 4: Bond Lengths, R_e (Å), and Dissociation Energies, D_e (eV) (in Parentheses), for MH^+ Ions

R_e (D_e)	Hg	(112)	Pb	(114)	Rn	(118)
ccsd(t)	1.553(2.63)	1.583(3.50)	1.783(1.49)	1.600(1.01)	1.618(2.47)	1.992(1.60)
ccsd	1.554(2.54)	1.543(3.41)	1.824(1.44)	1.648(0.94)	1.652(2.43)	1.923(1.53)
mp2	1.547(2.51)	1.558(3.48)	1.801(1.25)	1.687(0.80)	1.649(2.40)	1.892(1.43)
hf	1.582(1.28)	1.526(2.39)	1.781(0.73)	1.638(0.14)	1.670(1.54)	1.898(3.57)
expt	1.594(3.11, 2.4)[a]				1.6957(2.67)[b]	

[a] Reference 27. [b] Reference 16.

TABLE 5: Spectroscopic Constants of 6th and 7th Row p-Block Dimers

	Hg_2	$(112)_2$	Pb_2	$(114)_2$	Rn_2	$(118)_2$
ccsd(t)						
R_e (Å)	3.60	3.07	2.98	3.07	4.73	4.57
D_e (eV)	0.072	0.187	0.684	0.381	0.016	0.062
ccsd						
R_e (Å)	3.73	3.12	3.07	3.12	4.73	4.57
D_e (eV)	0.052	0.133	0.592	0.330	0.013	0.052
expt						
R_e (Å)	3.630[a]		2.930[b]		4.832[c]	
D_e (eV)	0.047		0.820		0.016[c]	

[a] Reference 19a. [b] Reference 27. [c] Reference 31a.

my directly calculated result.[14] This increase in ionization potential from Hg to (112) no doubt is because of increased relativistic stabilization of the valence *n*s shell. The discrepancy between the directly and indirectly calculated values might arise from some misrepresentation of the ground state of $(112)^+$ in the separated atom limit for $(112)H^+$ used in the Morse fit. In particular, Seth et al. find that the orbital eigenvalue of 7s shell lies between those of the $d_{3/2}$ and $d_{5/2}$ spin−orbit components the 6d shell.[15] It is therefore possible that the dissociated atom limit from the Morse fit corresponds to a $(112)^+$ ion in an excited state.

Inasmuch as the calculated gas-phase proton affinities (Table 3) indicate a relative degree of Lewis basicity, these data for Hg and element 112 at the CCSD(T) level differ by less than 10%, and both have values similar to my calculated proton affinity for radon.[16] Likewise, as a stand-in for atomic (ionic) radius, the bond lengths of the $(112)H^+$ and HgH^+ molecular ions differ only marginally.[17,18] Not surprisingly, the dissociation energy of $(112)H^+$ is ∼1 eV higher than that of HgH^+ because of the higher ionization potential of (112) (Table 4).

Although it is far from definitive, a common view holds that the interaction of two Hg atoms is predominantly dispersive, the metallic character of the condensed phase arising from many-body effects.[18] Accordingly, the data in Table 5 indicate that the bonding in Hg_2 is comparatively weak, 0.047 eV according to experimental results and 0.072 eV according to my CCSD(T) results.[19] Although there are several excellent studies in the literature that find Hg_2 dissociation energies in much better agreement with experiment, my results, which employ smaller basis sets and truncated virtual spaces, give qualitatively correct results for this property even as my calculated equilibrium bond length is in excellent accord with experiment.[20] (I should note here that there is some uncertainty in the dissociation energy of the mercury dimer with literature values ranging from 0.043 to 0.054 eV.)

That my dissociation energy is perhaps as much as 50% too large as compared to experiment likely owes at least in part to uncorrected basis set superposition errors. I have elected to not apply a counterpoise correction to the BSSE at the correlated level (there is essentially no BSSE at the HF level in this work). Although CP corrected potential energy surfaces do converge more smoothly to the basis set limit than do uncorrected results, it is also true that such corrections can have a tendency to overestimate the BSSE and can lead to results that are too repulsive.[21] The counterpoise correction may in fact lead to potential energy surfaces that actually deviate more from the basis set limit than does the uncorrected surface, especially as BSSE has a tendency to compensate for basis set incompletion error. While I recognize that by not correcting for basis set superposition error, I may (or may not) overestimate to some extent the binding energy, in electing to forego the CP correction I have avoided introducing other errors that are less well understood. As my purpose is not per se to reproduce the experimental (and in many cases, nonexistent) dimeric potential energy surfaces but rather to compare the results of homologous atoms, I find this choice to be defensible.

It is interesting then that the most striking difference I find between the properties of Hg and element 112 occurs for the dissociation energies and bond lengths of the homonuclear dimers (Table 5). I find that the bond between two (112) atoms is nearly twice as strong and 0.5 Å shorter than that I found for the mercury dimer. This suggests an interaction that is not as fundamentally dispersive and perhaps more covalent in $(112)_2$ than it is in Hg_2. While this doubling in cohesive energy from Hg to (112) is surprising given prevailing expectations about the relativity-induced inertness of element 112, it is consistent with unpublished density functional theory results of Fricke et al.[22] As I find no significant difference at any level of theory between the calculated polarizabilities of Hg and element 112, this suggests that some other mechanism is responsible for enhanced bonding in $(112)_2$. While the source of this possible enhanced stability is yet to be thoroughly examined, it seems there are two main possibilities. The first is simply that the smaller van der Waals radius of (112) as compared to Hg, 1.53 Å (=3.07 Å/2) for the former versus 1.80 Å for the latter, coupled with their relatively similar polarizabilities lead to a larger ($\sim\alpha/r^6$) dispersion term and therefore a stronger interaction. This argument is somewhat circular, however, in that the question remains whether the shorter bond length is a cause or a result of a stronger interaction.

It is also possible that the larger D_e of $(112)_2$ results from participation in bonding by formally unoccupied $7p_{1/2}$ spinors on each atom. These have a $^2/_3\pi$ character amenable to hybridization with 6d valence spinors having π character. It is already well established that 6d electrons are energetically destabilized and expanded relative to 7s in (112) and that the virtual $7p_{1/2}$ spinors are stabilized and contracted, which bring them close to the occupied manifold, facts that would invite such participation.[14] Such a $6d_{5/2}-7p_{1/2}$ π "resonance stabilization" model for the relative increase in bonding energy from Hg_2 to $(112)_2$ might also explain the results of Pershina et al. Although these authors find no enhanced intermetallic bonding in the pairwise interaction of E112 with other metal atoms (Hg, Pd, Au, Pt), they find that relativistically enhanced intermetallic dπ-like interactions seem to arrest a decrease in the bonding interaction in MAu_9 clusters from M = Hg to M = (112).[23] The dimeric interactions might be best described as "σ-like" and would be less influenced by interaction with primarily π-like $7p_{1/2}$ spinors than would be the case in the cluster calculations.

A more satisfying resolution to this issue will await a more detailed investigation. In any case, the bonding in $(112)_2$ is most likely more than simply dispersive as evidenced by the significantly shorter bond length in $(112)_2$, which contrasts with the relatively similar MH^+ bond lengths for M = Hg and (112). However, this reasoning too has its limitations.

Element 114 versus Pb. Unlike the relative similarity of element 112 and Hg, comparison of the various aspects of the chemistry of Pb to those of element 114 reveals that they are likely to have significantly different characteristics. At all levels of theory, element 114 has a polarizability about $^2/_3$ that of Pb for which my calculated values for α are perhaps 10% too large as compared to standard values.[12] In addition to other sources of disagreement between calculated and experimental polarizabilities is the fact that the $^3P_0$ ground state of Pb is described as a pure $7s^27p_{1/2}{}^2$ electron configuration and $J = 0^+$ state under jj-coupling. This likely results in an exaggerated contribution from the $^1S_0$ (p^2) Russell−Saunders term to the $J = 0^+$ ground state and an artificially inflated polarizability for Pb. Element 114 is not as subject to this source of error because extreme spin−orbit coupling means that the $J = 0_g$ designation under pure *jj*-coupling scheme is more descriptive of it than of Pb. Nevertheless, the extent to which the treatment of the two atoms is subtly different does not mitigate the conclusion that element 114 is significantly less polarizable than Pb. Viewed in isolation, this finding would suggest a much more inert element 114 as compared to Pb even in the absence of the ionization potential and proton affinity data reported in Tables 2 and 3, respectively. I calculated a value of 8.529 eV for the ionization potential of element 114, higher by more than 1 eV than a similarly calculated 7.156 eV for Pb, which in turn compares well to experiment.[13] Eliav et al. report an element 114 ionization potential of 8.45 eV using a Fock-space coupled cluster method, while Schwerdtfeger et al. find an IP of 8.36 using their energy-adjusted effective core potential.[24,25] Spin−orbit configuration calculations using the same ECP and basis set used in this study give an IP of 8.536 eV.[10] In any case, the data run counter to a trend of decreasing ionization potential down a column of the periodic table, in this case group XIV, but is fully in keeping with the anticipated consequences of severe spin−orbit coupling in the valence shell of element 114.

The proton affinity of element 114 is significantly lower than that of Pb, indicative of a much lower σ-donating capacity, and the bond dissociation energy of $(114)H^+$ is the lowest found for any of the MH^+ ions studied here. The latter is a full 50% lower than the D_e of PbH^+, which is itself comparatively low befitting the status of lead as a relatively inactive metal. At first blush, the weakness of the bond in $(114)H^+$ might seem surprising given the relatively high ionization potential of E114 coupled with the fact that the D_e here corresponds to a separated atom limit of H and $(114)^+$. However, the weakness is largely attributable to the diminution of σ character of the $7p_{1/2}$ spinor due to spin−orbit coupling. At the same time, the radial contraction of the $7p_{1/2}$ spinor leads to a bond in $(114)H^+$ that measures ~1.60 Å, only slightly longer than that in $(112)H^+$ or HgH^+ and significantly shorter than the nearly 1.80 Å of PbH^+. I can therefore probably expect E114 to be a relatively compact and unreactive element, certainly less active than Pb, but not likely to be completely inert. This finding is consistent with the results of others including Seth et al. and Landau et al.[1,24,25]

Because both Pb and E114 have a fully occupied $np_{1/2}$ valence spinor shell, the bonding in homonuclear dimers of these atoms could be fairly described as closed-shell−closed-shell interactions. The extent to which this description pertains depends on the magnitude of spin−orbit splitting in the valence shell, however, and therefore it is more apt for $(114)_2$ than for Pb_2. My results for Pb_2 are in generally good agreement with experimental and other theoretical results for the molecule.[26,27] My calculated Pb_2 dissociation energy is slightly lower than the experimental value, however, and this could be a result an underestimation of triplet ($^3\Pi_0$ and $^3\Sigma_0$) contributions to bonding in the $\Omega = 0^+$ ground state in my *jj*-coupled calculations. As is the case for the isolated atom, unaccounted for contributions from higher order Russell−Saunders terms would not be as significant a source of error in $(114)_2$, which is found to have a substantially lower dissociation energy than Pb_2. This underscores the enhanced closed-shell nature of the (114) atom relative to Pb. One would expect that there be less "open" shell triplet contributions to the ground state of $(114)_2$ because of the dominance of the $J = 0_g$ ground state in the element 114 atom. Still, despite the comparatively weak bond, the bond length for $(114)_2$ is only slightly longer than that for Pb_2, a finding that illustrates the importance of the relativistic contraction of the $7p_{1/2}$ spinor on chemical properties (atomic radius) of the atom. Clearly, my results would seem to describe a bond in $(114)_2$ that is less covalent than in Pb_2 but is more than a purely dispersive, closed-shell, van der Waals interaction. In this last regard, my $(114)_2$ results stand in contrast to those of Liu et al., who find a very low (~0.07 eV) dissociation energy for $(114)_2$ and a much greater bond length (~3.72 Å) than do I.[27] Their result, found using the same effective core potential that I employed, describes a much more noble element 114 than is suggested in my work. Interestingly, these same authors report a Pb_2 interaction in excellent agreement with mine, again using the same Pb ECP. There are two primary differences between the studies. First, their calculations on $(114)_2$ and Pb_2 excluded excitations from the $(n - 1)$s and $(n - 1)$p orbitals, whereas mine did not. While it is difficult to explain why this difference should have such a dramatic impact on calculated molecular properties for $(114)_2$ but not for Pb_2, I should note that in an examination I conducted on $(114)_2$ using a smaller and admittedly inadequate basis set, the exclusion of these 6s and 6p excitations results in a halving of the calculated dissociation energy.[28] The existence of some form of resonant stabilization of the interaction between two atoms of E114 or Pb would require the participation of (hybridization with) unoccupied valence $n\text{p}_{3/2}$ spinors on each atom. The exclusion of excitation amplitudes the 6s/6p spinors of element 114 may lead to an underestimation of the $7\text{p}_{3/2}$ contribution to bonding. Because the valence $6\text{p}_{1/2}$ and $6\text{p}_{3/2}$ spinors of Pb are not nearly as energetically or radially distinct as those of element 114, this may not prove an impediment to the contribution to bonding from $6\text{p}_{3/2}$ in Pb_2. Of course, this is merely speculation. Another major difference between the two studies is that as for $(112)_2$/Hg_2 I have elected to forego a counterpoise correction to any basis set superposition error in my results. Again, it is far from straightforward that basis set superposition error at the correlated level is always accounted for properly when the counterpoise correction is applied uncritically.[29] The magnitude of BSSE in the Pb/E114 dimers is likely to be comparable to that in the Hg/E112 couples, but because the dissociation energies are substantially larger for the group XIV elements, this is much less an issue. Finally, Liu et al. also report results of four-component Bejing density functional calculations that split the difference between their CCSD(T) work and mine, finding a $D_e((114)_2) \approx 0.20$ eV and $R_e\ ((114)_2) \approx 3.48$ Å.

Rn versus Element 118. The most striking differences I have found between the 7p elements and their 6p analogues occur for radon and element 118. The latter has an enormous polarizability; at more than 52 a.u. it is nearly twice the value I have calculated for radon and the largest reported for all of the atoms studied here (Table 1). If one extrapolates a simple empirical linear relationship between the known normal boiling points of the noble gases He−Xe and their atomic polarizabilities, then a bp of between 178 and 221 K would be expected for Rn (the accepted value is 211 K) and between 320 and 380 K for (118).[30] The lower limits in these reported ranges correspond to the raw polarizability data reported in Table 1 for Rn and (118), while the upper limits correspond to polarizabilities scaled to conform to the accepted value of α(Rn).[12] Even given the large uncertainties in this simplified analysis, it is difficult to argue that element 118 would be a gas under standard conditions. Indeed, because it has a proton affinity second only to Pb among the elements I have examined and an ionization potential lower than all but Pb, it would be similarly difficult to argue that element 118 should even be particularly noble despite its placement in the periodic table.

As noted in Table 2, the experimental and my calculated ionization potentials of radon are each more than 3 eV higher than those of Pb, an observation consistent with an increasing IP across a row of the periodic table. This trend is lost for E114 and E118, the latter having an ionization potential nearly identical to that of the former. The current calculated value for the IP of E118 is substantially higher than was reported in my earlier spin−orbit configuration interaction study, which found an IP of 7.32 eV, a result that does not contradict the trend reversal but that is interesting nonetheless.[10] While neither a new nor unexpected result, the relatively similar IPs of E114 and E118 do portend profound chemical implications for these elements that appear to have translated into the results of the current study. Just as the reason for the relative inertness of element 114 can be understood in terms of the relativistic energetic stabilization and radial contraction of its (fully occupied) $7\text{p}_{1/2}$ spinor, the reason for the apparent enhancement of chemical activity of element 118 relative to Rn is the energetic destabilization and radial expansion of its occupied $7\text{p}_{3/2}$ spinor shell.

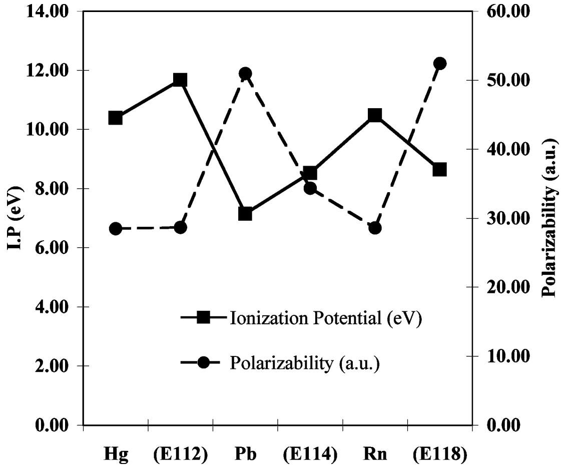

Figure 1. Ionization potentials and finite-field polarizabilities of 6p and 7p block atoms. The data correspond to calculations done at the CCSD(T) level of theory.

The dimer of element 118 exhibits a bonding interaction roughly equivalent to that calculated for Hg_2. Most likely, this is because of the very high polarizability of the element and is probably predominantly dispersive, although one might speculate that relativistic stabilization of the 8s valence orbital may allow some degree of 7p8s hybridization. It has been shown by Eliav et al. that element 118 does have an electron affinity, and therefore it is plausible that this interaction is in fact partly covalent.[31] I will explore this possibility further in multireference CI studies. In any case, my dissociation energy for $(118)_2$ is roughly 4 times that for Rn_2, the former measuring 0.062 eV as compared to 0.016 eV for the latter, a result for Rn_2 that agrees very well with the findings of Lee et al. and Pyykkö et al.[32] My calculated bond length in $(118)_2$ is shorter than the bond length in Rn_2 by 0.16 Å. Although a dimer bond energy that increases with increasing noble gas atomic weight is not unexpected, the magnitude of the increase from Rn_2 to $(118)_2$ is striking. That the bond shortening is indicative of a significant bonding interaction rather than simply a polarizability effect is evidenced by the fact that both the proton affinity and the MH^+ bond length for (118) are greater than those of Rn.

Salient Trends. The data in Figure 1 reflect the expected inverse relationship between ionization potential and atomic dipole polarizability.[33] Among the 6th row elements, polarizability increases sharply and ionization potential drops from Hg to Pb, while polarizability decreases and ionization potential increases from Pb to Rn as the greater nuclear charge stabilizes this valence shell. For the 7th row elements, however, although polarizability does increase modestly from element 112 to element 114, it rises dramatically from element 114 to element 118. At the same time, ionization potential decreases from element 112 to element 114 (although less dramatically than the decrease from Hg to Pb) but increases only marginally from element 114 to element 118. The differences between the trends in the 6p block relative to the 7p block can be understood to be the result of an electron shell closing at element 114. The $7\text{p}_{1/2}$ spinor shell is so profoundly stabilized that it very efficiently shields the $7\text{p}_{3/2}$ spinor from the nuclear charge and effectively establishes it as a separate subshell. This filling of the $7\text{p}_{1/2}$ spinor shell is nearly as important a feature of the electronic

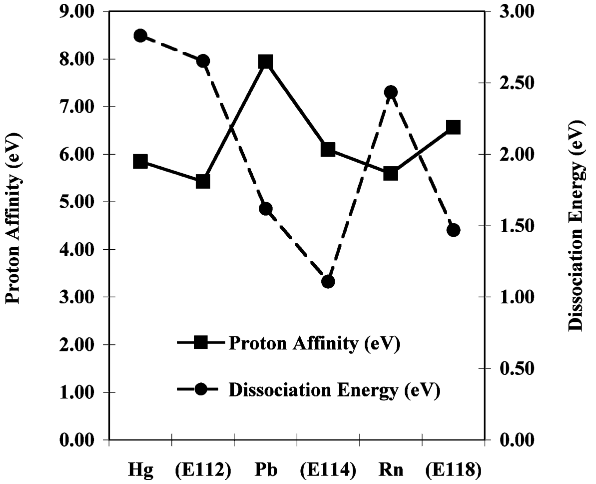

Figure 2. Proton affinities of M atoms and bond dissociation energies of MH^+ molecular ions. The dissociated atom limit corresponds to $M^+ + H$. The data correspond to calculations at the CCSD(T) level of theory.

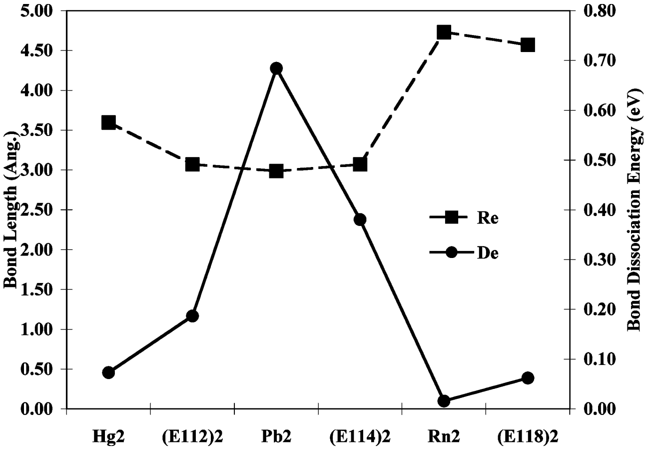

Figure 3. Spectroscopic constants of heavy and superheavy dimers. All data correspond to calculations done at the CCSD(T) level of theory.

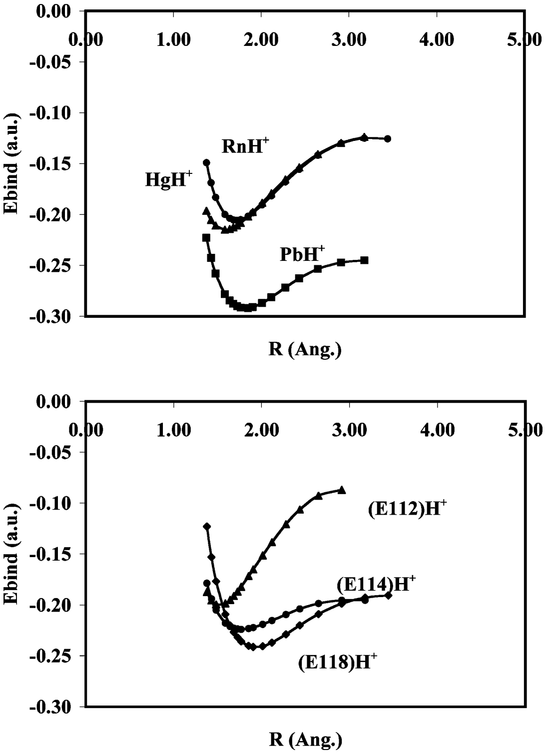

Figure 4. CCSD(T) potential energy surfaces for MH^+ molecular ions of 6p and 7p block elements. The binding energy is reported with respect to that of the isolated M atom.

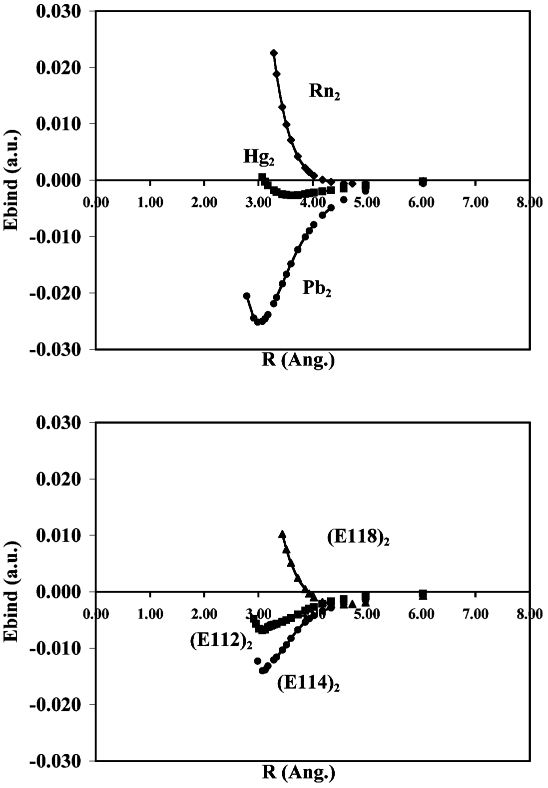

Figure 5. CCSD(T) potential energy surfaces of homonuclear dimers of 6p and 7p block elements. The binding energy is reported with respect to twice that of the isolated M atom.

structure in determining elemental characteristics as the completion of a period. A similar conclusion was reached by Schwerdtfeger et al. in their study of the polarizability of $(E119)^+$, which is, of course, isoelectronic to (118).[34]

Similar conclusions can be drawn with regard to the proton affinity and bond dissociation energy data presented in Figures 2−5. Mercury and radon have approximately equal proton affinities, which are both smaller than the PA of lead.[35] The latter is an unambiguously open-shell atom well suited to donate an electron pair to a strong acid, while the other two are clearly closed-shell atoms. The bond dissociation ($MH^+ \rightarrow M^+ + H$) energies of Hg and Rn are both larger than that of Pb; as much as anything, this is simply a reflection of their higher ionization potentials. Interestingly, while the proton affinities of element 112 and element 118 are comparable to those of their 6p analogues, the PA of element 114 is substantially lower than that of Pb. This is, no doubt, a result of the stabilization of the fully occupied $7p_{1/2}$ spinor of the atom coupled with the fact that this unhybridized (i.e., uncombined with $7p_{3/2}$) spinor has a reduced 1/3 σ-character. This last point also explains why the bond dissociation energy of $(114)H^+$ is the smallest of those studied despite the relatively high ionization potential of the atom; H can bond only through σ-like interactions. Interestingly, the shielding-destabilized $7p_{3/2}$ valence spinor of element 118 leads to that element having the second highest proton affinity among the elements studied here. The bond dissociation energy of $(118)H^+$ is also relatively low, however, in part because the $\omega = {}^1/_2$ projection of the $7p_{3/2}$ spinor also has a diminished σ character ($2/3\sigma$).

The experimental and my calculated equilibrium bond lengths of Hg_2 and Pb_2 are relatively similar, although this is not so of their bond dissociation energies. As a closed-shell−closed-shell interaction, the bonding in the former, a singlet, is usually described as the result of a nearly purely dispersive interaction. On the other hand, Pb_2 is known to have a $^3\Pi_0$ ground state amenable to the formation of a bond approaching covalency. Consequently, Pb_2 is relatively well bound, while the bond in Hg_2 is at best tenuous. Not unexpectedly for a noble gas, the D_e of Rn_2 is lower than that of Hg_2, although it is greater than that of any other known noble gas dimer.[36] The difference between the dimeric bond dissociation energies of element 112 and element 114 is much less than that between Hg and Pb. This is a result of both the (strangely) increased D_e of $(112)_2$ relative to Hg_2 and the more or less expected dramatic decrease in D_e from Pb_2 to $(114)_2$. The attractive interaction between two "noble gas" element 118 atoms is much stronger than it is in Rn_2, but it is still a fraction of that of even $(114)_2$.

Conclusion

For the most part, expectations relative to the anticipated effects of relativity on the chemistry of superheavy elements 112, 114, and 118 are borne out in my calculations. Element 112 is likely to be very similar in most respects to Hg, element 114 is likely to be significantly less active than Pb although not inert, and element 118 seems nearly certain to be far more active than Rn, or perhaps even element 114 or element 112. One notable exception is the anomalously high dissociation energy and short bond length of $(112)_2$, Hg_2. Although this finding is regarded as tentative and must be reexamined using larger basis sets and correlation virtual spaces, I suggest that relativistically enhanced π-like interactions available to element 112 might explain it. Element 114, on the other hand, although it is in the middle of the 7p block, behaves as a closed-shell atom albeit one with significant (particularly π) electron-donating capacity. Because of its tremendous polarizability, element 118 is expected to have a condensed phase standard state and an anomalously low ionization potential.

Finally, I can conclude that in contrast to "oddly ordinary" transactinide elements of the 6d block, the 7p elements would be predicted to exhibit a much different chemistry than their 6p analogues. This is principally due to the dramatic spin−orbit effects found in the 7p subshell, which effectively lead to a second valence shell closing at element 114 (lead) in addition to that expected for element 118 (radon). This secondary periodicity leads to an anomalously inert, compact, and unpolarizable element 114 (as compared to lead) and a similarly anomalous polarizable and diffuse element 118 (as compared to radon). Because of its relatively complex valence shell structure, the characteristics of element 112, which can be thought of as an intermediate in behavior between 6d and 7p transactinides, are distinct from those of both classes of atoms. This last question also requires further investigation.

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