Relativistic Quantum Chemistry of the Superheavy Elements. Closed-Shell Element 114 as a Case Study.

Peter Schwerdtfeger[*,a] **and Michael Seth**[b]

[a]*Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand*
[b]*Department of Chemistry, University of Calgary, Calgary, Canada T2N 1N4*

The chemistry of superheavy element 114 is reviewed. The ground state of element 114 is closed shell $[112]7s^2 7p_{1/2}^2$ and shows a distinct chemical inertness (low reactivity). This inertness makes it rather difficult to study the atom-at-a-time chemistry of 114 in the gas or liquid phase.

1. Introduction

The synthesis of the latest (proton-even) superheavy elements 114,[1] 116,[2] and 118[3] have been reported recently by the Dubna and Lawrence-Berkeley groups.[4] However, the unambiguous identification of these elements by spectroscopic methods still remains a challenge as the recent withdrawal from the observation of the α-decay chain of isotope $^{293}118$ shows.[5] One disadvantage was that the α-decay chain of $^{293}118$ does not end in the region of known isotopes.[3] Furthermore, the very small cross sections which lie in the picobarn region for such elements implicate a very small production rate of one atom per day or less.[6] The decay signal (usually by α decay or nuclear fission) has then to be singled out against a background of signals from other nuclear processes. Transfer of mass to the lighter nucleus in the collision (quasi-fission) may also inhibit the fusion process.[7] Another disadvantage is that the isotopes of superheavy elements of high nuclear charge Z are close to the proton drip-line making it increasingly more difficult to identify such new elements. The next generation of superheavy elements also requires less stable isotopes which implies the use of a radioactive beam facility. There is further evidence that magic nuclei above lead do not exist[8] and it will become increasingly more difficult to obtain elements with a lifetime in the second range or above.[9]

An important additional way for the positive identification of superheavy elements is by atom-at-a-time chemistry. Atom-at-a-time chemistry is currently the only experimental tool to gain valuable insight into the chemical behavior of superheavy elements.[9] Experiments have been carried out on element 106 (seaborgium) by Schädel's group at the GSI in Darmstadt[10] and preparations are currently underway to study 107–109, 112, and even 114.[11] The recently synthesized isotope $^{288}114$ has a α-decay half-life in the second range.[1] Before such experiments are carried out the chemical behavior has to be at least estimated from extrapolation of known chemistry of the lighter congeners in the periodic table.[12]

It is now well known that the chemistry of the heavier elements can be quite different compared to the lighter elements in the same group of the periodic table.[13] Table 1 shows a comparison of physical properties of Group 11 compounds.[14] It is evident that from these trends the chemistry of superheavy element 111 (eka-Au) cannot be deduced with great certainty from their lighter congeners. This is mainly due to relativistic effects which become increasingly more important for the heavier elements. Relativity can influence the chemical and physical properties of the heavier elements significantly leading to well known "Group-anomalies".[15] Relativistic quantum theory is therefore the only way to accurately predict the physical and chemical behavior of superheavy elements.[16] We note that whilst relativistic effects are important for *both* the inner shell

and the valence shell region, quantum electrodynamic (QED) effects such as the electron and photon self-energy can safely be neglected in the valence shell region.[17] The Breit interaction consisting of the magnetic (Gaunt) and retardation term should be included for very accurate calculations. For properties like K-shell ionization potentials (K-IP) of superheavy elements QED effects can be of the order of 1% of the total K-IP.[18]

A number of different techniques are in use to account for both relativistic and electron correlation effects. The most accurate way is a fully relativistic treatment at the Dirac-Hartree-Fock (DHF) level[19] including Breit interactions and other QED effects followed by well known correlation techniques such as coupled cluster theory (i.e. CCSD(T)).[20] A number of two-component techniques by eliminating the small component are used as well and a review has been given recently by Barysz and Sadlej.[21] The two-component (spin-orbit coupled) all-electron Hamiltonian is the ideal starting point for introducing spin-orbit coupled pseudopotentials.[22] Finally, scalar relativistic techniques are used as well at both the all-electron and the pseudopotential level.[23] The various relativistic Hamiltonians can be used in density functional theory.[24] We mention that our group has shown that the scalar relativistic pseudopotential approximation produces results almost as accurate as all-electron calculations[25] and we expect the same for two-component techniques, if the pseudopotential parameters have been adjusted carefully to the valence spectrum of the Dirac-Hamiltonian.

2. Chemistry of Element 114

Table 2 shows a comparison between calculated ionization potentials and excitation energies of element 114 at different levels of theory. The most accurate values are from Kaldor and co-workers Fock-space relativistic coupled cluster calculations using the Dirac-Fock-Breit solutions as a starting point.[26] Our DHF CCSD(T) calculations obtained earlier[27] are slightly below Kaldor et al.'s results. The results obtained by Liu et al.[28] using either the Nash pseudopotential[29] plus CCSD(T) or the Bejing four-component density functional program (BDF) are also close to Kaldor et al.'s data. Balasubramanian's results[30] are about 2 eV too low compared to the others. The pseudopotential used was the same as in Liu's calculations, hence we assume that either the basis set or the electron correlation procedure applied was insufficient. Furthermore, calculations with the same pseudopotential by Nash et al. gave 8.51 eV for the first ionization potential of 114 and 5.43 eV for the $^2P_{1/2}/^2P_{3/2}$ splitting of 114^+.[31] We also mention that early Hartree-Fock-Slater calculations carried out by Keller et al. gave 8.5 and 16.8 eV for the first and second ionization potential of 114.[32]

The most common oxidation states of group 14 elements are +2 and +4. However, the stability of the higher oxidation state in *p*-block elements decreases with increasing nuclear charge in one group which is often termed as the "inert pair ef-

*Corresponding author. E-mail: schwerd@ccu1.auckland.ac.nz. FAX: (64-9) 3737422.

TABLE 1: A comparison of properties of Group 11 elements.

Property	Cu	Ag	Au
Colour	bronze	silver	yellow
Specific resistivity / 10^{-8} Ωm	1.72	1.62	2.4
Thermal conductivity / $J \cdot cm^{-1}s^{-1}K^{-1}$	3.85	4.18	3.1
Electronic heat capacity / 10^{-4} $J \cdot K^{-1}mol^{-1}$	6.926	6.411	6.918
Melting point / $^\circ$C	1083	961	1064
Boiling point / $^\circ$C	2567	2212	3080
Atomic volume / cm^3mol^{-1}	7.12	10.28	10.21
Electronegativities	1.9	1.9	2.4
Cohesive energies / $kJ \cdot mol^{-1}$	330	280	370
Energy of O_2-chemisorption / eV	5.4	6.0	3.6
Desorption temperature of CO on metal / K	190–210	40–80	170–180
Common oxidation states	I, II	I	I, III
MF fluorides (solid)	unknown	AgF	unknown
Superconductors	many	rare	rare

TABLE 2: Electron affinity (EA), ionization potentials (IP), and electronic excitation energies (EE) for element 114 from various relativistic calculations. All values are given in eV.

Property		DHF[a]	DHF + B[b]	PP[c]	PP[d]	BDF[e]
EA	$6d^{10}7s^2p_{1/2}^2(^3P_0) \rightarrow 6d^{10}7s^2p_{1/2}^2p_{3/2}^1(^2P_{3/2})$	0.00	0.00			
IP1	$6d^{10}7s^2np_{1/2}^2(^3P_0) \rightarrow 6d^{10}7s^2p_{1/2}^1(^2P_{1/2})$	8.36	8.54	6.31	8.45	8.26
IP2	$6d^{10}7s^2p_{1/2}^1(^2P_{1/2}) \rightarrow 6d^{10}7s^2(^1S_0)$	16.55	16.87		16.74	16.62
IP3	$6d^{10}7s^2(^1S_0) \rightarrow 6d^{10}7s^1(^2S_{1/2})$	35.52	35.74		36.40	35.43
EE	$6d^{10}7s^2p_{1/2}^1(^2P_{1/2}) \rightarrow 6d^{10}7s^2p_{3/2}^1(^2P_{3/2})$	4.77	4.88	3.18		
EE	$6d^{10}7s^1(^2S_{1/2}) \rightarrow 6d_{3/2}^4d_{5/2}^37s^2(^2D_{5/2})$	2.09			1.94	

[a]DHF CCSD(T) from our group.[27]
[b]Fock-space coupled cluster calculations by Landau et al.[26]
[c]PP MRCI calculations by Balasubramanian.[30]
[d]PP CCSD(T) calculations by Liu et al.[28]
[e]Four-component density functional calculations by Liu et al.[28]

TABLE 3: Molecular properties of di- and tetravalent 114 compounds from scalar relativistic pseudopotential calculations at the MP2 level of theory. For the hydrides DHF structures are listed as well. Bond distances r_e in Å, H-(114)-H angles α_e in degrees (for the (114)X$_4$ molecules is the tetrahedral angle), and decomposition energies ΔU_0 in $kJ \cdot mol^{-1}$ (corrected for spin-orbit coupling) for the reactions (114)X$_4$ $\rightarrow$ (114)X$_2$ + X$_2$ and (114)X$_2$ $\rightarrow$ (114) + X$_2$.

Compound	Method	Relativistic			Nonrelativistic		
		r_e	α_e	ΔU_0	r_e	α_e	ΔU_0
(114)H$_2$	SRPP/MP2	1.865	89.7	−288	1.987	90.7	−44
	DHF	1.872	93.1		2.001	92.7	
(114)H$_4$	SRPP/MP2	1.750	109.5	−151	1.930	109.5	+32
	DHF	1.780	109.5		1.964	109.5	
(114)F$_2$	SRPP/MP2	2.128	97.1	+331	2.154	94.3	+833
(114)F$_4$	SRPP/MP2	2.136	109.5	−15	2.106	109.5	+585
(114)Cl$_2$	SRPP/MP2	2.498	99.7	+150	2.591	96.0	+543
(114)Cl$_4$	SRPP/MP2	2.477	109.5	−46	2.514	109.5	+340

fect".[33,34] From a one-center expansion within a Dirac-Hartree-Fock (DHF) scheme Grant and Pyper obtained heats of formation for di- and tetravalent 114 compounds which revealed rather low stability for the higher oxidation state.[35] This was recently supported by more accurate spin-orbit coupled relativistic pseudopotential calculations for the hydrides, chlorides, and fluorides of element 114, (114)X$_2$, and (114)X$_4$ (X = H, F, Cl).[27] All compounds are relativistically destabilized towards either decomposition, (114)X$_4$ $\rightarrow$ (114)X$_2$ + X$_2$ or (114)X$_2$ $\rightarrow$ (114) + X$_2$. In all cases the (114)X$_4$ decomposition is exothermic. Thus, element 114 is chemically more inert than the lighter elements Pb, Sn, or Ge.

Table 3 shows calculated bond parameters and decomposition energies of (114)X$_4$ and (114)X$_2$ compounds (X = H, F, and Cl) at various levels of theory. The basis sets used have been described elsewhere.[27] The calculations show that relativistic effects are significant. For (114)Cl$_4$, which could be a candidate for gas phase separation techniques, the higher oxidation state is destabilized by ca. 400 $kJ \cdot mol^{-1}$! Hence, the only oxidation state accessible for element 114 will be $+2$ in agreement with the prediction of Keller et al. more than 30 years ago.[32]

Relativistic effects in bond distances are smaller and less than 0.1 Å. For (114)F$_4$ relativistic effects lead to a slight increase in bond length which could be, however, due to inaccuracies in the pseudopotential or electron correlation procedure applied. Spin-orbit effects in bond distances and angles are small as well. Because of the spin-orbit contraction of the $7p_{1/2}$ orbital, spin-orbit coupling should decrease bond distances and increase bond angles. This is indeed calculated, i.e. for (114)H$_2$ we obtain $\Delta_{SO}r_e = -0.037$ Å, $\Delta_{SO}\alpha_e = +1.8^\circ$. We mention that the bond distance of (114)H$_4$ has been predicted earlier by Pyykkö and Desclaux to be 1.787 Å using a simple one-center Dirac-Fock approximation.[36]

114 is a closed-shell atom with an electronic configuration $7s^27p_{1/2}^2$. We therefore expect a rather low reactivity to form diatomic compounds in the gas phase. Indeed, all diatomic 114 compounds calculated by Liu et al. have lower dissociation energies compared to the corresponding lead compounds.[28] Similar results were obtained by Nash and Bursten.[31] Here spin-orbit effects are very large as a careful comparison between one- and two-component methods by Liu et al. showed.[28] In fact due to the increased chemical inertness, spin-orbit effects increase
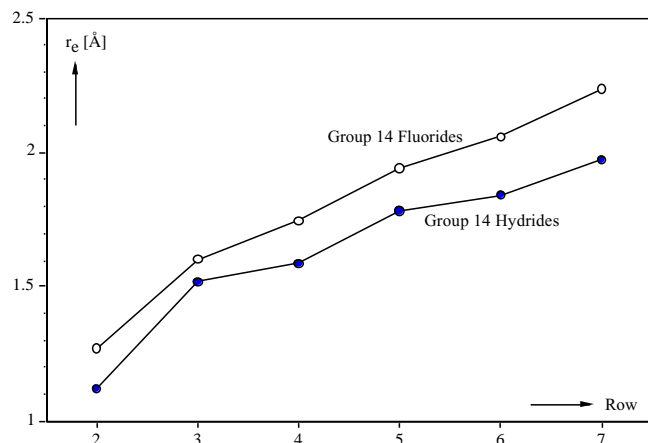
Figure 1. Experimental (from CX to PbX (X = H, F), Reference 37) and calculated bond distances (at the scalar relativistic CCSD(T) level if not available) for Group 14 diatomic hydrides and fluorides.

the bond distance in all diatomic (114)X compounds.[28] Hence, we do not expect a change in trend in bond distances down the Group 14 element compounds as shown clearly in Figure 1. Dissociation energies D_e of (114)X compounds decrease dramatically due to spin-orbit effects and for all diatomic (114)X compounds calculated so far D_e is lower than 200 kJ·mol^{-1}.[28]

3. Conclusion

Scalar relativistic and spin-orbit effects lead to an increased chemical inertness of superheavy element 114 making it rather difficult to form compounds in the gas phase. The behavior of 114 in solution is not known, however, and further theoretical calculations are needed to study the chemistry of 114 in solution. Nevertheless, we expect that charged complexes of 114 in solution are less stable compared to their lighter congeners in the periodic table.

References

(1) Yu. Ts. Oganessian, A. V. Yeremin, A. G. Popeko, S. L. Bogomolov, G. V. Buklanov, M. L. Chelnokov, V. I. Chepigin, B. N. Gikal, V. A. Gorshkov, G. G. Gulbekian, M. G. Itkis, A. P. Kabachenko, A. Yu. Lavrentev, O. N. Malyshev, J. Rohac, R. N. Sagaidak, S. Hofmann, S. Saro, G. Giardina, and K. Morita, Nature **400**, 242 (1999); Yu. Ts. Oganessian, V. K. Utyonkov, Yu. V. Lobanov, F. Sh. Abdullin, A. N. Polyakov, I. V. Shirokovsky, Yu. S. Tsyganov, G. G. Gulbekian, S. L. Bogomolov, B. N. Gikal, A. N. Mezentsev, S. Iliev, V. G. Subbotin, A. M. Sukhov, O. V. Ivanov, G. V. Buklanov, K. Subotic, M. G. Itkis, K. J. Moody, J. F. Wild, N. J. Stoyer, M. A. Stoyer, and R. W. Lougheed, Phys. Rev. C **62**, 041604 (2000).

(2) Yu. Ts. Oganessian, V. K. Utyonkov, Yu. V. Lobanov, F. Sh. Abdullin, A. N. Polyakov, I. V. Shirokovsky, Yu. S. Tsyganov, G. G. Gulbekian, S. L. Bogomolov, B. N. Gikal, A. N. Mezentsev, S. Iliev, V. G. Subbotin, A. M. Sukhov, O. V. Ivanov, G. V. Buklanov, K. Subotic, M. G. Itkis, K. J. Moody, J. F. Wild, N. J. Stoyer, M. A. Stoyer, R. W. Lougheed, C. A. Laue, Ye. A. Karelin, and A. N. Tatarinov, Phys. Rev. C **63**, 011301 (2000).

(3) V. Ninov, K. E. Gregorich, W. Loveland, A. Ghiorso, D. C. Hoffman, D. M. Lee, H. Nitsche, W. J. Swiatecki, U. W. Kirbach, C. A. Laue, J. L. Adams, J. B. Patin, D. A. Shaughnessy, D. A. Strellis, and P. A. Wilk, Phys. Rev. Lett. **83**, 1104 (1999).

(4) We loosely define superheavy elements as the trans-actinide elements (Z = 104) or elements with total nucleon number A = 250.

(5) D. Adam, Nature **412**, 122 (2001).

(6) Yu. Ts. Oganessian, Nature **413**, 465 (2001).

(7) A. C. Beriman, D. J. Hinde, M. Dasgupta, C. R. Morton, R. D. Butt, and J. O. Newton, Nature **413**, 144 (2001).

(8) S. Ćwiok, W. Nazarewicz, and P. H. Heenen, Phys. Rev. Lett. **83**, 1108 (1999).

(9) D. C. Hoffman, Chem. Eng. News **72**, 24 (1994); D. C. Hoffman, Radiochim. Acta **72**, 1 (1996); M. Schädel, Radiochim. Acta **70/71**, 207 (1995).

(10) M. Schädel, W. Brüchle, B. Schausten, E. Schimpf, E. Jager, G. Wirth, R. Günther, J. V. Kratz, W. Paulus, A. Seibert, P. Thorle, N. Trautmann, S. Zauner, D. Schumann, M. Andrassy, R. Misiak, K. E. Gregorich, D. C. Hoffman, D. M. Lee, E. R. Sylwester, Y. Nagame, and Y. Oura, Radiochim. Acta **77**, 149 (1997); M. Schädel, W. Brüchle, R. Dressler, B. Eichler, H. W. Gäggeler, R. Günther, K. E. Gregorich, D. C. Hoffman, S. Hübener, D. T. Jost, J. V. Kratz, W. Paulus, D. Schumann, S. Timokhin, N. Trautmann, A. Türler, G. Wirth, and A. Yakushev, Nature **388**, 55 (1997).

(11) M. Schädel, E. Jäger, E. Schimpf, and W. Brüchle, Radiochim. Acta **68**, 1 (1995); H. W. Gäggeler (personal communication, 2001).

(12) D. Bonchev and V. Kamenska, J. Phys. Chem. **85**, 1177 (1981).

(13) P. Pyykkö, Chem. Rev. **88**, 563 (1988).

(14) *CRC Handbook of Chemistry and Physics* (CRC Press, Cleveland, Ohio, 1977).

(15) P. Pyykkö and J. P. Desclaux, Nature **266**, 336 (1977); S. Siekierski, J. Autschbach, P. Schwerdtfeger, M. Seth, and W. H. E. Schwarz, J. Comput. Chem. **23**, 804 (2002).

(16) B. Fricke, Struct. Bond. **21**, 89 (1975); V. Pershina, Chem. Rev. **96**, 1977 (1996); P. Schwerdtfeger and M. Seth, *The Encyclopedia of Computational Chemistry*, edited by P. von R. Schleyer, N. L.Allinger, T. Clark, J. Gasteiger, P. Kollman, and H. F. Schaefer III (Wiley, New York, 1998).

(17) P. Pyykkö, M. Tokman, and L. Labzowski, Phys. Rev. A **57**, R689 (1998); L. Labzowski, I. Goidenko, M. Tokman, and P. Pyykkö, Phys. Rev. A **59**, 2707 (1999).

(18) N. Gaston, W. Nazarewicz, and P. Schwerdtfeger (unpublished results).

(19) Y. Ishikawa and M. J. Vilkas, J. Mol. Struct. (Theochem) **573**, 139 (2001).

(20) U. Kaldor and E. Kaldor, Adv. Quant. Chem. **31**, 313 (1999).

(21) M. Barysz and A. J. Sadlej, J. Mol. Struct. (Theochem) **573**, 181 (2001).

(22) H. Stoll, B. Metz, and M. Dolg, J. Comput. Chem. **23**, 767 (2002).

(23) R. Samzow, B. A. Hess, and G. G. Jansen, J. Chem. Phys. **96**, 1227 (1992).

(24) W. Liu, G. Hong, D. Dai, L. Li, and M. Dolg, Theor. Chem. Acc. **96**, 75 (1997).

(25) P. Schwerdtfeger, J. R. Brown, J. K. Laerdahl, and H. Stoll, J. Chem. Phys. **113**, 7110 (2000).

(26) A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, J. Chem. Phys. **114**, 2977 (2001).

(27) M. Seth, K. Faegri, and P. Schwerdtfeger, Angew. Chem. Int. Ed. Engl. **37**, 2493 (1998); Angew. Chem. **110**, 2669 (1998).

(28) W. Liu, C. van Wüllen, Y. K. Han, Y. J. Choi, and Y. S. Lee, Adv. Quant. Chem. **39**, 325 (2001).

(29) C. S. Nash, B. E. Bursten, and W. C. Ermler, J. Chem. Phys. **106**, 5133 (1997).

(30) K. Balasubramanian, Chem. Phys. Lett. **341**, 601 (2001). This paper appeared after the previously published results

by our (Reference 27) or Kaldor's group (Reference 26), but does not compare or mention any previous theoretical work on element 114.

(31) C. S. Nash and B. E. Bursten, J. Phys. Chem. **103**, 402 (1999).

(32) O. L. Keller, J. L. Burnett, T. A. Carlson, and C. W. Nestor, J. Phys. Chem. **74**, 1127 (1970).

(33) P. Schwerdtfeger, G. A. Heath, M. Dolg, and M. A. Bennett, J. Am. Chem. Soc. **114**, 7518 (1992).

(34) M. Laing, Ed. Chem. (Nov. issue), 160 (1999).

(35) I. P. Grant and N. C. Pyper, Nature **265**, 715 (1977); N. C. Pyper and I. P. Grant, Proc. R. Soc. Lond. A **376**, 483 (1981).

(36) P. Pyykkö and J. P. Desclaux, Nature **266**, 336 (1977).

(37) K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).