graphite monochromated Mo$_{K\alpha}$ radiation; $M_r = 464.76$; triclinic, space group $P1$ (no. 2), $a = 11.428(3)$, $b = 17.336(4)$, $c = 10.439(5)$ Å, $\alpha = 98.11(3)$, $\beta = 104.13(3)$, $\gamma = 106.02(2)^\circ$, $V = 1879(2)$ Å^3, $\rho_{calcd} = 1.643$ g cm^{-3}, $F(000) = 936$, $T = 293$ K, ($\lambda = 0.71069$ Å), $\mu(\mathrm{Mo}_{K\alpha}) = 12.0$ cm^{-1}, scan = $\omega/2\Theta$, scan rate = 8.0° min (in ω; 3 scans), scan width $(1.10 + 0.30\tan\Theta)^\circ$, $2\Theta_{max} = 50.1^\circ$. Of the 5734 reflections measured through a detector aperture 6.0 mm horizontal and 6.0 mm vertical, 5455 were unique ($R_{int} = 0.120$). A decay correction was applied following the intensities of three standard reflections measured after every 100 reflections (−6.80% during data collection). The absorption correction was neglegible and it was not applied. The data were corrected for Lorentz and polarization effects. A structural solution was found by direct methods (Patterson method, MITHRIL program).[24] The least-squares refinement was performed for a total of 415 parameters with 2976 reflections ($I > 3\sigma(I)$); minimization function: $\Sigma w(|F_o| - |F_c|)^2$, with least-squares weights: $4F_o^2/\sigma^2(F_o^2)$, p factor = 0.03. The non-hydrogen atoms were anisotropically refined and the hydrogen atoms were included at idealized positions and they were not refined. $R_F = 0.060$, $R_w = 0.070$, GOF = 2.03, maximum shift/error: 7.26. Accurate cell dimensions were obtained by least-squares refinement of 25 reflections ranged $13.40 < 2\Theta < 16.44^\circ$. All calculations were performed on a VAX 3520 station at the Servicio Central de Ciencias y Tecnologia de la Universidad de Cádiz. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101361 . Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[14] a) W. D. Jones, F. J. Feher, *Acc. Chem. Res.* **1989**, *22*, 91; b) M. R. Chin, L. Dong, S. B. Duckett, M. G. Partridge, W. D. Jones, R. N. Perutz, *J. Am. Chem. Soc.* **1993**, *115*, 7685.

[15] Compound **3** reacts rapidly with one equivalent of PMe_3 to give **1b**.

[16] The $^{13}C\{^1H\}$ NMR spectra of **3** in CD_2Cl_2 and CD_3OD are very similar. Since the signal assigned to the Pd-bonded aromatic quaternary carbon atom appears in both cases as a doublet ($^2J_{CP} = 7$ Hz) the π,η^1 arene interaction seems to be maintained in methanol.

[17] a) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 267; b) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005.

[18] S. I. Black, G. B. Young, *Polyhedron* **1984**, *8*, 585.

[19] a) R. F. Heck, *J. Organomet. Chem.* **1982**, *37*, 389; b) B. A. Markies, P. Wijkens, H. Kooijman, A. Spek, J. Boersma, G. van Koten, *J. Chem. Soc. Chem. Commun.* **1992**, 1420.

[20] a) D. C. Griffiths, L. G. Joy, A. C. Skapski, D. J. Wilkes, G. B. Young, *Organometallics* **1986**, *5*, 1744; b) M. E. Cucciolto, A. de Rienzi, F. Ruffo, D. Tesauro, *J. Chem. Soc. Dalton Trans.* **1998**, 1675.

[21] a) A. F. H. J. van der Ploeg, G. van Koten, K. Vrieze, A. L. Spek, *Inorg. Chem.* **1982**, *21*, 2014; b) J. E. Kickham, S. J. Loeb, *Organometallics* **1995**, *14*, 3584.

[22] M. J. Calhorda, J. M. Brown, N. A. Cooley, *Organometallics* **1991**, *10*, 1431; b) P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner, Z.-Q. Wang, *Chem. Commun.* **1996**, 1.

[23] F. Kawataka, Y. Yoshito, I. Shimizu, A. Yamamoto, *Organometallics* **1994**, *13*, 3517.

[24] G. J. Gilmore, *J. Appl. Crystallogr.* **1984**, *17*, 42–46.

Spin-Orbit Coupling versus the VSEPR Method: On the Possibility of a Nonplanar Structure for the Super-Heavy Noble Gas Tetrafluoride $(118)F_4$**

Clinton S. Nash and Bruce E. Bursten*

The discovery of the super-heavy elements 110, 111, and 112 by Armbruster and co-workers during the 1990s[1] has stimulated new interest in the properties and chemistry of newly discovered elements.[2, 3] Elements 110, 111, and 112 complete the 6d block of the periodic table. The next elements likely to be discovered are the representative 7p block elements, those with atomic numbers 113–118. The last of these, element 118, is predicted to be a noble gas with a closed-shell $7s^2 6d^{10} 7p^6$ electron configuration. As such, its properties are expected to resemble those of the heavy noble gases Xe and Rn, which are known to form compounds with electronegative elements such as F.[4]

The correct prediction of the structures of noble gas compounds was one of the great successes of the valence-shell electron-pair repulsion (VSEPR) model of Gillespie and Nyholm, in both its original[5] and more-refined current[6] formulations. This simple and pedagogically useful model correctly predicted that NgF_2 and NgF_4 (Ng = noble gas) should adopt linear and square-planar molecular geometries, respectively, based on trigonal-bipyramidal and octahedral electron-pair geometries. Herein, we will focus on the noble gas tetrafluorides XeF_4, which is known,[7] RnF_4, which has not been characterized definitively,[8] and $(118)F_4$. Our interest in the bonding in compounds of the super-heavy elements stems in part from the huge spin-orbit effects exhibited by these elements by virtue of their large atomic numbers.[9] These relativistic effects can have a remarkable influence on the properties of atoms and compounds of these elements. For example, Kaldor et al. have used relativistic coupled cluster calculations to predict that relativistic stabilization of the 8s orbital causes the element 118 to have a small electron affinity, making it unique among the noble gases.[10] We have recently predicted that spin-orbit effects will cause the super-heavy hydrogen halide H(117) to have an unusually long and strong bond.[11] Here we will report that the influence of spin-orbit effects on the bonding in $(118)F_4$ is so great as to favor a non-VSEPR tetrahedral structure for this molecule.

---

[*] Prof. B. E. Bursten
Department of Chemistry, The Ohio State University
Columbus, OH 43210 (USA)
Fax: (+1) 614-688-3306
E-mail: bursten.1@osu.edu

Dr. C. S. Nash
The Glenn T. Seaborg Institute for Transactinium Science
Lawrence Livermore National Laboratory
Livermore, CA 94550 (USA)
Fax: (+1) 925-422-3610
E-mail: nash6@llnl.gov

[**] This work was supported by the Division of Chemical Sciences, US Department of Energy (Grant DE-FG02-86ER13529), by the Ohio Supercomputer Center, and by the National Energy Research Supercomputer Center. We are grateful to W. C. Ermler, D. C. Hoffman, R. M. Pitzer, and P. Schwerdtfeger for helpful comments.

Correlated electronic structure calculations on XeF_4, RnF_4, and $(118)F_4$ have been carried out using the relativistic configuration interaction (RCI) method with the explicit inclusion (or exclusion) of a spin-orbit operator.[12] The Ng–F bond length was optimized by single-point calculations under the constraint of either a square-planar (D_{4h}) or tetrahedral (T_d) geometry. The results of these calculations are summarized in Table 1. Like other recent relativistic studies of XeF_4,[15, 16] our RCI calculations on XeF_4 greatly favor the experimentally observed square-planar geometry for this molecule. The calculated equilibrium Xe–F bond length, 1.95 Å, is in excellent agreement with the value obtained from neutron diffraction (1.951 Å)[17] and with that recently determined by high-resolution IR spectroscopy (1.935 Å).[16] At a bond length of 1.95 Å, the tetrahedral structure of XeF_4 lies roughly 5 eV higher in energy than the square-planar structure. We find a similar result for RnF_4: A square-planar structure with a Rn–F bond length of 2.05 Å is predicted, and the tetrahedral structure is about 2.5 eV higher in energy at this bond length. The bond length we predict for RnF_4 is close to the 2.025 Å bond length predicted by Dolg et al.[18] For both XeF_4 and RnF_4, the tetrahedral structure is considerably higher in energy than the square-planar structure over the entire range of bond lengths examined, both with and without the inclusion of spin-orbit coupling.

Table 1. Relative minimum energies and optimized Ng–F bond lengths from the relativistic configuration interaction calculations on XeF_4, RnF_4, and $(118)F_4$, without and with spin-orbit (SO) effects.

Molecule	Geometry	Without SO effects		With SO effects	
		E[a] [eV]	Ng–F [Å]	E[a] [eV]	Ng–F [Å]
XeF_4	D_{4h}	0.0	1.95	0.0	1.95
	T_d	5.66		4.96	
RnF_4	D_{4h}	0.0	2.04	0.0	2.05
	T_d	4.92		2.56	
$(118)F_4$	D_{4h}	0.0	2.13	0.24	2.15
	T_d	4.25		0.0	2.14

[a] The relative energy of the higher energy geometry is evaluated at the optimized Ng–F distance of the lower energy geometry.

Without spin-orbit coupling, the RCI calculations on $(118)F_4$ predict a square-planar structure, like that of XeF_4 and RnF_4, with a (118)–F bond length of 2.13 Å (Table 1). The tetrahedral structure is more than 4 eV higher at this bond length and is markedly higher in energy than the square-planar surface at all bond lengths examined (Figure 1). A separate SCF RECP geometry optimization under C_{2v} symmetry was used to sample the continuum of structures from square-planar (D_{4h}) to disphenoidal (sawhorse) (C_{2v}) to tetrahedral (T_d) under a common symmetry. In spite of the lowered symmetry constraints, these calculations also converged to a square-planar structure with a bond length of 2.124 Å. Clearly, in the absence of spin-orbit coupling, $(118)F_4$ adopts the geometry predicted by the VSEPR method.

The inclusion of spin-orbit coupling in the calculations on $(118)F_4$ drastically changes the situation, as shown in Figure 1. The potential energy surfaces for the tetrahedral and square-planar structures are nearly coincident; the tetrahedral structure is lower in energy by a small amount (<0.5 eV) at all bond lengths examined. The (118)–F bond lengths are calculated to be nearly the same in both geometries, namely 2.14 Å and 2.15 Å in the tetrahedral and square-planar geometries, respectively. We believe that our choice of configurations in these RCI calculations is such that the closeness in energy of these two surfaces is likely to remain even with the inclusion of more electron correlation. These results suggest a slight preference for a tetrahedral structure for $(118)F_4$ or, at minimum, an essentially nonrigid structure. Interestingly, a single-point RCI calculation in a C_{2v} geometry intermediate between the optimized tetrahedral and square-planar geometries gave a slightly higher energy than either of the higher symmetry structures.

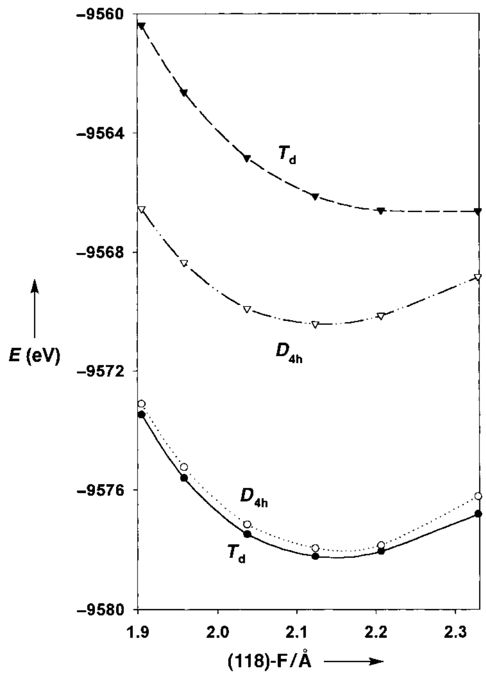

Figure 1. RCI energies of the $(118)F_4$ molecule as a function of (118)–F bond length under square-planar (D_{4h}) and tetrahedral (T_d) symmetry, without (▽ and ▼, respectively) and with (○ and ●, respectively) spin-orbit coupling.

In the VSEPR model, the square-planar geometry of NgF_4 molecules is attributed to the presence of six electron-pair domains, four of which are used to make Ng–F bonds. The results in Figure 1 clearly show that spin-orbit effects are responsible for the prediction of a non-VSEPR tetrahedral geometry for $(118)F_4$. Because spin-orbit coupling destroys the separation between spatial and spin coordinates, it is difficult to provide a simple orbital-based explanation for this apparently exceptional geometry. The most ready explanation involves the response of the valence atomic orbitals of (118) to the spin-orbit operator, which we have explored by using the atomic Dirac–Hartree–Fock relativistic calculations[19] that are summarized in Table 2. The 7s orbital of (118) undergoes its expected large energetic stabilization and radial contraction upon the inclusion of relativistic effects. Further, spin-orbit coupling dramatically splits the (118) 7p orbitals into lower energy $7p_{1/2}$ and higher energy $7p_{3/2}$ spinors. The

Table 2. Nonrelativistic Hartree–Fock and relativistic Dirac–Hartree–Fock orbital eigenvalues (ε) and radial expectation values ($\langle r \rangle$) for the ns and np orbitals of Rn and (118).

	Element Rn			Element 118	
Orbital	ε [eV]	$\langle r \rangle$ [Å]	Orbital	ε [eV]	$\langle r \rangle$ [Å]
	nonrelativistic			nonrelativistic	
6s	– 23.78	1.14	7s	– 21.06	1.28
6p	– 11.65	1.35	7p	– 10.73	1.49
	relativistic			relativistic	
$6s_{1/2}$	– 29.19	1.02	$7s_{1/2}$	– 36.25	0.96
$6p_{1/2}$	– 14.71	1.19	$7p_{1/2}$	– 20.29	1.09
$6p_{3/2}$	– 10.45	1.37	$7p_{3/2}$	– 8.25	1.58

$7p_{1/2}$ spinors are stabilized by 12 eV and radially contracted by 0.5 Å relative to the $7p_{3/2}$ spinors. As is evident in Table 2, these effects are much greater in (118) than for the corresponding orbitals in Rn. The large relative stabilization and radial contraction of the $7s_{1/2}$ and $7p_{1/2}$ spinors of (118) essentially make them unavailable for bonding interactions with the F atoms. Thus, the four electrons that can be described by these spinors are rendered as stereochemically inactive "inert pairs".[9c] From the point of view of the VSEPR model, the number of electron-pair domains has been reduced from six to four, consistent with a tetrahedral geometry within that model. The generation of inert pairs in conjunction with the expected large radius of (118) are consistent with our prediction that the tetrahedral and square-planar forms of $(118)F_4$ are practically isoenergetic, a remarkable consequence of large spin-orbit coupling.

Received: July 20, 1998 [Z 12183 IE]
German version: *Angew. Chem.* **1999**, *111*, 115–117

Keywords: electronic structure · noble gases · spin-orbit coupling · transuranium elements · VSEPR model

---

[1] a) S. Hofmann, V. Ninov, F. P. Hessberger, P. Armbruster, H. Folger, G. Muenzenberg, H. J. Schoett, A. G. Popeko, A. V. Yeremin, *Z. Phys. A* **1996**, *354*, 229; b) P. Armbruster, *Bull. Soc. Fr. Phys.* **1996**, *107*, 6.

[2] Examples: a) V. Pershina, *Chem. Rev.* **1996**, *96*, 1977; b) M. Jacoby, *Chem. Eng. News* **1998**, *76*(12), 48–54.

[3] Nomenclature: For unnamed elements, the atomic symbol is represented as (atomic number), such as (118).

[4] *Noble-Gas Compounds* (Ed.: H. H. Hyman), University of Chicago Press, Chicago, **1963**.

[5] R. J. Gillespie, R. S. Nyholm, *Q. Rev. Chem. Soc.* **1957**, 339.

[6] R. J. Gillespie, *Angew. Chem.* **1996**, *108*, 539; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 495.

[7] P. Laszlo, G. J. Schrobilgen, *Angew. Chem.* **1988**, *100*, 495; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 479.

[8] a) V. V. Avrorin, R. N. Krasikova, V. D. Nefedov, M. A. Toropova, *Radiokhimiya* **1981**, *23*, 879; b) L. Stein, *Inorg. Chem.* **1984**, *23*, 3670.

[9] Reviews of relativistic effects: a) K. S. Pitzer, *Acc. Chem. Res.* **1979**, *12*, 271; b) P. Pyykkö, J.-P. Desclaux, *Acc. Chem. Res.* **1979**, *12*, 276; c) P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563; d) W. C. Ermler, R. B. Ross, P. A. Christiansen, *Adv. Quantum Chem.* **1988**, *19*, 139; e) M. Pepper, B. E. Bursten, *Chem. Rev.* **1991**, *91*, 719; f) K. Balasubramanian, *Relativistic Effects in Chemistry, Part A: Theory and Techniques*, Wiley, New York, **1997**.

[10] E. Eliav, U. Kaldor, Y. Ishikawa, P. Pyykkö, *Phys. Rev. Lett.* **1996**, *77*, 5350.

[11] C. S. Nash, B. E. Bursten, unpublished results.

[12] Computational details: RCI calculations were carried out using Pitzer's modification of the COLUMBUS quantum-chemistry suite to allow inclusion of a spin-orbit potential.[13] Core electrons were replaced with shape-consistent relativistic effective core potentials (RECPs), which include spin-orbit operators.[14] The valence basis set consisted of (6p6sd1f) Gaussians contracted to [5p5sd1f]. The active space in the spin-orbit CI calculations consisted of single excitations of 24 electrons in 12 doubly occupied molecular orbitals into 14 virtual orbitals. Selected double excitations were also included in the active set. A typical calculation involved 3876 configurations and 24657 determinants under T_d symmetry and 1548 configurations and 9633 determinants under D_{4h}. Complete computational details will be given elsewhere.[11]

[13] a) R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lischka, P. G. Szalay, R. Ahlrichs, F. B. Brown, J. G. Zhao, *Int. J. Quantum Chem. Symp.* **1989**, *22*, 149; b) A. Chang, R. M. Pitzer, *J. Am. Chem. Soc.* **1989**, *111*, 2500.

[14] a) R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. LaJohn, P. A. Christiansen, *J. Chem. Phys.* **1990**, *93*, 6654, **1994**, *101*, 10198; b) C. S. Nash, B. E. Bursten, W. C. Ermler, *J. Chem. Phys.* **1997**, *106*, 5133.

[15] a) J. Styszynski, G. L. Malli, *Int. J. Quantum Chem.* **1995**, *55*, 227; b) J. Styszynski, X. Cao, G. L. Malli, L. Visscher, *J. Comput. Chem.* **1997**, *18*, 601.

[16] H. Bürger, S. Ma, J. Breidung, W. Thiel, *J. Chem. Phys.* **1996**, *104*, 4945.

[17] J. H. Burns, P. A. Agron, H. A. Levy, *Science* **1963**, *139*, 1208.

[18] M. Dolg, W. Küchle, H. Stoll, H. Preuss, P. Schwerdtfeger, *Mol. Phys.* **1991**, *74*, 1265.

[19] J. P. Desclaux, *At. Data Nucl. Data Tables* **1973**, *12*, 311.

A New Type of Metal-Organic Large-Pore Zeotype**

David M. L. Goodgame,* David A. Grachvogel, and David J. Williams*

The great industrial importance of zeolites, particularly in the petrochemicals industry, has fuelled the continuing interest in the synthesis and applications of new types of zeolites and related microporous materials (zeotypes). Particularly attractive avenues of further exploration include the incorporation of redox-active metals into such frameworks to provide novel heterogeneous catalytic systems[1] and the formation of zeotypes comprising microporous metal-organic ligand coordination arrays.[2] The latter approach offers, in principle, an extensive capability of custom-designing frameworks to gain better control of the pore sizes and shapes, whilst also permitting the incorporation of a wide range of metal ions, either as part of the framework or in the form of an

---

[*] Prof. D. M. L. Goodgame, Prof. D. J. Williams, D. A. Grachvogel
Chemistry Department
Imperial College of Science
Technology and Medicine
London SW7 2AY (UK)
Fax: (+44) 171-594-5804
E-mail: d.goodgame@ic.ac.uk

[**] This work was supported by the Engineering and Physical Sciences Research Council. The University of London Intercollegiate Research Service is thanked for the provision of facilities for solid-state NMR spectroscopy.