

Electronic Structure and Properties of the Transactinides and Their Compounds

Valeria G. Pershina

Gesellschaft für Schwerionenforschung, Planckstrasse 1, Postfach 11 05 52, D-64200 Darmstadt, Germany

Received November 28, 1995 (Revised Manuscript Received July 19, 1996)

Contents

I. Introduction	1977	A. Experimental Investigations of Volatility	1999
II. Relativistic Effects on Atomic Properties of Rf, Ha, and Sg	1979	1. "One-Atom-at-a-Time" Chemistry	1999
A. Methods for Calculating the Electronic Structure of Heavy Atoms and Ions	1979	2. Macrochemistry for the Lighter Homologs	1999
B. Results of Relativistic Atomic Calculations	1980	B. Theoretical Interpretation of Volatility of the Transactinide-Containing Compounds	1999
1. Electronic Configurations	1980	1. Empirical Extrapolations	1999
2. Orbital Energies and Ionization Potentials	1981	2. Dependence on Geometry	2000
3. Radial Charge Distributions and Atomic/Ionic Radii	1982	3. Estimates of Volatility on the Basis of MO Calculations	2000
III. Electronic Configurations and Sublimation Enthalpies of the Transactinide Metals	1983	XI. Oxidation States of Rf, Ha, and Sg in Aqueous Solutions	2001
IV. Relativistic Quantum-Chemical Methods for Molecules	1985	A. Characterization of Oxidation States	2001
A. Dirac–Fock One-Center Expansion (DF-OCE)	1986	B. Redox Potentials in Aqueous Solutions	2001
B. Local Density Functional Methods (LDF)	1986	1. Group 4	2001
1. Quasirelativistic Hartree–Fock–Slater (QR-HFS)	1986	2. Group 5 (Redox Reactions)	2001
2. Quasirelativistic Multiple Scattering (QR-MS)	1986	3. Group 6	2002
3. Dirac–Slater Multiple Scattering (DS-MS)	1986	XII. Forms of the Transactinides in Aqueous Solutions	2002
4. Dirac–Slater Discrete Variational (DS-DV)	1986	A. Experimental Study of Solvent Extraction	2002
C. Relativistic Core Potential Methods (RCP)	1987	B. Theoretical Study of Complex Formation and Extraction	2003
1. Quasirelativistic Pseudopotentials (QRP)	1987	1. Anionic Halide and Oxyhalide Complexes of Group 5 Elements in Acid Solutions	2003
2. Relativistic Core Potentials	1988	2. Complexes of Group 6 Elements	2004
D. All-Electron <i>ab Initio</i> Methods	1988	XIII. Summary	2006
1. <i>Ab Initio</i> Relativistic Dirac–Fock SCF Calculations for Diatomics	1988	XIV. References	2006
2. Dirac–Fock SCF Methods for Polyatomics	1989		
V. Transactinide Hydrides	1990		
VI. Transactinide Halides	1991		
A. Fluorides	1991		
B. Chlorides and Bromides	1992		
1. Group 4 Chlorides	1992		
2. Group 5 Chlorides and Bromides	1992		
3. Group 6 Chlorides	1994		
4. Comparison of Groups 4, 5, and 6 Highest Chlorides	1994		
5. Other Chlorides	1996		
VII. Transactinide Oxides	1996		
A. Monoxides	1996		
B. Trioxides	1997		
VIII. Transactinide Oxyhalides	1997		
A. Group 5 Oxytrihalides	1997		
B. Group 6 Oxytetrachlorides	1998		
C. Group 6 Dioxydichlorides	1998		
IX. Other Compounds of the Transactinides	1998		
A. The Sg Carbonyl	1998		
X. Volatility of the Halides and Oxyhalides	1999		

I. Introduction

During the last 20 years the end of the periodic table has been a subject of both experimental and theoretical interest. Discovery of new elements and their long-lived isotopes have given an impact to investigations of their physical and chemical properties. Apart from general interest, this knowledge is important for the chemical separation of these elements which is one of the methods of their detection.

Starting with element 104, the transactinides represent the last transition element series, with element 112 being discovered¹ just few months ago and elements 110 and 111 a year before.² Names for elements 104–109, which were proposed by scientists who produced them and approved in 1994 by the ACS for their use in the United States are the following: 104, rutherfordium (Rf); 105, hahnium (Ha); 106, seaborgium (Sg); 107, nielsbohrium (Ns); 108, hassium (Hs); and 109, meitnerium (Mt).

On the basis of their location in the periodic table, the transactinides are expected to exhibit chemistry analogous to that of other transition elements, where



Valeria G. Pershina was born in Cheliabinsk, Russia, in 1953. She received her Diploma from Mendeleev University of Chemistry and Technology (Moscow, 1977) and her Ph.D. degree (with Professors G. Ionova and V. Spitsyn) from Institute of Physical Chemistry, USSR Academy of Sciences (Moscow, 1983). In the following years she worked as a researcher at the same Institute of Physical Chemistry. Since 1990 she has been at the University of Kassel (with Professor B. Fricke) and Gesellschaft für Schwerionenforschung, Darmstadt, Germany. In 1994 she made a habilitation at the Institute of Physical Chemistry, Russian Academy of Sciences, Moscow. Her scientific interests are physical chemistry, relativistic quantum chemistry, the electronic structure of transition element, actinide, and transactinide compounds.

the filling of the $(n-1)d$ valence shell takes place. Special interest in these elements is dictated by the fact that in this area of the periodic table relativistic effects have such a strong influence on their electronic structure and the structure of their compounds, that it might result in a deviation from trends in properties found within the lighter analogs. Among these properties are oxidation states (redox potentials), ionic radii, complexing ability, etc. which are important for their chemical separation.

Although almost all the transactinides are presently known, studies of chemical properties have only been performed on Rf and Ha, which have rather long-lived isotopes ^{261}Rf (65-s) and ^{262}Ha (35-s). The known isotopes of elements Sg and Ns live only 0.9 and 0.1 s, respectively, and of the further elements, only few milliseconds. Recently, however, new estimates of the half-lives of two longer-lived isotopes of Sg of the order of ≈ 10 –30s have been reported.^{3a} There are some predictions of the existence of longer lived isotopes (of the order of few seconds) of Ns.^{3b}

Such short half-lives and low production rates of the heavy elements (beyond Fm) make experimental investigations of their atomic and molecular properties very difficult. For this case special "fast-chemistry" techniques have been developed. They are based on the principle of the chromatographic separation, which has advantages over other methods, since each of the few available atoms experiences many adsorption–desorption cycles thus ensuring a statistical chemical behavior. The experiments are subdivided into two large groups: gas-phase chromatography experiments^{4–9} studying volatility of the heavy elements and their compounds, and liquid chromatography technique,^{10–12} studying complex formation in aqueous solutions.

Results of these experiments^{4–13} on the chemistry of elements 103 (Lr), 104 (Rf), and 105 (Ha) provided strong evidence that the actinide series ends at Lr and a new series begins with element 104. Rf was

found to be an analog of the group 4 elements, Zr and Hf, and Ha an analog of the group 5 elements, Nb and Ta, and their chemical behavior was characteristic of the elements of these groups.

These experiments, however, revealed that the properties within the groups do not change smoothly and that there is a break in periodicities. Thus, in the gas-phase chromatography experiments rutherfordium tetrachloride and bromide were found to be more volatile than analogous HfCl₄ and HfBr₄^{7b,8a,e,g} while hahnium pentabromide was substantially less volatile than NbBr₅ and TaBr₅.^{9a,f} In the solvent extraction experiments,¹² Ha was found to be extracted together with Nb (and Pa) and not with Ta, which means that the trend for the formation of a particular type of complex in the group is broken in going from Ta to Ha. New experiments are in preparation to study the chemical behavior of Sg.¹³ Reviews covering experimental research in this area are given in refs 14–25.

Complexity and the high costs of the experiments on the transactinides make theoretical investigations and predictions highly desirable. The first of such predictions of chemical properties based on results of relativistic atomic calculations, different qualitative theories, and general knowledge about the periodic system were made more than 20 years ago.^{26–35} These works gave an insight into trends in fundamental properties of elements belonging to the transition 6d, 7d, and 8d series. These properties were ionization potentials, ionic/atomic/metallic radii, electronic configurations, stabilities of oxidation states, etc. As a result, a conclusion about similarity in properties and chemical behavior between the transactinides and the lighter 4d and 5d analogs has been made. Reviews covering this area can be found in refs 14, 37, and 38.

Later, results of more accurate (multiconfiguration Dirac–Fock) relativistic atomic calculations^{39–43} provided new values for the atomic properties. Some papers^{43,44} have been published on predictions of properties of Rf compounds (enthalpies of formation of halides and redox potentials) using the results of the new calculations and some semiempirical models.

The number of publications devoted to the investigations of properties of transactinide-containing compounds based on results of molecular calculations up to 1989 and 1990 was considered negligible. Only a few publications^{45,46} have shown the possibility of the application of modern relativistic quantum-chemical codes to calculate the electronic structure of the heavy and superheavy element compounds. In refs 47 and 48 the influence of relativistic effects on bond lengths in model tetra- and hexahydrides of Rf and Sg has been analyzed. Only relatively recently did some calculations^{49,50} of the electronic structure of Rf halides appear, with the final aim of interpreting the results of the recent experiments. A more systematic study as a part of the joint program on the investigation of properties of the transactinide-containing compounds was started in 1990, with the results being presented in refs 51–64. Some related publications^{65–68} from other groups appearing in the

literature show growing interest in this quickly developing area.

The main purpose of this review is to present an overview of the results of studies concerning the electronic structure and properties of transactinide-containing compounds based on molecular-orbital calculations, on very recent atomic calculations and on different qualitative or quantitative theories.

In the next section, recent achievements in the development of relativistic atomic codes and results of the calculations together with their application are presented. Section III is devoted to estimates of sublimation enthalpies of the metals. In section IV, relativistic molecular codes and their application to the transactinide-containing compounds are described. In the subsequent sections, V–IX, results of the calculations of the electronic structure of hydrides, halides, oxides, oxyhalides, and other compounds of the transactinides are presented. Volatility of the transactinide halides and oxyhalides is discussed in section X. Sections XI and XII are devoted to the solution chemistry of the transactinides: to redox potentials (section XI) and to the electronic structure and extractability of neutral and anionic complexes (section XII).

II. Relativistic Effects on Atomic Properties of Rf, Ha, and Sg

Relativistic effects, which increase proportionally with respect to Z^2 for atomic electronic shells, are the reason for a strong energetic stabilization of the s and p orbitals and their spatial contraction, and, as a secondary effect, a destabilization and expansion of the (outer) d and f orbitals. In the 5d elements, such changes in the valence 6s and 5d orbitals result in quantitative and qualitative alterations in properties of their compounds. Much larger changes in the energy and spatial distribution of the valence 7s, 7p, and 6d electrons in the transactinides result in larger changes in properties, leading in some cases to deviations from the trends found within the lighter analogs. Among these properties are electronic configurations, ionization potentials, ionic/atomic radii, oxidation states (redox potentials), complexing ability, etc.

A. Methods for Calculating the Electronic Structure of Heavy Atoms and Ions

Fundamental predictions of chemical properties of the transactinides based on results of relativistic atomic calculations have been made by Mann, Waber, and co-workers²⁹ and by Fricke and Greiner.^{28,70} The calculations of the heavy element atoms and ions have been performed by using the single-configuration Dirac–Fock (DF) method^{26,29,36,69} and analogous local-density model, the Dirac–Slater (DS).^{27,28,31,37,38,70} Results and their application to the interpretation of chemical properties are summarized in early reviews of Fricke.^{37,38} To the list of references presented there calculations of Desclaux³⁶ should be added. (The full list of atomic calculations up to 1985 can be found in ref 71.)

Starting in 1980, multiconfiguration Dirac–Fock (MCDF) calculations^{39–42} for the very heavy elements

appeared, showing in some cases significantly different results than those which were expected on the basis of a straightforward extrapolation of the periodic table or from the DS or DF calculations.

The MCDF method is known to take into account most of the correlation effects while retaining only a reasonable number of configurations.⁷² In its relativistic version, it has the advantage of working *ab initio* in the intermediate coupling scheme thus allowing convergence to a well-specified state. The method nevertheless largely omits dynamic correlation and some core polarization, since excitations of the type $(nj) \rightarrow (n'j)$ cannot be handled. A detailed description of the method is given in ref 72c; the general theory, in refs 72a,b.

Another method, successfully treating correlation effects in many-electron systems is the relativistic many-body perturbation theory (MBPT).⁷³ The method is however more suitable for highly charged atoms⁷⁴ (where few terms of the perturbation series suffice), but less suitable for neutral atoms (where higher orders of the series are nonnegligible). Calculations of atoms as heavy as Rb,⁷⁵ Rn, Hg,⁷⁶ Cs, and Tl^{74,77} have been reported.

The drawbacks of the MBPT method are eliminated in the coupled-cluster (CC) formalism,⁷⁸ an all-order method, where infinite subclasses of contributions are summed. (For a recent review of the nonrelativistic CC method see ref 79.)

Both relativistic MBPT and CC methods are based on the solution of the four-component one-electron Dirac–Fock–Breit (DFB) equation.^{80,81} The relativistic Hamiltonian in the “no-virtual pair” approximation contains the Coulomb potential (describing the instantaneous electrostatic interaction) and the Breit potential (describing magnetostatic terms).^{73,78} Inclusion of the latter term increases the accuracy of the calculated fine-structure splittings and inner-electron binding energies. The relativistic effects are included to second order in the fine-structure constant α . Correlation effects in the CC method are then incorporated by the CC formalism in the Fock space,^{82–86} Hilbert space,⁸⁷ or other approximations.⁸⁸

Developed in a discrete global analytical four-component spinor basis, the relativistic multireference Fock-space CC method⁸³ takes into account the effects of virtual single and double excitation (CCSD) as well as their products and powers to all orders. It proved to be the most accurate for a large variety of systems. The method takes into account most of the dynamic correlations, omitted from MCDF, and a core polarization. At present it is limited to one and two particle valence sectors of the Fock space, i.e., it can only treat the states which can be reached from a closed shell by adding or removing no more than two electrons. In addition, the computational costs are very high.

The CCSD method has been applied to the calculations of the electronic structure of the very heavy elements: Lr, Rf, and 111–113.^{84–86} Calculations for other superheavy elements are in progress.

B. Results of Relativistic Atomic Calculations

1. Electronic Configurations

Lr was the first element where a strong relativistic stabilization of the $7p_{1/2}$ orbital was supposed to result in an unusual ground-state electronic configuration. This state, $7s^27p$, was first proposed by Mann,^{29c} and later by Brewer,⁸⁹ although the DF calculations of Desclaux³⁶ predicted $7s^26d$. For Rf and heavier elements, DF calculations³⁶ predicted an $(n-1)d^mns^2$ ground-state configuration (n is the number of the period and m goes from 1 to 10).

In 1980, calculations of Desclaux and Fricke,³⁹ using the MCDF method, have shown that spin-orbit stabilization plays a dominant role in Lr, so that the ground-state electronic configuration is $7s^27p(^2P_{1/2})$ in contrast to the earlier expected $7s^26d$, assumed by analogy with Lu. In these calculations the energy difference between the $(n-1)d$ and np configurations of Y, La, and Lu was about 0.3 eV lower compared to the experimental value. The calculated energy difference for Lr was corrected by this value which resulted in the $7s^27p$ ground-state configuration. The first excited state at about $(1.5 \pm 1) \times 10^3 \text{ cm}^{-1}$ ($J = 3/2$) was $7s^2d$.

Calculations^{40,41} for Rf using the same MCDF method have also obtained an electronic configuration which is different from that expected from the periodic table. By taking into account 468 jj configurations,⁴⁰ the ground state was shown to be $J = 2$ consisting of $6d7s^27p_{1/2}$ (80%), with the first excited-state configuration $6d^27s^2$ (95%) being 0.5⁴⁰ or 0.24 eV⁴¹ higher in energy. The $7s^27p^2$ electronic configuration, proposed in ref 16 as the ground state, turned out to be 2.9 eV above the ground state.

Recent calculations⁸⁴ using the CCSD method have given a different electronic configuration for Rf than the one obtained by the MCDF method, but in agreement with the early predictions:³⁶⁻³⁸ $7s^26d^2(^3F_2)$. The $7s^27p6d(^3D_2)$ state was found to lie about 0.30 eV above the ground state. The difference between the MCDF and CCSD calculations was explained by the fact that the former take into account only nondynamic correlations of the outer four electrons. The CCSD calculations performed without correlated f electrons resulted in the same relation between the two electronic configurations like that obtained by using the MCDF method. Inclusion of the f electrons and electrons with higher l number (up to 6) resulted in an inversion of these levels. Thus, the dynamic correlation of the system, requiring virtual orbitals with l up to 6, turned out to be responsible for the reversal. The Breit interaction was shown to have a large effect on total energies, but a very small effect on correlation and transition energies in the outer shells.

The CCSD calculations⁸⁶ for Lr confirmed the $7s^2-7p$ ground-state electronic configuration obtained in the MCDF calculations.³⁹ The next excited state, $7s^26d_{3/2}(^2D_{3/2})$, is found to be about 0.16 eV higher in energy, which is in good agreement with the corrected value of 0.186 eV from the MCDF calculations.³⁹ The $7s^27p_{1/2}$ configuration was confirmed to be a result of the relativistic stabilization of the $^2P_{1/2}$ state.

Table 1. Recent Physicochemical Data for Rf, Ha, and Sg

property	Rf		Ha	Sg
	MCDF ^{a,b}	CCSD ^c	MCDF ^d	MCDF ^e
chemical group	4	4	5	6
ground-state configuration	$6d7s^27p$	$6d^27s^2$	$6d^37s^2$	$6d^47s^2$
first excited configuration	$6d^27s^2$	$6d7s^27p$	$6d^37s7p$	$6d^37s^27p$
excitation energy, eV	0.5; ^a 0.24 ^b	0.30	1.90	1.64
$R_{\text{max}}(M^{z+})$, Å ($z = \text{max}$)	0.706 ^b	—	0.685	—
IR (M^{z+}), Å ($z = \text{max}$)	0.79 ^b	—	0.74	—
$\Sigma^n \text{IP}$ ($n = \text{max}$), eV	76.80 ^b	—	126.38	—
IP(0)-(1+), eV	6.50 ^b	6.01	6.89	7.10
most stable oxidation state	4+	4+	5+	6+ (4+ ?)

^a Reference 40. ^b References 41 and 43. ^c Reference 84. ^d Reference 42. ^e Reference 90.

For Ha, the MCDF calculations⁴² have given $6d^3-7s^2$ as the ground-state electronic configuration, in accordance with earlier predictions.^{37,38} The relativistic stabilization of the $7p_{1/2}$ orbital manifests itself in the first excited configuration of this element, $6d^3-7s7p$, lying at 1.9 eV higher in energy. The d^4s configuration, which was expected earlier to be the next excited state, turned out to be 2.0 eV above the ground state.

Preliminary MCDF calculations⁹⁰ have shown a similar situation for Sg: the ground-state electronic configuration is $6d^47s^2$ and the first excited state is $6d^37s^27p$, located 1.64 eV higher in energy. Results of the recent MCDF and CCSD calculations for elements Rf through Sg are shown in Table 1.

For element 111, the CCSD calculations^{85a} have shown that in contrast to the lighter group 11 elements, the atomic ground state is $6d^97s^2(^2D_{5/2})$; the $^2D_{3/2}$ state is higher by 2.69 eV, and the $6d^{10}7s$ configuration lies 2.95 eV above the $^2D_{5/2}$. The reversal is ascribed to relativistic effects. These results are very close to the relativistic Hartree-Fock-Slater calculations of Keller et al.³⁰ The $6d^{10}-7s^2$ ground state was confirmed for element 112.^{85b} A recent CCSD result for the ground state of element 113 is $6d^{10}7s^27p_{1/2}(^2P_{1/2})$.^{85c}

Thus, the results of the atomic calculations have shown that a strong relativistic stabilization of the $7s$ electrons manifests itself in the stabilization of the $7s^2$ pair over the entire transactinide series. The effect of the ns electron stabilization was already observed^{28,37,38,91,92} in the $5d$ elements in contrast to the $4d$ ones (the change of the configuration from $5s4d^m$ to $6s^25d^{m-1}$, see Table 2). Nevertheless, in the case of Au the tendency to fill the d shell is still stronger than the relativistic stabilization of the $6s^2$ pair, while in the case of element 111, the relativistic stabilization of the $7s^2$ pair is predominant.^{85a}

The stabilization of the $7s^2$ pair with increasing Z is particularly seen for the +1 ionized state of the transactinides in contrast to their $5d$ analogs (with some exceptions like Hf^+) having the $(n-1)d^mns$ configurations. Thus, e.g., the lowest configuration of the Ha^+ state is $6d^27s^2$ (93%) in contrast to the

Table 2. Ground and First Ionized States for Group 4–6 Elements

	group 4			group 5			group 6		
	Zr	Hf	Rf	Nb	Ta	Ha	Mo	W	Sg
M	4d ² 5s ²	5d ² 6s ²	6d ² 7s ^{2a}	4d ⁴ 5s	5d ³ 6s ²	6d ³ 7s ²	4d ⁵ 5s	5d ⁴ 6s ²	6d ⁴ 7s ²
M ⁺	4d ² 5s	5d6s ²	6d7s ²	4d ⁴	5d ³ 6s	6d ² 7s ²	4d ⁵	5d ⁴ 6s	6d ³ 7s ²

^a Reference 84; according to ref 41 the configuration is 6d⁷s²7p.

(*n*−1)d³s configurations of V⁺, Nb⁺, and Ta⁺ (Table 2). (For the higher oxidation states of Ha (2+ and 3+), the (*n*−1)d³ main configuration has a large admixture, up to 16%, of the 6d^m7s¹ configuration⁴²). The relativistic stabilization of the 7s orbitals was also shown⁸⁵ to lead to the 6d⁸7s² and 6d⁹7s² ground states of the 111⁺ and 112⁺ ions, rather than the 6d⁹s and d¹⁰s states of the lighter group 11 and 12 elements, respectively.

The theoretically predicted relativistic stabilization of the 7p_{1/2} and 7s² electrons was a reason to think about stability of the +1 oxidation state of Lr (ref 16) and Rf (ref 40), of the +3 state of Ha and the +4 state of Sg (ref 38) in addition to the stability of their maximum oxidation states. Estimates of the stability of these and other states will be discussed in section XI.

Availability of the 7p_{1/2} electrons in the ground-state electronic configuration was also thought to lead to a pronounced p character in the properties of these elements. (See discussions of volatility of Lr in section III.) Results of the later MO calculations^{49–52} have shown that a larger participation of the 7p_{1/2} orbitals of the transactinides in chemical bonding in comparison with the lighter analogs in the groups does not change the basic d character of bonding of their compounds.

2. Orbital Energies and Ionization Potentials

The strength of the chemical bonding in a compound is known to be determined by the energies of atomic valence shells and their spatial distribution. The influence of relativistic effects on the atomic and molecular properties for elements lighter than the transactinides has been extensively discussed in the literature (see, e.g., refs 92–99).

In ref 57, the influence of relativistic effects on the electronic structure and properties of the transactinides has been analyzed on the basis of HFS and DS atomic calculations, as well as on the HF and DF data of Desclaux.³⁶ As an example, in Figure 1 binding energies for group 5 elements, including Ha and Pa, obtained as a result of the nonrelativistic HF and relativistic DF calculations are shown. The ratio of the relativistic DS to the nonrelativistic HFS eigenvalues for the valence electrons of Nb, Ta, and Ha are given in Table 3.

The following opposite trends have been observed for the relativistic and nonrelativistic valence orbitals in going from Nb to Ha: the nonrelativistic s and p_{1/2} orbitals become more destabilized, but (*n*−1)d orbitals become stabilized, while the relativistic s and p_{1/2} orbitals become more stabilized, but the (*n*−1)d orbitals—destabilized. However, if the trends in the nonrelativistic and relativistic valence orbital changes are the same in going from Nb to Ta, they become opposite in going from Ta to Ha. Thus, nonrelativ-

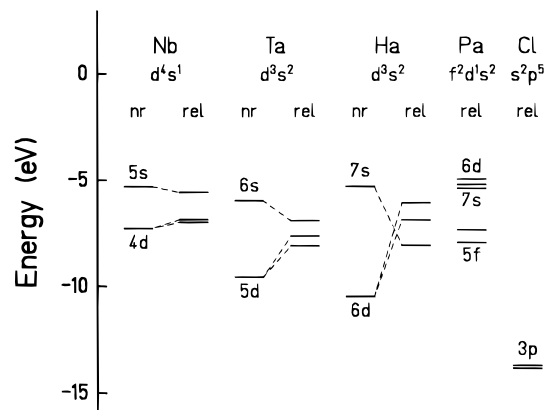


Figure 1. Binding energies of the valence electrons for Nb, Ta, and Ha as a result of the DF relativistic and HF nonrelativistic calculations.³⁶

Table 3. Ratio of the Relativistic (DS) to Nonrelativistic (HFS) R_{\max} and Eigenvalues (E) for the Valence Electrons of Nb, Ta, and Ha (Ref 57)

atom	<i>ns</i>	<i>np</i> _{1/2}	<i>np</i> _{3/2}	(<i>n</i> −1)d _{3/2}	(<i>n</i> −1)d _{5/2}
	$E^{\text{rel}}/E^{\text{nr}}$				
Nb(d ⁴ s)	1.0715	1.0879	0.9695	0.9341	0.8762
Ta(d ³ s ²)	1.1833	1.1458	0.7521	0.7543	0.6164
Ha(d ³ s ²)	1.5245	1.4612	0.4480	0.5514	0.3264
	$R_{\max}^{\text{rel}}/R_{\max}^{\text{nr}}$				
Nb(d ⁴ s)	0.9702	0.9660	0.9989	1.0080	1.0186
Ta(d ³ s ²)	0.9089	0.9080	1.0191	1.0081	1.0453
Ha(d ³ s ²)	0.7945	0.7870	1.0596	1.0127	1.0962

istic description of the wave functions for the transactinide elements will result in prediction of wrong trends in properties within the groups.

In order to compare the transactinides with pseudoanalogs within the actinides (e.g., Ha with Pa) binding energies of Pa are also shown in Figure 1. One can see that in addition to the 7s and 6d orbitals, Pa has also the 5f orbitals in the valence region. Being located at the beginning of the actinide series, Pa has much less stabilized 7s (and 6d) electrons than Ha, which has a filled 5f shell and, thus, experiences the actinide contraction since the 7s orbitals are not well screened and attracted to the core. Thus, the bonding made by the valence orbitals of Pa will be different from that of Ha.

The same effect was found in ref 68 for Sg with respect to U. There, relativistic and nonrelativistic energies of the atomic valence orbitals have been compared for W, U, and Sg. A trend in their changes with increasing atomic number was found to be similar to that for the group 5 elements (see ref 57 and Figure 1). The 7s orbital of Sg is stabilized by 2.54 eV and contracted by about 0.34 Å by relativistic effects.

In ref 100, the same opposite action of the orbital and relativistic effects for the *ns* and *np*_{1/2} electrons has been demonstrated for Rf and elements 111–115.

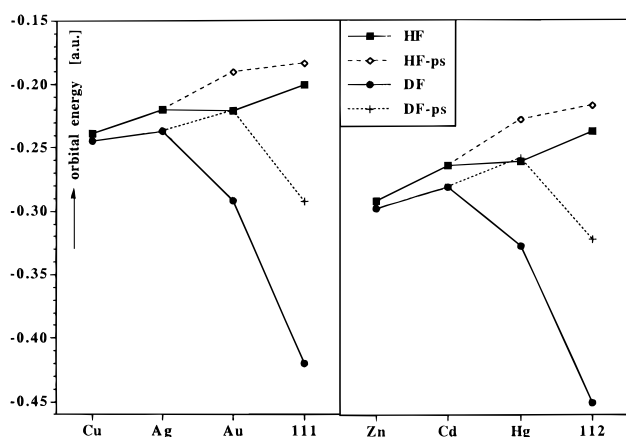


Figure 2. Orbital energies of the valence ns electrons ($n = 4-7$). HF-ps and DF-ps indicate nonrelativistic and relativistic calculations for the pseudoatoms, respectively, (i.e., atoms with 4f or 5f electrons removed). (Reproduced with permission from ref 100. Copyright 1995 American Chemical Society.)

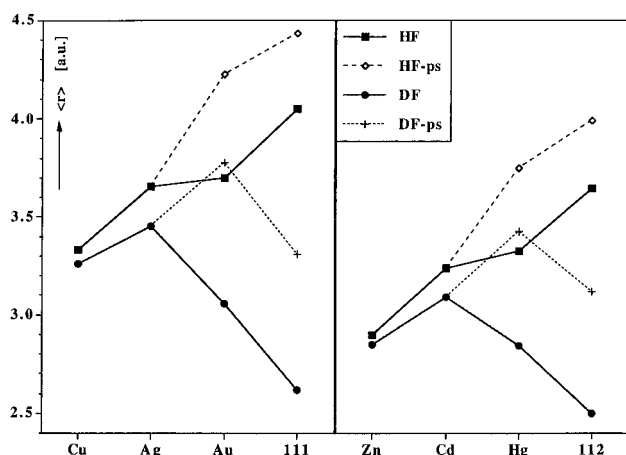


Figure 3. $\langle r \rangle$ expectation value of the valence ns orbitals ($n = 4-7$). HF-ps and DF-ps indicate nonrelativistic and relativistic calculations for the pseudoatoms, respectively, (i.e., atoms with 4f or 5f electrons removed). (Reproduced with permission from ref 100. Copyright 1995 American Chemical Society.)

In this work an effect of the filled 5f shell on the atomic energies and expectation values of the valence electrons has been demonstrated. Relativistic and f-shell effects were shown not to be additive. The orbital stabilization of the ns (or destabilizations of the $(n-1)d$ electrons) due to the filled f shell is increased by relativistic effects. (Obviously, relativistic f orbitals are more diffuse than their nonrelativistic counterparts and their screening of the nuclear charge is even less pronounced). The result of the f shell's and relativistic effects' influence on the orbital energies and wave functions is shown in Figures 2 and 3.

The first and multiple DFS ionization potentials (IP) for elements 104–112 are given in ref 38. Recently, the MCDF^{40,41} and CCSD^{84,85} values have been provided for Rf, Ha, and elements 111–113. For Rf, the MCDF calculations⁴¹ have shown the first ionized electron to be a $7p_{1/2}$, with the IP($6d7s^27p \rightarrow 6d7s^2$) of 6.50 eV. (This value was obtained by normalization and extrapolation over experimental values for the lighter analogs.) The CCSD calculations⁸⁴ have given a corrected value of the first IP of

6.01 eV with the first ionized electron being 6d ($6d^2-7s^2 \rightarrow 6d7s^2$). The next IPs are the following:⁴¹ IP($Rf^+ \rightarrow Rf^{2+}$) $7s^26d \rightarrow 7s^2$ of 14.80 eV (the CCSD calculations⁸⁴ give 14.36 eV for this ionization); IP($Rf^{2+} \rightarrow Rf^{3+}$) $7s^2 \rightarrow 7s$ of 23.80 eV; IP($Rf^{3+} \rightarrow Rf^{4+}$) $7s \rightarrow$ core of 31.90 eV. The IP($Rf \rightarrow Rf^{4+}$) $7s^26d7p \rightarrow$ core of 76.50 eV. The first through fifth MCDF IPs for Ha are given in ref 42.

Since relativistic effects in the transactinides destabilize 6d AOs and split them by the spin-orbit interaction, the relativistic first IP and some others of the transactinides are lower than the nonrelativistic ones, and they are lower than those of the analogous 5d elements. The relativistic decrease in IP for the transition from the neutral to the maximum oxidation states (Table 4) enhances the stability of the maximum oxidation states of Rf and Ha. The same would probably hold for Sg which is still awaiting the final results of the MCDF calculations.

3. Radial Charge Distributions and Atomic/Ionic Radii

Spatial distribution of the various electrons as $\langle r^n \rangle$ ($n = -3, -1, 1, 2, 4, \text{ and } 6$) for elements up to 120 as a result of the DF calculations are given by Desclaux.³⁶ Radii of maximum radial charge density in the outermost shells for Rf and Ha and their ions along with those values for the analogous elements obtained as a result of the MCDF calculations are given in refs 40–42. Atomic (AR) and ionic radii (IR) of these elements in different oxidation states have been estimated by normalization and extrapolation of R_{\max} over known experimental values.^{41,42}

According to the MCDF calculations,⁴¹ AR(Rf) is larger than those of the analogs since the outer electron is a 7p: AR(Hf,6s) = 0.161 and AR(Rf,7p) = 0.178 au. Taking into account the results of the CCSD calculations,⁸⁴ AR(Rf) should be different (and probably smaller) since the outer electron is the 7s. (For Zr, Hf, and Rf the DF values³⁶ of $R_{\max}(ns)$ are 3.291, 3.048, and 2.972 au, respectively). For the +1 oxidation state of group 4 elements, IR decrease in going down the group due to a decrease in $R_{\max}(ns)$.⁴¹

Along the transactinide series, the ns function becomes more contracted so that the smallest $R_{\max}(ns)$ will be at element 112.³⁶⁻³⁸ In ref 100, the 5f-shell effect on the space distribution of the ns and $np_{1/2}$ orbitals (their contraction) was shown to be enhanced by relativistic effects (Figure 3). A much smaller $R_{\max}(7s)$ for elements 111 and 112 compared to Ag, Au and Cd, Hg, respectively, was supposed to result in the smallest bond lengths 111–X and 112X in the series MX.

The MCDF IR(Rf^{4+}) and IR(Ha^{5+}) have been obtained by an extrapolation and normalization of R_{\max} of outer electrons of the filled 6p shell over known experimental IR (Table 4).^{41,42} The data of Table 4 show that IR(M^{4+}) and IR(M^{5+}) of the 4d and 5d elements, respectively, are almost equal due to the lanthanide contraction (of about 0.020 Å) which was shown⁴⁸ to be up to 86% a nonrelativistic effect. The IR of the corresponding transactinide ions are larger than those of the 5d elements due to the shell-structure expansion of the outer $6p_{3/2}$ orbitals enhanced by relativity. Due to the actinide contraction (of 0.030 Å), which is a mostly relativistic effect, IR

Table 4. Multiple Ionization Potentials (0–4+) and (0–5+), Radii of Maximum Radial Charge Density (R_{\max}) and Ionic Radii (IR) for M^{4+} and M^{5+}

group 4				group 5			
element	$\Sigma IP, eV^a$	$R_{\max}, \text{\AA}^b$	IR, \AA^c	element	$\Sigma IP, eV^a$	$R_{\max}, \text{\AA}^d$	IR, \AA^c
Ti	91.15	0.47	0.61	V	162.64	0.44	0.54
Zr	77.29	0.62	0.72	Nb	135.05	0.59	0.64
Hf	77.50	0.63	0.71	Ta	132.03	0.60	0.64
Rf	76.80 ^b	0.71	0.79 ^b	Ha	126.38 ^d	0.69	0.74 ^d

^a Reference 101. ^b Reference 41. ^c Reference 102. ^d Reference 42.

of the transactinides are smaller than the radii of the corresponding actinides.

The MCDF ionic radii for the +2, +3, and +4 oxidation states of group 5 elements, including Ha, increase with increasing atomic number due to the relativistic and orbital expansion of the d orbitals.

Thus, as it was concluded earlier,^{37,38} larger ionic and covalent radii, smaller ionization energies, and close spacing of the energies of the valence orbitals of Rf and Ha, compared to their lighter analogs will facilitate stability of their maximum oxidation states and will be the basis for a rich chemistry of complex ions in solutions.

An analysis of the influence of relativistic effects on R_{\max} and on the involvement of different orbitals in chemical bonding in the transactinides has been done in refs 57, 67, and 68. Relativistic radial contraction or extension of the valence orbitals can be seen in Table 3 and Figures 4–6 for group 5 elements, as an example.⁵⁷ Thus, R_{\max} for different valence orbitals changes in a different way within the groups: due to the relativistic contraction of the ns and $np_{1/2}$ orbitals, their relativistic R_{\max} decreases with increasing Z , while the nonrelativistic values show just the opposite trend (Figures 4 and 5). (For these orbitals relativistic and orbital effects act in opposite directions. According to the DS calculations⁵⁷ of the elements for electronic configurations which they have in compounds, e.g. in MCl_5 , the relativistic shift in $R_{\max}(ns)$ Nb, Ta, and Ha is 3, 9.1, and 20.5%, respectively.) For relativistic $np_{3/2}$, $(n-1)d_{3/2}$ and $(n-1)d_{5/2}$ electrons R_{\max} increases in going down the group with the relativistic effect enhancing the orbital effect for the $(n-1)d_{5/2}$ orbitals (Figure 6).

The opposite behaviors of the relativistic and nonrelativistic valence ns and $np_{1/2}$ orbitals were shown to result in different trends in chemical bonding in going from the 5d to the 6d compounds (see results of the molecular calculations in section VI).

III. Electronic Configurations and Sublimation Enthalpies of the Transactinide Metals

Knowledge of the sublimation energies of the transactinide metals, ΔH_s , is very important not only for studying properties of individual atoms, but also for calculating different properties of their compounds, such as enthalpies of formation, sublimation, etc. Since the transactinides are available only in "one-atom-at-a-time" quantities, it is impossible to measure their ΔH_s from the bulk metallic state.

An indirect way to estimate ΔH_s from experimental data for single atoms was proposed in ref 103. Heats of adsorption of Cf, Es, Fm, and Md on a metallic

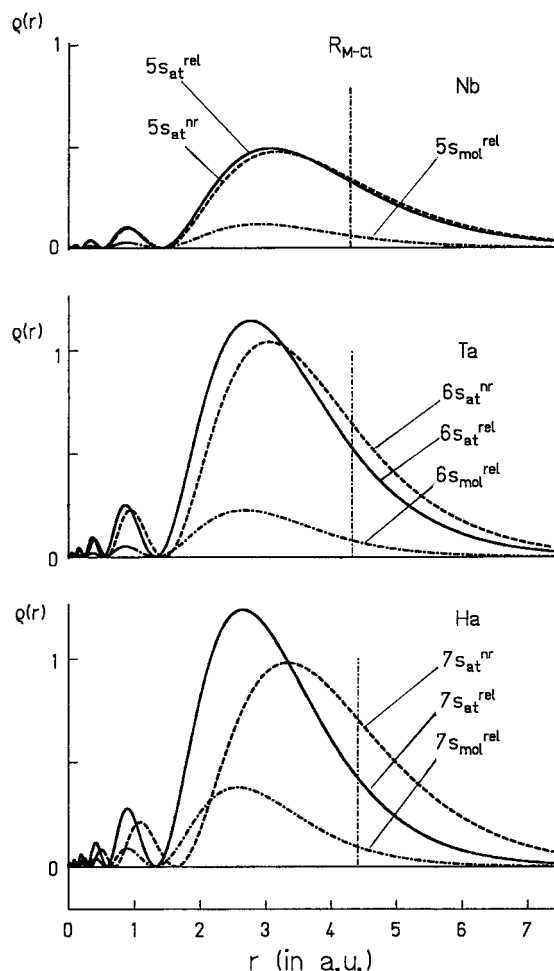


Figure 4. Radial distribution of the ns electrons in Nb, Ta, and Ha as a result of atomic DS relativistic (full line) and HF nonrelativistic (dashed line) calculations. The dashed-dotted (mol) are relativistic calculations of the metal ions for electronic configurations obtained in the molecular DS DVM calculations for MCl_5 . (Reproduced from ref 57. Copyright 1993 American Institute of Physics.)

surface of the chromatography column, measured in the gas-phase chromatography experiments, were shown to be proportional to the sublimation enthalpies of their metals.^{103,104} Since the electronic environment is different when the atom is adsorbed on a surface and when it is in the bulk material, the choice of the right surface was claimed to be important to ensure the proportionality between these two values. This technique, however, would not be useful for the transactinides, since it is extremely difficult to stabilize elements in the atomic state at temperatures higher than 1000 °C applied there. Thus, theoretical predictions become the only way to obtain the information about ΔH_s .

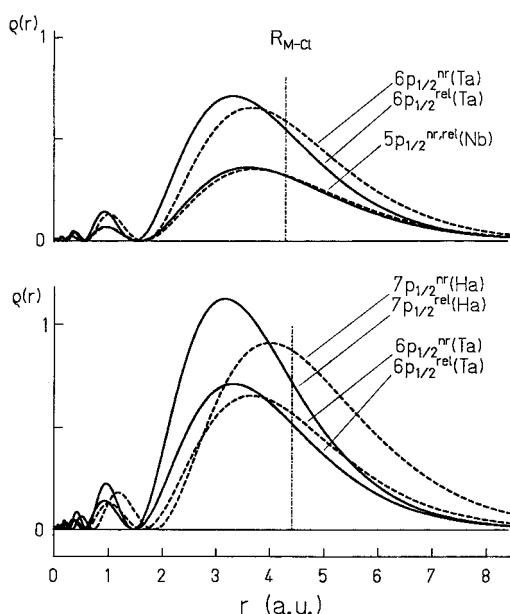


Figure 5. The radial density of the relativistic (full line) and nonrelativistic (dashed line) $np_{1/2}$ electrons in the molecules MCl_5 . (Reproduced from ref 57. Copyright 1993 American Institute of Physics.)

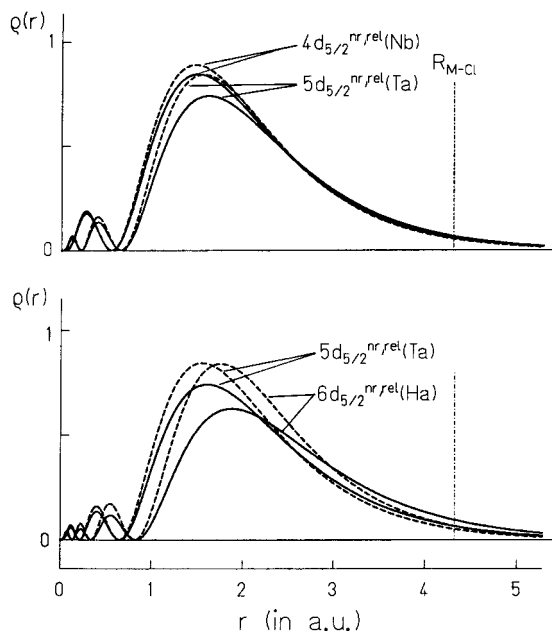


Figure 6. The radial distribution of the relativistic (full line) and nonrelativistic (dashed line) $(n-1)d$ electrons in the molecules MCl_5 . (Reproduced from ref 57. Copyright 1993 American Institute of Physics.)

Estimates of the sublimation enthalpies of the unknown elements, as well as of some other properties, were mostly made by using the periodic law.

Among heavy elements, Lr was a special subject of interest due to the (calculated³⁹) $7s^27p$ ground-state electronic configuration. This element was believed to be as volatile as other p elements, e.g., Tl having the $6s^26p$ configuration.

First Keller¹⁶ and then Eichler¹⁰⁵ used a linear correlation between ΔH_s and the atomic number of elements Al–Ga–In–Tl to estimate $\Delta H_s(p)$ for Lr (as a “p” element). The value obtained was 135 kJ/mol (32.26 kcal/mol) which means that the volatility of Lr would be as high as that of the other p elements.

$\Delta H_s(d)$ for Lr (as a d element) was estimated using the following relation

$$\Delta H_s = E_b - \Delta E \quad (1)$$

where E_b is the binding energy and ΔE is the difference between electronic configurations in the metallic and gaseous states. E_b was shown^{106–108} to vary smoothly with atomic number, and for the lanthanides and actinides to be nearly a constant value. The obtained $\Delta H_s(d)$ for Lr were 414 kJ/mol (98.9 kcal/mol);^{107,108} 351 kJ/mol (83.9 kcal/mol),¹⁰⁹ and 410 kJ/mol (98 kcal/mol).¹¹⁰ Thus, the difference between $\Delta H_s(d)$ and $\Delta H_s(p)$ was found to be ≈ 4 eV, which could have been detected easily in experiments.

Attempts to separate Lr(p) from the other actinides using the high-temperature gas-phase chromatography in quartz and Pt columns⁴ nevertheless failed. Conducted at temperatures around 1000 °C in the reducing atmosphere of He/H₂ (to keep Lr in the atomic state), the experiment has given a lower limit for the adsorption enthalpy for Lr of ≥ 290 kJ/mol, which is significantly higher than the expected value for Lr(p). Thus, Lr was found to be as nonvolatile as the other actinides. The results, however, did not exclude existence of Lr(p). It is possible, that when interacting with the surface of the column the atom easily reaches its excited $7s^26d$ state, which is only 0.24 eV above the ground state, thus losing its “p” character.

For the heavier elements, first estimates of ΔH_s have been obtained through an extrapolation versus the row of the periodic table.^{15,38} Later, some more elaborate schemes were used to obtain ΔH_s for Rf through Sg. For example, in ref 49 $\Delta H_s(Rf)$ was calculated by using the relation 1, with E_b being shown to have a linear dependence on the atomic number in group 4. (The electronic configuration of the Rf metal was assumed to be $6d^37s$ by analogy with Zr and Hf). Since the calculated^{40,41} MCDF ground state electronic configuration was $6d7s^27p_{1/2}$, $\Delta E = E(d^3s) - E(ds^2p)$ was larger than $\Delta E = E(d^3s) - E(d^2s^2)$, so that the estimated ΔH_s of Sg of 610 ± 25 kJ/mol (145.8 kcal/mol) was below that value of Hf. The $6d^27s^2$ ground-state configuration would result in an increase in the sublimation energy up to 655 ± 25 kJ/mol (156.5 kcal/mol). In ref 44 an estimate of $\Delta H_s(Rf)$ of 540 kJ/mol was given by comparison with $\Delta H_s(Hf)$. The proposed value is obviously too low. The predictions are summarized in Table 5.

An experiment¹¹¹ designed to check for the “p” or “d” behavior of Rf according to the proposed different ground-state electronic configurations has only given a lower limit of the sublimation enthalpy of 370 kJ/mol (88 kcal/mol). This indicated that Rf is not as volatile as Sn or Pb, but rather nonvolatile like analogous d elements. It was also concluded that this sort of experiment was not the proper one to be able to distinguish between a “p” or “d” character of the element, since it is difficult to stabilize the transactinides in the atomic state at the required temperatures (above 1500 °C).

Another empirical approach to estimate ΔH_s for the transactinides was proposed by Eichler.^{104,112} He

Table 5. Electronic Configurations and Sublimation Enthalpies (ΔH_s) of Metals for Rf, Ha, and Sg

element	electronic configuration		ΔH_s , kJ/mol	ref
	gas	metal		
Rf	$d^2s^2(^3F_4)$	$d^3s(^5F_5)$	633.5 ± 30	63
	$d^2s^2(^3F_4)$		655	49
	$ds^2p(^3D_2)$		610.5 ± 25	49
			540	44
			648	112e
Ha	$d^3s^2(^4F_{3/2})$	$d^4s(^6D_{9/2})$	767.8 ± 30	63
			700	44
			821	112e
			835	112c
			795	15
			807	63
			862	63
Sg	$d^4s^2(^5D_4)$	$d^5s(^7S_3)$	900...1156	112d
		$d^5p + d^4sp(^5P_3 + ^7F_6)$	858	15

used linear correlations (within the groups) either between $\log \Delta H_s$ and the entropy of sublimation of a metal, $S(g)$, or between ΔH_s and the electronic metal density n_{ws} , which in turn was expressed via $S(g)$. The latter values were obtained via a linear correlation with $\ln A$, where A is the atomic weight. These two correlations resulted for Ha in two different values of ΔH_s of 835 and 700 kJ/mol (199.6 and 167.3 kcal/mol), respectively. For Sg, estimated in this way^{112d} enthalpies of formation span a large range of values: 900–1156 kJ/mol (215–276 kcal/mol), so preventing their use in unambiguous predictions of properties. This empirical approach does not take into account electronic configurations of elements and metals and their possible change caused by strong relativistic effects.

To eliminate the discrepancies between different models, a systematic approach was attempted in refs 63a–d. A new semiempirical model was proposed to estimate sublimation enthalpies for all the transition elements. The model appeared as a generalization of different electronic correlations^{113–115} used to estimate various properties of metals such as cohesive energy, $E_c(\Delta H_s)$, type of crystal lattice, phase transitions, etc.

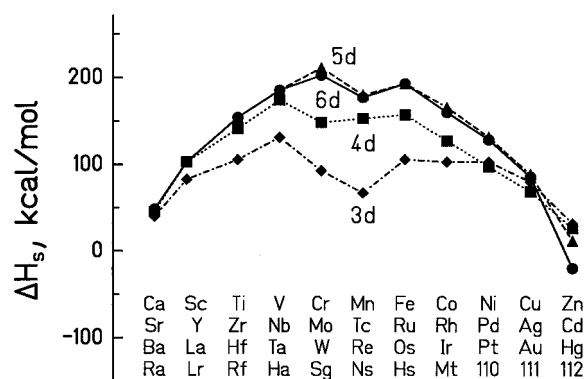
The following equation has been proposed to calculate the cohesive energy of a metal⁶³

$$E_c = C_{nd}(Z/\gamma) \quad (2)$$

where C_{nd} is an empirically determined coefficient, Z is the atomic number, and γ is equal to the following

$$\gamma = \frac{\sum_L (2L + 1)_M}{\sum_L (2L + 1)_M + (2L + 1)_A} \quad (3)$$

where “M” and “A” denotes “metal” and “atom”, and $(2L + 1)$ is the degree of degeneracy of each L state. A character of the dependence of ΔH_s on Z along a transition element series is defined by $1/\gamma$. Any change in the electronic configuration of the free atom, or participation of the p orbital in the formation

**Figure 7.** Calculated in ref 63 sublimation enthalpies of the transition-element metals.

of the metallic state, will influence the character of the dependence of ΔH_s on Z .

In eq 2 the choice of C_{nd} is very important. C_{nd} was shown to decrease exponentially from the third to the sixth period

$$C_{nd} = ba^x + y \quad (4)$$

where $x = k\Delta Z$, and ΔZ is the difference in the number of valence electrons between an element of the nd series and a corresponding element of the 3d series; $k = 0.1$ is an empirical coefficient, and a , b , and y are parameters, determined from the known ΔH_s for each group of elements.¹¹⁶

The ΔH_s , calculated via eq 2, for all the d elements are shown in Figure 7. An exponential form of eq 4 results in ΔH_s for the transactinides being within those values for the 5d elements. One can see that there is no simple increase in ΔH_s in going down a group, and in some groups the trend is reversed. (Thus, e.g., a decrease in ΔH_s in group 12 results in element 112 being a gas, as it was supposed earlier^{37,104}). Obviously, simplified extrapolations of ΔH_s within the groups would result in large errors.

A good agreement between the calculated and experimental values for the lighter d elements gives a hope for the reliability of the proposed method. On the basis of this model, approximate electronic configurations of the transactinide atoms in metals have been predicted. For Rf through Sg they are given in Table 5. Two values of $\Delta H_s(\text{Sg})$ correspond to the two proposed electronic configurations in the metallic state: d^5s and $d^5p + d^4sp$. In the same work^{63d} $\ln p(T)$ (where p is the equilibrium vapor pressure over a substance) for Rf was calculated.

In ref 56, thermodynamic functions, the entropy, free energy and enthalpy, for Ha in the electronic configurations d^3s^2 , d^3sp , and d^4s and +5 ionized state have been calculated as a function of temperature. These values have been obtained on the basis of results of the MCDF calculations⁴² of fine-structure components of the corresponding electronic states of Ha. The data can be used to estimate the volatility of the element as a function of temperature.

IV. Relativistic Quantum Chemical Methods for Molecules

Application of modern relativistic codes to individual transactinide-containing compounds and their

homologs within the lighter elements enables one to study molecular properties such as IPs, electron affinities (EA), crystal-field and spin-orbit effects, electronic density distribution, and bonding. Only by knowing these properties and trends in their changes can one judge about the analogy of the transactinides with the lighter elements.

Usually molecular calculations are divided into two main groups: those where accurate calculations are performed for very small molecules, and those, where approximate calculations are done for chemically interesting, more sophisticated systems.

Methods which can be used for calculating the electronic structure of the transactinide-containing compounds are the same relativistic methods, which can be applied with sufficient accuracy to calculations of other heavy systems. The methods and their application to transition element molecular systems have been overviewed in the literature.^{66a,92,95-99,117} Application of modern codes to actinide-containing compounds is demonstrated in ref 118. In the following section, we will briefly describe presently available relativistic molecular programs arranged roughly in order of increasing sophistication of the method. Additional attention will be paid to the all-electron *ab initio* methods: within a very short time the DF theory and methodology have received much development (see ref 119) and these methods are beginning to be applied to heavy molecular systems.

A. Dirac-Fock One-Center Expansion (DF-OCE)

This is a fully relativistic, self-consistent method with the full (nonlocal) exchange. It is developed¹²⁰ as an extension of the numerical atomic DF codes for hydride molecules, MH_n . Since all the AOs share a common origin, integrals are easily calculated in spherical polar coordinates by numerical methods. The review of the method is given by Desclaux.¹²¹

The method is known to give reasonable bond lengths and force constants, and it was applied to studies of relativistic effects on molecular geometries and bond energies.^{122,123} The electronic structures of group 4 and 6 hexahydrides, including RfH_4 and SgH_6 ,^{47,48} have been calculated by using this method.

B. Local Density Functional Methods (LDF)

In this group of methods the Slater's local exchange approximation is used leading to the replacement of the Hartree-Fock nonlocal exchange potential with the local exchange. The LDF equations are then solved either by multiple-scattering X_α methods, or by various basis-set expansion methods based on the discrete variational approach.

1. Quasirelativistic Hartree-Fock-Slater (QR-HFS)

The method¹²⁴ is an extension of the perturbative Hartree-Fock-Slater (P-HFS) one,¹²⁵ which was based on the nonrelativistic discrete variational method of Ellis.¹²⁶ The method uses analytical basis functions. Relativistic effects of higher orders are taken into account by perturbation operators. In this way, the relativistic changes to the valence charge density are included. The method gives potential energy curves and was extensively applied to the

analysis of bonding and relativistic contributions.^{127,128} No calculations of the transactinide molecules have been reported.

2. Quasirelativistic Multiple Scattering (QR-MS)

In this method the four-component Dirac equation is replaced by an approximate one-component equation. In the Pauli approximate Hamiltonian the mass-velocity and Darwin terms are included. In some versions of the method¹²⁹⁻¹³¹ QR-MS calculations give one-electron non-spin-orbit split MOs; in other versions,¹³² the spin-orbit interaction is put on top of the self-consistent solutions by using the first- and second-order relativistic perturbation operator. The radial functions are solved numerically in atomic spheres and plane waves are used between the spheres.

The method is used for predicting optical and photoelectron spectra. It gives reasonable orbital energies and descriptions of bonding. Inaccuracies are arising from the "muffin-tin" approximation, but the computational costs are relatively low. The first calculations⁵¹ of the electronic structure of the Rf tetrachloride have been performed using this method.

3. Dirac-Slater Multiple Scattering (DS-MS)

The method is similar to the previous one, but it includes the spin-orbit coupling explicitly: the full Dirac-Slater equations are solved giving four-component MOs. The method gives reliable photoelectron energies, description of bonding, spin-orbit splittings, hyperfine tensors. Slightly different versions of the method are described by Case and Yang^{133,134} and Soldatov.¹³⁵ The method is reviewed in ref 136. Calculations of the electronic structure of the Rf tetrachloride along with its lighter analogs have been published.⁴⁹

4. Dirac-Slater Discrete Variational (DS-DV)

Developed by Rosen and Ellis,¹³⁷ this is a fully relativistic, self-consistent field method based on the numerical solution of the Dirac-Fock equations, without approximations except for local exchange (leading to the Dirac-Slater equations). Thus, all the relativistic effects, including spin-orbit coupling, are explicitly calculated. A review of the method is given in ref 138.

The method uses four-component basis functions Φ_j which are symmetry orbitals determined via a LCAO (linear combination of atomic orbitals) expansion. The molecular integrals between these functions are calculated in a numerical, three-dimensional grid. The Hamiltonian matrix elements are given by

$$h_{i,j} = \sum w_k \Phi_i^*(r_k) h_D \Phi_j(r_k) \quad (5)$$

w_k being the weight factor for grid point r_k and h_D is the Dirac Hamiltonian

$$h_D = \alpha\pi + (\beta - 1)c^2 + V \quad (6)$$

The potential is the sum of three parts

$$V = V_n + V_c + V_x \quad (7)$$

with V_n the nuclear, V_c the Coulomb, and $V_x = -3\alpha(3\rho/8\pi)^{1/3}$ the exchange potentials. Most of the correlation effects are included in the exchange-correlation term.

The diagonalization

$$(h - \epsilon_r S)c_i = 0 \quad (8)$$

gives the molecular orbitals (MO)

$$\Psi_i = \sum c_j \Phi_j \quad (9)$$

The symmetry molecular orbitals for double point groups are constructed using the projection operator method¹³⁹ implemented into the program.¹⁴⁰

The method provides reliable MOs and orbital energies. By using the Slater transition-state procedure the ionization potentials and optical spectra can be calculated quite well. The Mulliken population analysis¹⁴¹ gives the possibility to interpret the bonding in terms of ionic and covalent contributions (overlap population, OP). The program also includes a least-squares fitting procedure¹²⁸ for the charge distribution. The calculated orbital or total energies have a numerical accuracy of about ± 0.1 eV.

Later improvements of the integration schemes and introduction of the elliptic-hyperbolic coordinates enabled one to calculate accurate total energies for diatomic molecules.¹⁴³ Further improvement^{144a} was achieved by minimization of the error in the total energy. In this case another (a weighted) fitting procedure for the potential was used to create a variationally consistent total energy functional. Calculations^{144b} of the relativistic systems by using this version have shown good agreement with experiment. For Au_2 , e.g., equilibrium distances and dissociation energies are $R_e = 4.75$ Å and $D_e = 3.16$ eV which can be compared with the experimental values $R_e = 4.67$ Å and $D_e = 2.30$ eV. Calculations of Tl_2 , Pb_2 , and Bi_2 have been reported.¹⁴⁵

Further improvement, the inclusion of the integration scheme of Boerringer et al.,¹⁴⁶ enabled one to calculate potential energy curves for three-dimensional molecules.¹⁴⁷ The calculated binding energy for Hg_3^+ is $D_e = 2.87$ eV, which is in a good agreement with the experimental value of 2.4 eV. To achieve better agreement with experimental data, work is being carried out to improve the exchange-correlation functional and replace it by the nonrelativistic and relativistic functionals of Becke¹⁴⁸ and Engel.¹⁴⁹

The DS-DV method has been successfully applied to many transition element molecules and recently to the calculations of a large series of the transactinide-containing molecules.^{45,46,51-62,68}

C. Relativistic Core Potential Methods (RCP)

An efficient way to solve the many-electron problem by using *ab initio* methods is to apply the effective core potential (ECP) approach. According to this approximation, frozen inner shells are omitted and in the Hamiltonian an additional potential energy term replaces the core electrons. As a result, the number of basis functions is drastically diminished, and, hence the number of two-electron integrals. Then the one-electron integrals are solved for

the valence basis functions and this additional term by applying *ab initio* schemes at the SCF level or with electron correlation included. The ECP are generated by using the results of the all-electron atomic calculations and fitting them to a linear combination of Gaussian functions. The development of these methods and their application to a variety of relativistic systems have been overviewed in refs 98 and 150.

Since the variational principle holds for *ab initio* methods, accurate total energies can be obtained. The potential curves are reliable, enabling predictions of molecular geometries and bond strengths. In contrast to the LDF methods, explicit treatment of spin enables calculations of the excited-state spectra. Nevertheless, application of sophisticated correlation schemes often comes at the expense of an ease of interpretation of the wave function.

1. Quasirelativistic Pseudopotentials (QRP)

In this approximation, atomic calculations, which are used for generating ECP, are two-component wave functions. The Hamiltonian includes the Darwin and mass-velocity terms, but omits spin-orbit effects. In the Hay-Kahn-Cowan version¹⁵¹ the spin-orbit effects are included via the perturbation theory after the wave functions have been obtained. The limitation of the method is the absence of the spin-orbit *ab initio* operator. The method has been applied to many transition-metal systems,¹⁵² as well as to the actinides,¹⁵³ and it is implemented into the commercial system "Gaussian 92". For molecules as heavy as HgCl_2 , the calculated¹⁵² R_e and D_e are 2.301 Å and 2.52 eV, respectively, which can be compared with experimental values of 2.29 Å and 4.51 eV.^{154a}

Another version of the QRP is the quasirelativistic energy-adjusted pseudopotential which uses energy-optimized valence basis sets.¹⁵⁵ In contrast to the Hay-Kahn-Cowan method, based on one-particle properties, this method uses quantum mechanical observables for generating ECP. These potentials have been developed for almost all the elements of the periodic table. In a new version of the method,⁶⁵ two-component (without averaging over spin-orbit effects) quasirelativistic DF pseudopotentials are generated. The method of adjustment for the two-component pseudopotentials is based on general multiconfiguration wave functions, i.e., linear combinations of many-electron wave functions with appropriate total angular momentum J and parity belonging to a single relativistic configuration. The method of energy adjustment allows a generation of pseudopotentials in the intermediate coupling scheme, since linear combinations of the wave functions are used for nearly all nonrelativistic reference configurations. This method was applied to the calculations⁶⁵ of the group 5 oxides MO , where $\text{M} = \text{Nb}, \text{Ta},$ and Ha . The CASSCF + ACPF (complete active space and averaged coupled-pair functional calculations) results corrected for the spin-orbit interaction by spin-orbit splitting give the following equilibrium distances and dissociation energies for NbO : $R_e = 1.675$ Å and $D_e = 6.91$ eV (the experimental values are $R_e = 1.691$ Å and $D_e = 7.8$ eV); and for TaO , $R_e = 1.691$ Å and $D_e = 7.45$ eV (the experimental values are $R_e = 1.688$ Å and $D_e = 8.2$ eV).

Table 6. Comparison of Different Methods Taking into Account Correlation Effects for the Spectroscopic States of AuH

method	R_e , Å		D_e , eV		ref
	sd	sspd	od	ospd ^e	
DK ^a + MP2	1.505	1.498	2.942	3.042	159
DHF ^b + MP2	1.503	1.497	2.996	3.114	159
RECP ^c + MP2	1.519	1.512	2.965	3.075	159
DK + CCSD	1.525		2.93		189
exp	1.524		3.36		212

^a Douglas–Kroll method of Hess, ref 190. ^b DHF method of Dyall, ref 178. ^c RECP of Christiansen, Ermler, and Ross, ref 160. ^e The effects of correlation are examined for both the valence (σ) and the outer core (ospd) electrons.

Relativistic PP calculations with (SOPP) and without spin–orbit coupling including correlation at the CCSD level for 111H and 112H⁺, and at the MP2 level for 112H⁺, 112F₂, and 112F₄ have been reported recently^{67a,b} and those of 111Li are in progress.

2. Relativistic Core Potentials

The method is described in detail by Pitzer.^{156a} The RCPs are generated from all-electron numerical Dirac–Fock atomic calculations. Spin–orbit effects are included in this way from the beginning and full four-component atomic wave functions are obtained.^{156b} The nonempirical spin–orbit operators were introduced and with some simplifications implemented in the program.^{157,158} In this way, the calculation of CI became feasible. Thus, correlation effects can be included through MCSCF (multiconfiguration SCF) or CI calculations. Since the spin states are treated explicitly, the excited states and electronic spectra can be calculated. The calculations, however, are associated with high computational costs.

RCP results for AuH¹⁵⁹ including electron correlation at the second-order Møller–Plesset (MP2) perturbation theory level along with those obtained by all-electron relativistic *ab initio* methods are shown in Table 6.

The RCPs are presently developed for all the lanthanides and actinides,¹⁶⁰ and calculations of some actinide systems like U_2 , $U(\text{cot})_2$, actinocenes, or actinofullerenes have been published.^{161a–c} A set of RECPs has been developed for elements Am through 112.¹⁶² No calculations of the transactinide systems have been reported until now.

D. All-Electron *ab Initio* Methods

Although ECP methods are useful in calculating such properties as binding energies and optimal geometries, the consequence of using a frozen core or ECP in relativistic molecular calculations have not been fully investigated.^{66a}

During recent years the DHF theory and methodology have been considerably developed. The formulation of the principle of kinetic balance and its extension¹⁶³ have given a strong foundation to the employment of the finite basis sets in the DHF calculations.

The calculations are based on solution of the Dirac–Fock–Coulomb (DFC) or Dirac–Fock–Breit (DFB) Hamiltonians. The former is expressed in the following way

$$H_{\text{DC}} = \sum_{i=1}^N H_{\text{D}}(i) + \sum_{i>j} 1/r_{ij} \quad (10)$$

where $H_{\text{D}}(i)$ is the Dirac's kinetic energy operator and $1/r_{ij}$ is the instantaneous Coulomb repulsion. The inclusion of the Breit interaction (B_{ij}), which is a magnetostatic term, leads to the Dirac–Coulomb–Breit Hamiltonian:

$$H_{\text{DCB}} = H_{\text{DC}} + \sum_{i<j} B_{ij} \quad (11)$$

Here

$$B_{ij} = -1/2[(\alpha_i \alpha_j)/r_{ij} + (\alpha_i r_{ij})(\alpha_j r_{ij})/r_{ij}^3] \quad (12)$$

Among the existing programs the following should be mentioned: an earlier Slater-based code for linear molecules of Lee and McLean,^{164–167} the Gaussian codes for linear molecules of Laaksonen et al.,¹⁶⁸ for polyatomic molecules of Aerts and Nieuwpoort,^{169–180} the more recent linear code of Matsuoka¹⁸¹ and polyatomic codes of Dyall,^{182–185} and of Saue,¹⁸⁶ as well as the numerical code of Pyper and Malli.^{187,188}

Correlation methods based on four-component spinors began to be available only recently.^{175–177,159} Correlation effects, which are as important as relativistic ones for heavy systems, are taken there into account by using the CI or many-body perturbation theory (MBPT) capabilities. Very recently the RCC method⁷⁸ (the CCSD version⁸³) was applied to the four-component methods.¹⁷⁸ Earlier, the CCSD method^{82–86} was combined with the one-component relativistic method of Hess¹⁹⁰ (see ref 189).

The amount of calculations performed by using the DHF all electron four-component methods is still small. The computational efforts applied there are tremendous and much higher than for similar quality nonrelativistic systems. The computational costs are extremely high.

1. *Ab Initio* Relativistic Dirac–Fock SCF Calculations for Diatomics

The DF-SCF *ab initio* approach for diatomics has been developed by Malli and Pyper.^{187a} Details of the method are given elsewhere.^{187b–e} The basic idea of the method is to express the wave function for the diatomic molecule in terms of the Dirac–Fock numerical atomic functions supplemented with Slater functions. The frozen core approximation is used. All electron calculations are also possible, although even for the 48-electron system, CdH⁺, they are prohibitively expensive at present, even using supercomputers. In contrast to the ECP and relativistic pseudopotentials schemes, this method explicitly incorporates the core orbitals and takes into account core–valence exchange. Electron correlation effects are neglected.

The method, originally developed for the closed-shell molecules, has been extended to a general class of open-shell molecular systems¹⁸⁸.

Calculations^{66a} using this method give predictions of bond length in good agreement with experiment, though the dissociation energies are about 30–50% of the experimental values. (For example, predicted

Table 7. Spectroscopic Parameters for the Ground States of PtH and PtH₂

mole- cule	R_e , Å			D_e , eV		
	MOLFDIR	DHF ^c	exp ^d	MOLFDIR	DHF ^c	exp ^e
PtH	1.518 ^a	1.551	1.528	2.98 ^a	2.03	3.6 ± 0.4
PtH ₂	1.508 ^b	1.525	—	2.69 ^b	1.52	—

^a Multireference CI, ref 177. ^b Kramers-restricted CCSD (KRCCSD), ref 178. ^c No correlation, ref 184. ^d Reference 191. ^e Reference 192.

bond length and dissociation energy for TlI are 5.604 au and 1.723 eV, which can be compared with experimental values of 5.3171 au and 2.76 eV, respectively). The discrepancy is ascribed to the electron correlation effects. Calculations of the superheavy diatomic 117Cl have been reported recently.^{66a}

2. Dirac-Fock SCF Methods for Polyatomics

Recently calculations of 111H have been performed^{67a} by using the four-component SCF-DF method (for polyatomics) of Saue.¹⁸⁶ The developed DIRAC program is set up to do both conventional and direct SCF calculations in a finite (Gaussian) basis on the basis of the Dirac-Coulomb-Hamiltonian. Time reversal symmetry is exploited which results in a compact formalism in terms of quaternion algebra. The nuclear charge distribution is modeled by a Gaussian function. The program presently treats closed shells, but it will be extended to one open shell shortly. An extension for treating correlation effects at the MP2 perturbation level exists in the program. Calculations of 111H have been performed without electron correlation (results will be discussed in section V). Calculations of 117H are in progress.^{186c}

Another group of molecular DHF calculations with Gaussian basis sets is represented by works of Dyall et al.^{159,182-185} In contrast to the DIRAC program,¹⁸⁶ where expansion of the wave function is done in a scalar one-component basis, a two-spinor basis expansion is used. SCF-DHF calculations of as heavy systems as PbO₂ and PbH₄¹⁸² have been published. The original single-reference four-component DHF program has been extended to perform Kramers-restricted open-shell calculations for doublet states, where the unpaired electron can be a single electron outside or a hole inside a closed-shell core, and for states of linear molecules with two electrons in open shells. Some results for PtH and PtH₂¹⁸⁴ are shown in Table 7. Very recently a correlation part has been added to the program at the MP2 perturbation level.¹⁵⁹ In ref 159, a consistent comparison of different methods including electron correlation has been made on the example of AuH. The best results are shown in Table 6 along with those from the RECP¹⁵⁹⁻¹⁶⁰ and Douglas-Kroll (DK)¹⁹⁰ ones, although the RECP results are strongly dependent on the chosen basis sets.

A DF four-component method for polyatomics, which presently incorporates correlation effects, is that of Nieuwpoort et al.¹⁷⁵⁻¹⁷⁹ Developed within the last few years a program MOLFDIR¹⁷⁹ is an implementation of the Dirac-Fock-Roothaan method for polyatomic molecules. It uses Gaussian functions for

the expansion of the components of the molecular spinors. Originally the program was developed for closed shells.¹⁷⁰ Then an open-shell CI version appeared¹⁷⁵ where the open shells were handled by defining a suitable averaged Dirac-Fock operator. Later, a multireference CI extension was added.¹⁷¹ The method in its different versions has been applied to the following systems: PbH₄¹⁷⁴ and UF₆ (closed shell Dirac-Fock-Gaunt)¹⁸⁰, EuO₆⁹⁻¹⁷⁵ and UF₆⁻ (open-shell Dirac-Fock),¹⁸⁰ IrF₆²⁻ (charge transfer CI),¹⁷⁶ PtH (multireference CI).¹⁷⁷

Recently¹⁷⁸ a Kramers-restricted version of the closed-shell coupled cluster for single and double approximations (CCSD) has been presented, which was combined with the MOLFDIR program. The method has been applied to PtH₂ molecule. Some results on PtH and PtH₂ are shown in Table 7 in comparison with those of Dyall.¹⁸⁴ (The binding energy for PtH₂ is enhanced by 27 kcal/mol by correlation in comparison with the DHF results of Dyall.¹⁸⁴) The calculated bond lengths for PtH agree within 0.02 Å with the experimental data. The excitation energies differ from measured values by less than 0.03 eV.

Typical resources necessary for this kind of calculations are 3-5 Gbytes of disk storage and 20-40 h of CPU time on a CRAY computer.

One of the heavy systems calculated by using the MOLFDIR program (closed-shell version) was UF₆.¹⁸⁰ The calculated $R_e = 1.994$ Å can be compared with the experimental value $R_e = 1.999 \pm 0.003$ Å,^{193a} and the calculated $D_e = 22.7$ eV is about 70% of the experimental value of 31.9 eV.^{193b}

DF SCF and DFB calculations have also been reported by Malli et al.^{66b-e} for a number of molecular systems containing actinides: ThF₄^{66d} and UF₆.^{66e} They used their recently developed highly accurate universal gaussian basis set for DF and DFB calculations with the MOLFDIR package (uncorrelated version). The dissociation energies for ThF₄ obtained as a result of the calculations are 19.34 (DF) and 19.30 (DFB) eV, which are about 70% of the experimental value of 27.7 eV.^{66f} For UF₆, the DF and DFB dissociation energies^{66e} are 23.53 and 23.27 eV, respectively, which are about 73% of the experimental value of 31.9 eV.^{193b} The discrepancy with the experimental result of the DF calculations^{180,66d,e} is assigned to the lack of correlation.

At present, these DF-SCF calculations^{66b} are performed for the group 4, 5, and 6 highest halides, including Rf, Ha, and Sg. Some preliminary results have already been obtained for MF₄, MCl₄ (M = Zr, Hf, and Rf), MF₆, MCl₆ (M = Mo, W, and Sg), 110F₆, and 110Cl₆. They will be discussed in section VI. Calculations of the bromides of these elements are in progress.

An inexpensive, reliable alternative to the DHF method (if spin-orbit effects are small) was demonstrated to be the second-order DK method, developed by Hess.¹⁹⁰ According to the Douglas-Kroll transformation¹⁹⁴ the large and small components are decoupled to second order in the external potential and the spin-orbit terms are neglected in the resulting Hamiltonian. Using one-component wave functions decreases drastically the computational efforts.

Table 8. Equilibrium Distances R_e and Dissociation Energies D_e (in au) for MH_4 and MH_6 (from Refs 47 and 48)

molecule	R_e		D_e		molecule	R_e		D_e	
	nr	rel	nr	rel		nr	rel	nr	rel
TiH ₄	3.244	3.246	0.788	0.783	CrH ₆	3.192	3.181	0.572	0.581
ZrH ₄	3.608	3.615	1.006	0.984	MoH ₆	3.526	3.496	0.777	0.822
HfH ₄	3.626	3.605	0.977	0.999	WH ₆	3.595	3.492	0.796	0.920
RfH ₄	—	3.670	—	0.632	SgH ₆	—	3.607	—	0.980

The spin-averaged quantities can be used to a good approximation, e.g., for compounds with nondegenerate singlet ground states. In ref 189 the one-component DK method¹⁹⁰ has been combined with the Fock-space coupled-cluster method⁸³ and applied to the calculations of AuH. The results shown in Table 6 are in good agreement with experiment: the error in the bond length is only 0.001 Å.

Recently the DK method has been used for calculations of the electronic structure of 111H.⁶⁷ This simple molecule, to which relativistic *ab initio* codes can be applied without difficulties, was chosen as an object to study relativistic and correlation effects in the very heavy element area. Results of calculations for 111H performed by different methods (see next section) are presented in ref 67a, with those of the four-component all-electron *ab initio* ones with electron correlation at the CCSD level still missing.

V. Transactinide Hydrides

Transactinide hydrides are the simplest molecular systems which were used as models to study the influence of relativistic and correlation effects on bonding and molecular structure.

Calculations of group 4 and 6 hydrides, including RfH₄ and SgH₆, have been performed using the DF-OCE method.^{47,48} Equilibrium bond lengths (R_e) and dissociation energies (D_e) for these molecules as a result of relativistic and nonrelativistic calculations are given in Table 8. The results were shown to be dependent on the basis set selected for the valence orbitals. If the $(n-1)d$ valence orbitals are chosen as the valence ones for the $ns^2(n-1)d^m$ electronic configurations of the elements, the relativistic R_e are larger than the nonrelativistic ones, and the relativistic D_e are smaller. Adding the $(n-1)p$ valence orbitals to the basis set results in the opposite effect: the relativistic R_e become shorter than the nonrelativistic ones, and the relativistic D_e become larger than the nonrelativistic ones. Initially, this was explained by the fact, that the relativistic contraction of the p orbitals compensates the relativistic expansion of the d orbitals. Later, this statement was corrected,⁹⁹ and it was shown that the relativistic contraction of orbitals and the relativistic contraction of bond lengths are two parallel but largely independent effects. (The force behind the bond contraction was found¹²⁸ to be the diagonal core-core contribution in the valence MO.)

The data from Table 8 show that for nearly all the compounds (except TiH₄ and ZrH₄) relativistic effects decrease the bond lengths. The bond contraction expressed as $C = [R_e(nr) - R_e(rel)]/R_e(nr)$ was found to be -0.05, -0.19, and 0.58% for TiH₄, ZrH₄, and HfH₄, respectively.⁴⁷ For CrH₆, MoH₆, and WH₆ these values are 0.35, 0.81, and 2.81%, respectively.⁴⁸

Such estimates, unfortunately, have not been made for RfH₄ and SgH₆, since nonrelativistic R_e and D_e have not been calculated. One can get an idea about bond contraction in the transactinide compounds by using the equation $C(\%) = c_z Z^2$, where c_z is dependent on the group.¹²² However, the bond contraction obtained in the calculations^{47,48} is smaller than the one obtained by using this formula.

Thus, relativistic effects are responsible for the bond lengths of the 4d and 5d compounds being nearly equal. For RfH₄ the predicted bond length (or covalent radius) is 0.03 Å larger than that for HfH₄, and for SgH₆ is 0.06 Å larger than that for WH₆. Such a small increase in the covalent radii of the 6d elements relative to those of the 5d elements is explained, in addition to the relativistic bond contraction, by a large actinide contraction of 0.30 Å, which is mainly a relativistic effect.

Relativistic effects increase dissociation energies of the compounds under study. An increase in relativistic D_e of the 5d relative to the 4d compounds was explained by a larger contraction of the relativistic 6s and 6p_{1/2} orbitals and a larger participation of the more expanded 5d orbitals in bonding. The analysis of the contribution of valence orbitals in bonding in the transactinides has not been given. A decrease from 0.999 to 0.639 au and from 0.405 to 0.395, for D_e and the force constant k_2 , respectively, was found when going from HfCl₄ to RfH₄, while in going from WH₆ to SgH₆, k_2 remains essentially constant and D_e increases from 0.92 to 0.98 au. This trend was supposed to be caused by relativistic effects.^{47,48}

In ref 67a relativistic and correlation effects have been studied for 111H by using various relativistic methods. The following calculations have been carried out: nonrelativistic (NR) all-electron and pseudopotential (PP) HF; NR-CCSD; relativistic pseudopotential with (SOPP) and without (ARPP) spin-orbit coupling including electron correlation at the CCSD level; perturbative all-electron calculations using the mass-velocity and Darwin term of the Pauli Hamiltonian (MVD); relativistic all-electron Douglas-Kroll (DK) including electron correlation at the CCSD, multireference CI (MRCI) and average coupled pair functional level (ACPF); and all-electron DF (without correlation). Except for the MVD approximation, all the methods yielded similar molecular properties at both the uncorrelated and correlated levels, although correlation increases the dissociation energy by about 1.5 eV. The accuracy of the coupled cluster level (SOPP + CCSD) was considered to be sufficient to discuss trends in molecular properties.

Relativistic effects were shown to be very large for 111H, resulting in large changes in molecular properties. They diminish the metal-hydrogen bond distance significantly for AuH and even more for 111H, so that the calculated bond distance of 111H

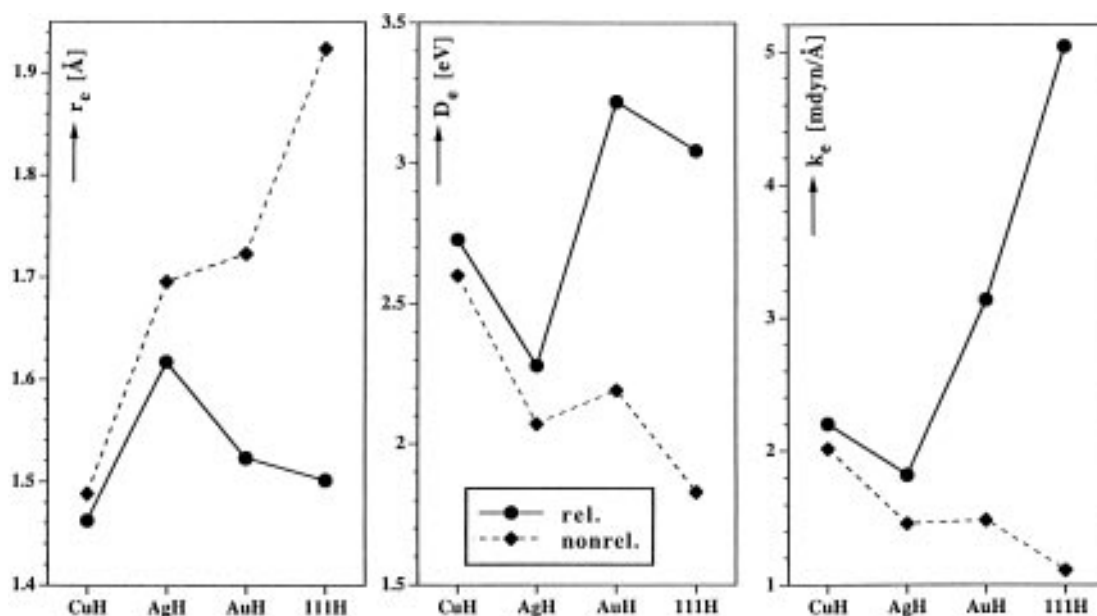


Figure 8. Nonrelativistic and relativistic molecular properties for the group 11 series of hydrides. The data for CuH, AgH, and AuH are from refs 212, 159, 189, 194e. (Reprinted from Seth, M.; Schwerdtfeger, P.; Dolg, M.; Faegri, K.; Hess, B. A.; Kaldor, U. Large Relativistic Effects in Molecular Properties of the Hydride of Superheavy Element 111 *Chem. Phys. Lett.* **1996**, *250*, 461–465. Copyright 1996, with kind permission of Elsevier Science-NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

is less than those of both AgH and AuH (Figure 8). Electron correlation effects were found to be small for the 111–H bond. Nonadditivity of relativity and correlation has been demonstrated.

An interesting result is that relativistic effects do not increase dramatically dissociation energies in going from AuH ($\Delta D_e = 1.0$ eV) to 111H ($\Delta D_e = 1.2$ eV) (Figure 8). This was attributed to the spin–orbit coupling of the ground state, $^2D_{5/2}$ (and not $^2S_{1/2}$), split by 2.7 eV and resulting in a spin–orbit destabilization of 111H. (The SOPP + CCSD results relative to the ARPP + CCSD ones show that D_e decreases from 3.79 to 3.05 eV due to the spin–orbit coupling).

Relativistic effects increase the force constant in 111H and change the dipole moment by 4 Debye. It is remarkable that relativistic effects change effective charges from $111^{+0.33}H^{-0.33}$ to $111^{-0.07}H^{+0.07}$. The orbital populations are increased by one electron for the 7s orbital and decreased by 0.6 electron for the 6d orbital. This was a reason to conclude there was an enhanced participation of the 6d orbitals in the chemical bonding, and therefore a more “typical” d-block behavior of 111 in contrast to Cu, Ag, or Au. Similar relativistic effects on D_e and R_e were observed^{67b} for $112H^+$ relative to CdH^+ and HgH^+ .

VI. Transactinide Halides

Rf, Ha, and Sg were found^{6–9,11,13} to form the highest chlorides and bromides of the form MX_4 , MX_5 , and MX_6 by analogy with group 4 and 5 lighter elements. These are rather stable, volatile compounds, which are monomers in the gas phase. For the lighter analogs, the stability of the maximum oxidation state is known to decrease in going from fluorides, to chlorides, and further to bromides and to iodides. The stability of the compounds in a particular oxidation state decreases in going from group 4 to group 6.

Due to high temperatures applied in the gas-phase chromatography experiments, a question about the stability of the highest chlorides and bromides of the transactinides is of primary importance. In this case a comparative study proves to be very useful since the properties of the lighter compounds have been well investigated.

A. Fluorides

Some preliminary calculations have been reported on RfF_4 by using the all-electron *ab initio* DF method.^{66b} The calculations with a basis set constructed for the $7s^26d^2$ ground state configuration of Rf have given $D_e = 29.06$ eV, $R_e = 1.95$ Å, and $Q_M = 1.96$. A stabilization effect of 1.08 eV was found for the binding energy in case of the basis set constructed for the $7s^26d7p$ configuration. Thus, the corresponding data are 30.14 eV, 1.96 Å, and 1.96.

The electronic structure of the highest fluorides of group 6 elements including Sg, MoF_6 , WF_6 , and SgF_6 , has been calculated by Rosen et al.⁴⁶ using the DS-DV method.

Results of the calculations have shown the relative ordering of the highest occupied (HOMO) and lowest unoccupied MOs (LUMO) in SgF_6 to be similar to those for the lighter analogs, although there is a reordering of the valence levels in SgF_6 , so that a γ_8^- level becomes the last occupied, whereas in all lighter systems this is a γ_8^+ level. The spin–orbit splitting of the t_{2g} (first vacant, of d character) level increases from 0.5 to 1.2 eV in going from WF_6 to SgF_6 and becomes of the same order of magnitude as the crystal–field splitting.

First ionization energies have been calculated by performing the transition-state procedure and are equal to 14.4, 14.5, and 14.4 eV for MoF_6 , WF_6 , and SgF_6 , respectively. Correcting these values with respect to the experimental ones for the fluorides of

Mo and W (15.1 and 15.5 eV, respectively) gives the first IP for SgF_6 of 15.4 eV.

Ab initio all-electron calculations^{66b} for WF_6 and SgF_6 have given 19.51 and 18.20 eV, respectively, for the dissociation energies, and 1.82 and 1.92 Å, respectively, for the equilibrium bond distances.

DS-DVM calculations have been performed for 110F_6 .^{45a} (This molecule was supposed to be used in the process of extraction of superheavy elements from a target which was bombarded by a heavy ion beam.) Earlier, nonrelativistic calculations^{45b} (within the muffin-tin approximation) for 110F_6 were published. The relativistic results show the lowering of levels with a large contribution of the s orbitals and a large spin-orbit splitting of the d levels. The crystal-field splitting of the d levels is however smaller in the relativistic case than in the nonrelativistic one due to the stabilization of the e_g level. The stabilization of the lowest level of d character results in a slight decrease in the energy gap between bonding and antibonding levels. Relativistic effects stabilize the bonding levels of the $2p(\text{F})$ character.

The calculated (via the transition-state procedure) ionization energy for 110F_6 of 13 eV turned out to be very close to the theoretical ionization energy for PtF_6 . Thus, a similarity in properties between 110F_6 and PtF_6 was proposed. Some optical transitions and trends relative to PtF_6 were predicted for 110F_6 . These predictions are important for detecting this compound with the use of lasers in resonance ionization spectroscopy or resonance fluorescence. *Ab initio* DF calculations were performed for 110F_6 .^{66b}

In ref 67b the SOPP calculations were performed for 112F_2 and 112F_4 with the correlation at the MP2 level. 112F_4 was shown to be stable due to relativistic effects.

B. Chlorides and Bromides

1. Group 4 Chlorides

Calculations of the electronic structure of MCl_4 , where $\text{M} = \text{Ti}, \text{Zr}, \text{Hf},$ and Rf , have been performed in a few studies using the QR-MS,⁵¹ DS-MS,⁴⁹ the DS-DV^{50,61} and the all-electron *ab initio* DF^{66b} methods. All the results agree that the electronic structure of RfCl_4 is similar to that of HfCl_4 (and not to that of PbCl_4) and that the bonding is typical of the transition d-element compounds. There are some unessential discrepancies in values of effective charges and overlap populations (Table 9).

From Table 9 one can see that the results of the calculations from refs 50 and 61 agree, although in the former case the interatomic distance $R_{\text{Rf-Cl}}$ is too large. Both results show the same trend in the values of the effective charges within the group: a decrease in the ionicity but with the minimum at Hf. According to the calculations in ref 49 all MCl_4 are more ionic and the effective charge on Rf is the lowest in the series.

The DF calculations^{66b} show a steady decrease in the values of the effective charges (see Table 9), which are larger than those obtained in the DS-DV calculations.

The DS-DV results of ref 50 show no increase in the OP(metal-ligand) of RfCl_4 compared to HfCl_4 due

Table 9. Effective Charges on the Metal Atom (Q_M) and Overlap Populations (OP) in MCl_4 , where $\text{M} = \text{Zr}, \text{Hf},$ and Rf , Obtained as a Result of Different Calculations

molecule	Q_M				OP	
	DS-MS ^a	DS-DV ^b	DS-DV ^c	DF ^d	DS-DV ^b	DS-DV ^c
ZrCl_4	2.36	1.03	1.18	1.90	0.63	0.48
HfCl_4	2.34	0.91	1.04	1.44	0.69	0.55
RfCl_4	2.30	0.96	1.07	1.40	0.69	0.57

^a Reference 49; calculations for $R_{\text{Zr-Cl}} = 2.32$ Å, $R_{\text{Hf-Cl}} = 2.33$ Å, and $R_{\text{Rf-Cl}} = 2.39$ Å. ^b Reference 50; calculations for $R_{\text{Zr-Cl}} = 2.32$ Å, $R_{\text{Hf-Cl}} = 2.33$ Å, and $R_{\text{Rf-Cl}} = 2.50$ Å. ^c Reference 61; calculations for $R_{\text{Zr-Cl}} = 2.32$ Å, $R_{\text{Hf-Cl}} = 2.316$ Å (ref 200), and $R_{\text{Rf-Cl}} = 2.36$ Å, which was chosen taking into account an increase in the covalent radius of Rf relative to Hf (see ref 47). ^d Reference 66b, as a result of the calculations $R_{\text{Zr-Cl}} = 2.36$ Å, $R_{\text{Hf-Cl}} = 2.32$ Å, and $R_{\text{Rf-Cl}} = 2.32$ Å. (The last value is for the basis set constructed for the $7s^26d^2$ ground-state configuration of Rf. For the $7s^26d7p$ basis set $R_{\text{Rf-Cl}} = 2.40$ Å and $Q_M = 0.68$.)

to a larger metal-ligand distance in the former compound, although the calculations⁶¹ for the more realistic bond lengths give an increase in the OP of RfCl_4 . (As was shown,^{52,61} a change in the metal-chlorine bond distance of 0.01 Å gives rise to a change in the total OP(metal-chlorine) of 0.01.) Partial OP, obtained in the calculations^{49,61} show that the increase in the covalency in RfCl_4 relative to HfCl_4 comes at the expense of a larger participation of the $7s_{1/2}$ and $7p_{1/2}$ orbitals in bonding.

Thus, the results of the calculations^{49,50,61,66b} lead to the conclusion that RfCl_4 is a rather covalent compound, with its covalency being the largest in the series. In ref 61 estimates of the bond energies as a sum of the ionic and covalent parts (see Mulliken¹⁴¹) are given. Direct calculations of dissociation energies using the latest version of the DS-DV method¹⁴⁷ are in progress.^{64b}

In ref 66b, DF-SCF dissociation energies of 16.32, 14.26, and 15.55 eV have been calculated for ZrCl_4 , HfCl_4 , and RfCl_4 , respectively, where the last value is for the $\text{Rf}(7s^26d^2)$ basis set. The calculated D_e for ZrCl_4 and HfCl_4 are 80 and 70% of the thermochemical ΔH_{diss} of 20.35 (or 20.05^{154b}) and 20.55 eV, respectively (see ref 57). (The difference between D_e and ΔH_{diss} should be kept in mind.) Optimized bond lengths are 2.36, 2.32, and 2.32 Å for the tetrachlorides of Zr, Hf, and Rf, respectively (the experimental values for the first two compounds are 2.32 and 2.316 Å, respectively).^{200a} (By taking into account the much larger $\text{IR}(\text{Rf}^{4+})$ in comparison with $\text{IR}(\text{Hf}^{4+})$ (see Table 4) equal bond lengths of HfCl_4 and RfCl_4 seem improbable.)

The calculations performed for RfCl_4 with the basis set constructed for the $7s^26d7p$ ground-state configuration of Rf have given $D_e = 16.90$ eV, showing a stabilization effect of 1.35 eV relative to the ground-state configuration; $R_e = 2.40$ Å, and $Q_M = 0.68$. To have a qualitative comparison of the Rf results with those for the lighter analogs it would be logical to study the basis set effects in the lighter compounds as well. The discrepancy with the experimental data can be explained by the lack of correlation.

2. Group 5 Chlorides and Bromides

a. Influence of Relativistic Effects on the Electronic Structure and Related Properties.

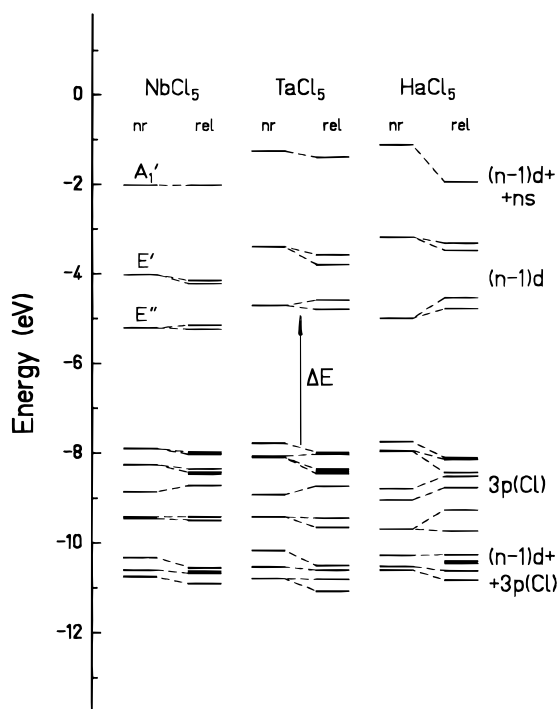


Figure 9. Energy level diagrams for NbCl₅, TaCl₅, and HaCl₅ as a result of the HFS nonrelativistic (nr) and DS DVM relativistic (rel) calculations. (Reproduced from ref 57. Copyright 1993 American Institute of Physics.)

The most complete study of the electronic structure, bonding, trends in properties of the highest chlorides and bromides within the group, and influence of relativistic effects on them has been done in refs 52, 53, 57, and 61 by using the DS-DV method.

Molecular Orbital Energies. Energy eigenvalues for MCl₅ (M = Nb, Ta, and Ha) as a result of the relativistic and nonrelativistic calculations^{52,57} are shown in Figure 9. One can see that the relative ordering and positions of energy levels for HaCl₅ are similar to those of the lighter analogs. The spin-orbit and crystal-field splittings of the relativistic MO increase in going from NbCl₅ to HaCl₅, although there is a strong relativistic stabilization of the highest vacant d orbital in HaCl₅, which has a large admixture (about 58%) of the 7s-AO. (In TaCl₅ this orbital has only 5% of the 6s character).

Opposite trends were found in the change of the following properties in the relativistic treatment on the one hand and the nonrelativistic treatment on the other hand in going from TaCl₅ to HaCl₅. The relativistic HOMO is stabilized, which results in an increase in molecular IP, while the nonrelativistic HOMO is destabilized which results in a decrease in IP. The relativistic LUMO is destabilized which results in a decrease in EA, while the nonrelativistic LUMO is stabilized which results in an increase in EA. The value of the energy gap ΔE between the binding levels of the 3p(Cl) character and vacant metal levels increases in the relativistic case, while it decreases in the nonrelativistic case. As a result, in the relativistic case the energies of the charge-transfer transitions $E_{\pi-d}$ increase from TaCl₅ to HaCl₅, which leads finally to an increase in the stability of the maximum oxidation state of the metal atom in HaCl₅. In the nonrelativistic case $E_{\pi-d}$ decrease. Thus, relativistic effects were found to

Table 10. Partial Overlap Populations of the Metal Valence Orbitals with All Chlorine Valence Orbitals (OP) for MCl₅ as a Result of Nonrelativistic (nr)^a and Relativistic (rel) Calculations (from Ref 57)

molecule	OP(s _{1/2})	OP(p _{1/2})	OP(p _{3/2})	OP(d _{3/2})	OP(d _{5/2})
	nr				
NbCl ₅	0.23	0.12	0.24	0.83	1.25
TaCl ₅	0.27	0.16	0.33	0.83	1.25
HaCl ₅	0.21	0.14	0.28	0.84	1.26
	rel				
NbCl ₅	0.28	0.14	0.24	0.83	1.25
TaCl ₅	0.41	0.22	0.30	0.84	1.28
HaCl ₅	0.48	0.29	0.20	0.87	1.33

^a The nonrelativistic data are for the molecules with experimental bond lengths.

Table 11. Effective Charges on Atoms (Q_M) and Total Overlap Populations (OP) for MCl₅ as a Result of Relativistic (rel) and Nonrelativistic (nr) Calculations (from Ref 57)^a

molecule	Q_M		OP	
	nr	rel	nr	rel
VCl ₅	1.12	1.12	1.70	1.70
NbCl ₅	0.97	0.93	1.92	2.04
TaCl ₅	1.12	0.95	2.09	2.49
HaCl ₅	1.19	0.81	1.82	2.60

^a The bond lengths for NbCl₅ and TaCl₅ are 2.338 (ax), 2.241 (eq) and 2.369 (ax), 2.226 (eq),^{200b} respectively; the ones for VCl₅ and HaCl₅ of 2.21 (ax), 2.18 (eq) and 2.42 (ax), 2.28 (eq), respectively, are estimates.⁵²

define the following trends in properties in the group: an increase in IP, a decrease in EA, an increase in ΔE , in $E_{\pi-d}$ and in E_{SO} .

Charge Density Distribution and Bonding. The relativistic charge-density distribution differs from the nonrelativistic distribution due to the electron reorganization at a given interatomic distance and due to the relativistic change of it. Different trends were found for relativistic and nonrelativistic populations of the valence ns and $np_{1/2}$ orbitals in going from TaCl₅ to HaCl₅ (an increase in these values in the first case and a decrease in the second), and as a result, for the effective charges Q_M . A gradual stabilization and contraction of the relativistic ns and $np_{1/2}$ orbitals with increasing Z is a reason for their enhanced electron population. This results in Q_M for Nb and Ta being nearly equal and in a much smaller Q_{Ha} in comparison with the lighter analogs (Table 10). This (as well as an expansion of the valence d orbitals) is also a reason for their greater participation in bonding and, as a result, an increase in the covalency in going down the group (see the OP data in Tables 10 and 11). The nonrelativistic treatment of the wave functions results in a decrease in the OP(ns -Cl) and OP($np_{1/2}$ -Cl) in going from TaCl₅ to HaCl₅ and, finally, in a decrease in the covalency. Thus, without relativity HaCl₅ would be rather similar to VCl₅, which is not stable.

Estimates of the bond energies (or ΔH_{diss}) are given in ref 52.

Stability of Oxidation States. Relativistic effects are responsible for an increase in the stability of the maximum oxidation state in the group. A linear correlation between the relativistic energies of the charge-transfer transitions $E_{\pi-d}$ and reduction po-

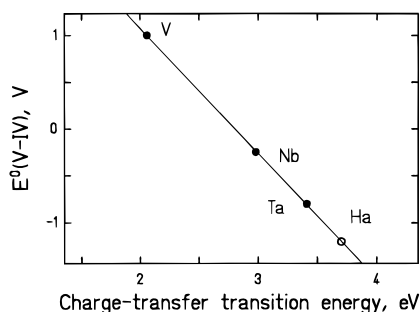


Figure 10. A correlation between redox potentials $E^{\circ}(\text{V-IV})$ and relativistic energies of the lowest charge-transfer transitions in MCl_5 ($\text{M} = \text{V}, \text{Nb}, \text{Ta},$ and Ha). Experimental data for E° are from ref 223. (Reproduced from ref 52. Copyright 1992 American Institute of Physics.)

tentials, corresponding to the transition from the +5 to the +4 state, results in $E^{\circ}(\text{V-IV})$ of -1.0 V, thus indicating that the stability of the +5 oxidation state in the group changes in the following way: $\text{V} < \text{Nb} < \text{Ta} < \text{Ha}$ (Figure 10). Without relativity Ha^{5+} would have been less stable than Nb^{5+} .

Group 5 Bromides. In ref 53 the electronic structure and properties of the group 5 pentabromides including Ha have been studied. The results show that the trends in the properties are the same as for the corresponding chlorides with the former compounds being more covalent.

b. Pseudoanalogs of the Transactinides. Despite the fact that Pa in many of its compounds exists in a pentavalent state, it can hardly be considered as an analog of the group 5 elements. Calculations⁵² of the electronic structure of PaCl_5 have shown the bonding to be made by the valence 5f, 6d, and 7s electrons (see also Figure 1) and by their hybridization. Such a hybridization accounts for a different geometrical configuration of the molecule, a square-based pyramid (C_{4v} symmetry), while the d-element pentachlorides are in a trigonal-bipyramid form (D_{3h} symmetry). In addition, PaCl_5 is much more ionic than MCl_5 ($\text{M} = \text{Nb}, \text{Ta},$ and Ha).

The possibility of HaCl_5 having a different geometry (C_{4v}) has also been discussed in ref 52.

3. Group 6 Chlorides

The electronic structure of group 6 hexachlorides has been calculated by using the DS-DV method.⁶¹ Bond lengths for SgCl_6 were chosen 0.06 Å larger than those for WCl_6 , taking into account the ionic radii of W and Sg estimated by Pykkö.⁴⁸ MO energies, IPs, energies of the electronic transitions, spin-orbit and crystal-field splittings, etc. obtained as a result of the calculations, as well as estimates of the bond strengths are given in ref 61. Q_M and OP are shown in Table 12. According to these data, Sg-Cl bonding will be obviously weaker than the W-Cl bond. Direct calculations of the dissociation energies using the latest DS-DV version¹⁴⁷ are in progress.^{64b}

The DF-SCF dissociation energies^{66b} for MoCl_6 , WCl_6 , and SgCl_6 have been obtained as 6.73, 11.49, and 12.71 eV, respectively, showing an increase in the metal-chlorine bond strength with increasing atomic number of the metal. These values are, however, about 35 and 53% of ΔH_{diss} of 19.2 and 21.6 eV, respectively, calculated for MoCl_6 and WCl_6 via

Table 12. Effective Charges (Q_M) and Overlap Populations (OP) for One M-Cl Bond for Group 4, 5, and 6 Chlorides (from Ref 61)

	MCl_4		MCl_5		MCl_6	
Q_M	Zr	1.18	Nb	0.93	Mo	0.79
	Hf	1.04	Ta	0.95	W	0.74
	Rf	1.07	Ha	0.81	Sg	0.59
OP (M-Cl)	Zr	0.48	Nb	0.41	Mo	0.36
	Hf	0.55	Ta	0.50	W	0.46
	Rf	0.57	Ha	0.52	Sg	0.45

the Born-Haber cycle (see ref 57). (The DF W-Cl average bond energy was given as 44 kcal/mol,^{66b} while the thermochemical values are 73.7 kcal/mol^{201b} and 83.2 kcal/mol.⁵⁷) The obtained DF equilibrium bond lengths for MoCl_6 , WCl_6 , and SgCl_6 are 2.25, 2.31, and 2.38 Å. The experimental values are 2.25–2.26 and 2.26 Å for MoCl_6 and WCl_6 , respectively.^{201a,c} Relativistic effects were shown to increase the binding energy of SgCl_6 from 9.4 to 12.71 eV.^{66b}

The results of the calculations of the binding energy of SgCl_6 , and—what is more important—the trend in its change in going from WCl_6 to SgCl_6 are different in refs 61 and 66b. In the first case the energy is estimated as a sum of the ionic and covalent parts of the binding energy which for SgCl_6 are both smaller than the corresponding parts of WCl_6 , resulting in a smaller total binding energy of SgCl_6 . In ref 66b direct calculations of the binding energy are performed, although the DF method used does not take into account electron correlation, which gives up to 30–40% of the binding energy. Thus, the DF results should be considered within the approximation used.

4. Comparison of Groups 4, 5, and 6 Highest Chlorides

a. The Electronic Structure and Bonding.

The MO for the highest chlorides of elements Rf, Ha, and Sg, obtained as a result of the DS-DVM calculations,⁶¹ are shown in Figure 11. All the halides have similar energy level structures, with the MO being more stabilized with increasing atomic number of the

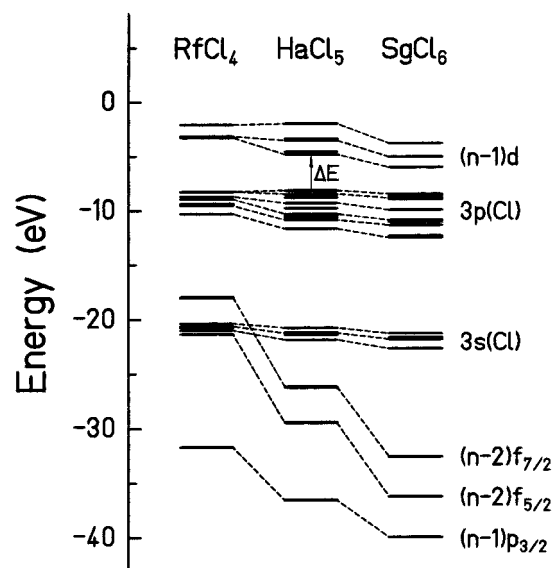


Figure 11. Energy eigenvalues for the highest chlorides of Rf, Ha, and Sg, as a result of the DS DVM calculations. (Reproduced from ref 61. Copyright 1994 American Chemical Society.)

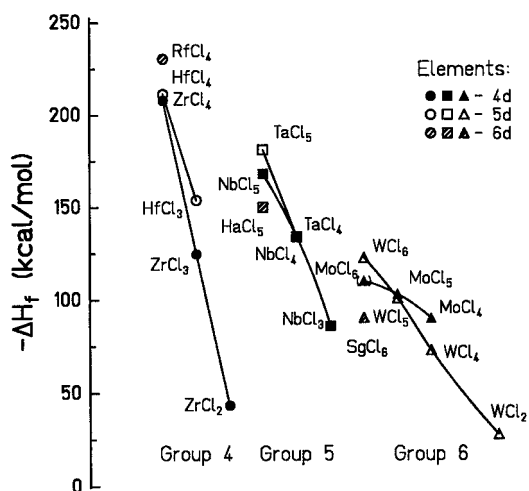


Figure 12. Formation enthalpies (negative) of gaseous chlorides of groups 4–6. Experimental values for the 4d and 5d chlorides are from refs 202–204. (Reproduced from ref 61. Copyright 1994 American Chemical Society.)

metal. The energy gap (ΔE) between the occupied and vacant d levels decreases from 4.98 to 3.25 and to 2.46 eV for RfCl_4 , HaCl_5 , and SgCl_6 , respectively.

Effective charges and total overlap populations for a single M–Cl bond of these compounds are given in Table 12. The obtained OPs reflect experimentally found regularities:^{196,201} a decrease in the bond strength in going from the group 4 to the group 6 chlorides, and an increase in it of the 5d relative to the 4d compounds. (The lowest value of OP for MoCl_6 corresponds to the instability of this compound.)

These data also show that although the groups are basically similar, there are some differences. The basic similarity is an increase in the covalency within the groups with increasing Z . Nevertheless, SgCl_6 is probably less stable than WCl_6 due to smaller both ionic and covalent contributions, while the chemical bonding of RfCl_4 is stronger than that of HfCl_4 due to an increase in both the ionic and covalent parts. Thus, a tendency to a decrease in the M–Cl bond strength in going from group 4 to group 6, known for the lighter elements, will be even more pronounced for the transactinides. This will obviously result in the decomposition at 25 °C of SgCl_6 by analogy with MoCl_6 , with the enthalpy of the reaction $\text{SgCl}_6 \rightarrow \text{SgCl}_5 + 1/2\text{Cl}_2$ of 22.5 kcal/mol. This result is important for the gas chromatography experiments conducted at high temperatures.

b. Enthalpies of Formation. Heats of formation for the highest chlorides of Rf, Ha, and Sg were calculated in ref 61 via the Born–Haber cycle using estimated ΔH_{diss} ^{52,61} and ΔH_s of metals.⁶³ The calculated ΔH_f along with experimental data^{202–206} for the lighter chlorides are shown in Figure 12. The figure reflects trends in the stability of the transition element chlorides: (1) the chlorides of the 5d elements are more stable in high oxidation states, but the 4d compounds are more stable in the low oxidation states; (2) toward the right of the periodic table the stability of the maximum oxidation state of the elements in chlorides falls rapidly (for Mo the maximum oxidation state is not stable in the chloride; for no element beyond group 6 is the maximum oxidation state attainable as a binary chloride); (3) the groups

are not equivalent with respect to the stability of the transactinides: RfCl_4 is more stable than the lighter analogs, while SgCl_6 is probably even less stable than MoCl_6 .

ΔH_f for crystalline compounds of Rf has been calculated by Bratsch and Lagowski^{44b} using a model to estimate $\Delta H_f(\text{MX}_n)$ and $\Delta H_{\text{hydr}}(\text{M}^{z+}, \text{aq})$ for the lanthanides and actinides. The basis of this model lies in the same principle of Born–Haber, only for the formation of crystalline compounds. Thus

$$\Delta H_f^\circ(\text{MX}) = \Delta H_f^\circ(\text{M}^{z+}, \text{g}) + A/(r_{\text{M}^{z+}} + r_{\text{X}}) + B \quad (13)$$

where $r_{\text{M}^{z+}}$ is the ionic radius of a cation, r_{X} is the ionic radius of the anion, and A and B are determined by fitting to experimental data. $\Delta H_f^\circ(\text{M}^{z+}, \text{g})$ is calculated by

$$\Delta H_f^\circ(\text{M}^{z+}, \text{g}) = \Delta H_f^\circ(\text{M}, \text{g}) + \sum_1^z \text{IP}(\text{M}) + 2.5zRT \quad (14)$$

In this way ΔH_f for different chlorides of Rf were calculated using coefficients A and B , obtained by fitting the equation to the experimental data for the actinides. This ionic model, however, can hardly be applied to the transactinides, since the crystal structure of the transactinide chlorides is different from that of the actinide chlorides, and the former compounds would form molecular crystals with highly covalent bonding. (In addition, the assumed $\Delta H_f^\circ(\text{M}, \text{g})$ for Rf was too low.) All this resulted in $\Delta H_f^\circ(\text{RfCl}_4)$ of -828 kJ/mol , which is less negative than those values for ZrCl_4 and HfCl_4 of -980.52 and -990.35 kJ/mol , respectively.²⁰²

Johnson⁴³ used the same model of Bratsch and Lagowski and corrected their values of ΔH_f just by using the MCDF IPs and IR for Rf (ref 41). He obtained ΔH_f of -970 and -847 kJ/mol for IR of 0.079 and 0.082 nm, respectively. Estimates of ΔH_f of other halides of Rf, RfX_2 and RfX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) also have been given in this work.

The model of Bratsch and Lagowski when applied to the group 4 compounds, was checked in ref 207. This time, coefficients A and B (eq 13) were obtained for isostructural MCl_4 compounds. Using $\Delta H_f^\circ(\text{Rf}, \text{g})$ ⁶³ and MCDF potentials,⁴¹ a new value of $\Delta H_f^\circ(\text{RfCl}_4)$ of -884.83 kJ/mol has been obtained, which is still less negative in comparison with ΔH_f for ZrCl_4 and HfCl_4 . Obviously, since the covalent interaction is not taken into account in this model, an increase in $(r_{\text{M}^{z+}} + r_{\text{X}})$ will always result in a decrease in the crystal energy, thus reducing the stability of a system.

Eichler et al.¹¹² obtained $-\Delta H_f$ of the compounds simply via a linear correlation with ΔH_s for the corresponding metals in the groups. Estimated in this way ΔH_f of $\text{RfCl}_4(\text{s})$ and $\text{RfCl}_4(\text{g})$ are -1031.2 and -909.1 kJ/mol , respectively, and of $\text{HaCl}_5(\text{s})$ and $\text{HaCl}_5(\text{g})$ are -899.4 and -805.2 kJ/mol , respectively. (Estimated $\Delta H_f^\circ(\text{M}, \text{g})$ used in this case are 648 and 821 kJ/mol for Rf and Ha, respectively, which were obtained by a linear correlation with $\ln A$, where A is an atomic mass.) The theoretical justification for this approach is nevertheless lacking.

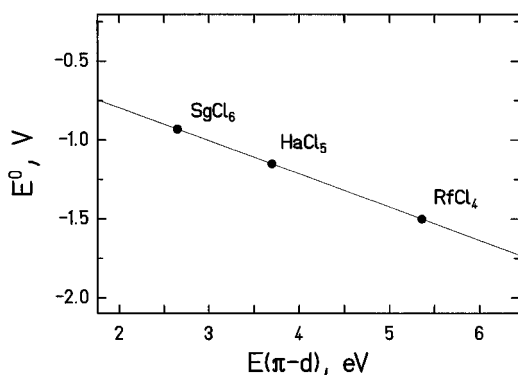


Figure 13. A correlation between redox potentials, E^0 , corresponding to electronic transitions from the highest to the next lower oxidation state and related energies of the lowest charge-transfer transitions, $E(\pi-d)$, in RfCl_4 , HaCl_5 , and SgCl_6 calculated via the transition-state procedure in the DS DV method. (Reproduced from ref 61. Copyright 1994 American Chemical Society.)

c. Stability of the Maximum Oxidation States.

Besides a decrease in the M–Cl bond strength in the highest transactinide chlorides with increasing atomic number of the metal atom, the stability of the maximum oxidation state also decreases. This is seen from a linear correlation between calculated (via the transition-state procedure) energies, $E_{\pi-d}$, of the charge-transfer transitions in MCl_n , corresponding to transitions from the highest to the next lower oxidation states, and related redox potentials (Figure 13). (See also section XI.)

5. Other Chlorides

Diatomics of heavy elements, including 117Cl, have been studied by Malli et al.^{66a} using the *ab initio* Dirac–Fock method. The results have shown a relativistic increase in the bond strength up to 0.70 eV, in comparison with the nonrelativistic value of 0.009 eV. The nonrelativistic bond length was found to be 4.99 bohr, while the relativistic value is 5.25 bohr. Thus, the results predicted a larger bond distance, smaller force constant, and about 2 orders of magnitude greater binding energy for 117Cl in the relativistic case compared to the nonrelativistic one. (A larger bond distance in the relativistic case is explained by the predominant $\pi-\pi$ bonding of $7p\pi$ and $3p\pi$ DFAOs of element 117 and Cl atom, which results from the more expanded and destabilized $7p_{3/2}$ orbitals of element 117 and $3p_{3/2}$ orbitals of Cl.)

VII. Transactinide Oxides

A. Monoxides

Although the simple transactinide oxides (where the metals are in lower oxidation states) have not yet been produced, the knowledge of the metal–oxygen bonding in these systems can be useful to understand the bonding in the more complex oxyhalide compounds, which are formed along with the highest halides.

The lighter group 4–6 oxides have been well studied. In the gas phase group 5 oxides VO and NbO are known to have a $4\Sigma^-$ ground state with three unpaired electrons, while TaO has a $2\Delta_{3/2}$ ground

Table 13. Calculations⁶⁵ of Molecular Constants for MO, Where M = Nb, Ta, and Ha

MO	state	$R_e, \text{Å}$		D_e, eV		w_e, cm^{-1}		μ_e, D
		theor	exp ^c	theor	exp ^c	theor	exp ^c	
NbO ^a	$4\Sigma^-$	1.675	1.691	6.91	7.80	1033	0000	3.39
TaO ^b	$2\Delta_{3/2}$	1.691	1.688	7.45	8.20	1022	1029	2.12
	$2\Delta_{5/2}$	1.690	1.686			1024	1031	
HaO ^b	$2\Delta_{3/2}$	1.750	–	7.95	(8.75)	1026	–	3.77
	$2\Delta_{5/2}$	1.747	–			1028	–	

^a Spin-orbit averaged CASSCF + ACPF (complete active space + averaged coupled-pair functional) calculations. ^b Spin-orbit corrected ACP calculations. ^c Reference 212.

state with one unpaired electron.^{205,208} In addition, removing one electron in TaO results in strengthening the metal–oxygen bond: the dissociation energy D_e and the bond length R_e for TaO are 191.5 ± 3 kcal/mol and 1.6872 Å , respectively, while those for TaO^+ are 238 ± 20 kcal/mol and 1.6667 Å , respectively.²⁰⁹ In group 4, only TiO has a 3Δ ground state, while ZrO and HfO have a $1\Sigma^+$ state without unpaired electrons. The question about electronic configurations of RfO and HaO and bonding was therefore of high interest.

In ref 210, a $2\Delta_{3/2}$ ground-state electronic configuration for HaO was proposed assuming that relativistic stabilization of the $7s$ and $7p$ orbitals in HaO results in an increase in the $n\sigma 2s\sigma + n\sigma 2p\sigma + n\pi 2p\pi$ interaction. The dissociation energy for HaO has been estimated by using the formula:²¹¹

$$D_e = k\gamma \exp(R_{\text{O}_2}/R_{\text{M-O}}) \text{ (kcal/mol)} \quad (15)$$

where $k = 23.069$ kcal/mol, $\gamma = (I_{\text{M}^{2+}} + I_{\text{O}})/(I_{\text{M}^{2+}} - I_{\text{O}})$, $R_{\text{O}_2} = 1.36 \text{ Å}$, and $I_{\text{O}} = 13.614$ eV. The values obtained for VO, NbO, TaO, and HaO are 148.46, 174.38, 193.91, and 183.60, respectively, which can be compared with experimental values^{205,212} of 150 ± 5 , 180 ± 3 , 191.5 ± 3 kcal/mol for VO, NbO, and TaO, respectively. Thus, D_e for HaO was found to be between those values for NbO and TaO.

The fact that the electronic configurations of VO and NbO are different from those of TaO (and HaO) was used as an explanation of the different behavior of their solid-state compounds when heated: oxygen-containing compounds of Nb (K_2NbOCl_5 , KNbOCl_4 , etc.) evolve NbOCl_3 when heated, while those of Ta evolve TaCl_5 . The reason for that was proposed to be the following.²¹⁰ The formation of the bond with three Cl in MOCl_3 needs three unpaired electrons, while TaO has only one. Thus, the energy, necessary to unpair the electrons $\text{Ta}^{2+}(\text{d}^1)\text{d}^1 \rightarrow \text{d}^1\text{d}^1$ will destroy the Ta=O bond, especially when the two coupled d electrons are shifted into it. The same would obviously hold for Ha.

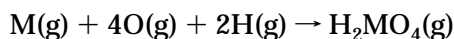
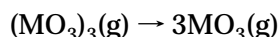
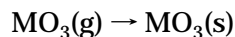
The $2\Delta_{3/2}$ ground-state electronic configuration for HaO was also obtained as a result of the QRP calculations.⁶⁵ Nonrelativistic and quasirelativistic energy-adjusted *ab initio* calculations have been performed for group 5 oxides MO, where M = Nb, Ta, and Ha. Results are summarized in Table 13. The calculations have shown that due to strong relativistic effects the ground state in HaO is 2Δ arising from the $\sigma^2\sigma^2\pi^4\delta^1\sigma^2$ configuration ($\text{Ha}^{+0.74}$; $7s^{1.76}7p^{0.17}6d^{2.27}$). Nonrelativistic calculations have given a $4\Sigma^-$ ground state of the $\sigma^2\sigma^2\pi^4\delta^1\delta^1\sigma^1$ config-

uration ($\text{Ha}^{+0.66}$, $7s^{0.85}7p^{0.12}6d^{3.30}$). Thus, a differential relativistic effect of 2.74 eV stabilizing the $^2\Delta$ state with respect to the $^4\Sigma^-$ has been observed. The relativistic effects have also stabilized the dissociation energy in HaO by 1.93 eV, although for the bond lengths (and vibrational constants) a surprisingly small effect of less than 0.03 Å was observed.

The results have shown a monotonic increase in the equilibrium distances, dissociation energies and dipole moments for the $^2\Delta$ state. The vibrational frequencies remain roughly constant. In case of the $^4\Sigma^-$ state, there is a monotonic increase in both the bond lengths and dipole moments, whereas the dissociation energies and vibrational frequencies are nearly constant.

B. Trioxides

In some gas-phase chromatography experiments^{13b,213} for studying chemical properties of Sg, a mixture of oxygen and steam is to be used instead of a halogenating agent. This seems to provide better selectivity with regard to the other transactinides, actinides or interfering α emitters. To predict the behavior of the trioxides MO_3 , formed under these conditions, or volatile acids H_2MO_4 , in ref 112d the heats of the following reactions have been estimated:



Here, the formation enthalpies (absolute values) of MO_3 and H_2MO_4 have been obtained as a linear function of the atomization enthalpy $\Delta H_f(\text{g})$ of the metals, with $\Delta H_f(\text{Sg}, \text{g})$ being estimated as (900–1156) kJ/mol. The obtained values are $\Delta H_f(\text{SgO}_3, \text{s}) = -873$ to -1016 , $\Delta H_f(\text{SgO}_3, \text{g}) = -346$ to -390 . The limitation of this approach has already been mentioned in section VI.4. (Thus, e.g., there is a decrease in the absolute values of $\Delta H_f(\text{WO}_3)$ relative to $\Delta H_f(\text{MoO}_3)$, while $\Delta H_f(\text{Mo})$ and $\Delta H_f(\text{W})$ are 615.0 and 845.2 kJ/mol, respectively).

By using $\Delta H_f(\text{Sg}, \text{g})$ of 807 (862 kJ/mol)⁶³ (see section III), and by assuming that ΔH_{diss} of the oxygen-containing compounds of Sg is at least as large as ΔH_{diss} for the W compounds, the lower limits (in absolute values) of $\Delta H_f(\text{SgO}_4, \text{g})$ of -330 (-280.3) kJ/mol and $\Delta H_f(\text{H}_2\text{SgO}_4, \text{g})$ of -990.8 (-940.6) kJ/mol have been estimated²¹⁴ with the use of the Born–Haber cycle.

On the basis of these data the following has been concluded: increasing stability of the trioxides and the acids; and decreasing volatility of the trioxides.^{112d}

The present data permit an estimation of the adsorption behavior of Sg in its oxide or hydroxide forms at the quartz surface in the gas chromatography experiments.

VIII. Transactinide Oxyhalides

By analogy with 4d and 5d oxide halides, transactinide oxyhalides are formed in the presence of

Table 14. Effective Charges (Q_M), Overlap Populations (OP), and Dipole Moments (μ) for MOCl_3 , Where M = V, Nb, Ta, Ha, and Pa (from Ref 54)

property	VOCl_3	NbOCl_3	TaOCl_3	HaOCl_3	PaOCl_3
Q_M	1.17	0.98	1.02	0.90	1.14
OP (M=O)	0.59	0.63	0.72	0.79	0.42
OP (M–Cl)	0.40	0.38	0.48	0.49	0.29
μ , D	0.48	0.91	0.99	1.27	0.88

oxygen in the gas-phase chromatography column simultaneously with pure halide formation. The lighter homologs are known to be more stable toward thermal decomposition and have higher formation enthalpies^{196,204,215} than the corresponding halides. Their stability, however, decreases in going from group 4 to group 6. Thus, predictions of properties of transactinide oxychlorides, especially their thermodynamic and thermochemical stability, are very important for the gas-phase chromatography experiments. These predictions will also be used for identification of the produced species.

A. Group 5 Oxytrihalides

The electronic structure and properties of MOX_3 (M = V, Nb, Ta, Ha, and Pa), which are monomers in the gas phase,^{201,216} have been studied in ref 54 on the basis of results of DS DVM calculations. The calculated properties were shown to have the same trends in the group as those for the corresponding pentahalides. Some of them (the electron density distribution data and dipole moments) are presented in Table 14.

An interesting result is that in contrast to expectations the oxyhalides proved to be more ionic than the corresponding pentahalides (compare Q_M and OP data in Tables 14 and 11). The OP data from Table 14 show that a tendency to form a double bond with oxygen increases in going from Nb to Ha. (Partial OP analysis has shown that an increase in the metal–oxygen bonding in HaOCl_3 is due to a larger contribution of the valence 7s and $7p_{1/2}$ orbitals.)

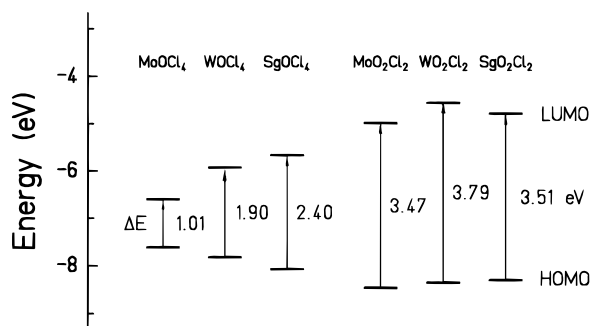
The calculated data for PaOCl_3 , as a pseudoanalog of Ha, show the bonding to be more ionic due to the participation of the more localized 5f electrons. The oxyhalides have dipole moments and their values increase in the direction of the Ha oxychloride.

ΔH_{diss} for HaOCl_3 was estimated as 20.82 eV, which is lower than the ΔH_{diss} for NbOCl_3 and TaOCl_3 of 21.6 and 22.52 eV, respectively, calculated via the Born–Haber cycle. ΔH_f for HaOCl_3 obtained via the Born–Haber cycle is -151.2 ± 7 kcal/mol, which is less negative than those values for the oxytrichlorides of Nb and Ta of -179.8 and -186.6 kcal/mol, respectively.²⁰⁴

It is interesting to compare here the results of the *ab initio* quasirelativistic calculations⁶⁵ for MO and the DS-DVM calculations⁵⁴ for MOCl_3 with respect to the trend in the metal–oxygen bonding in the group. The DS-DVM calculations used the same increase (of 0.05–0.07 Å) in the Ha=O bond lengths relative to the Ta=O as was later obtained (0.059 Å) in the *ab initio* calculations.⁶⁵ Estimated⁵⁴ (by using Q_M and OP) M=O bond energies are 8.29, 8.47, and 8.22 eV for NbOCl_3 , TaOCl_3 , and HaOCl_3 , respectively, which are comparable with the experimental

Table 15. Effective Charges (Q_M), Energy Gaps (ΔE), Overlap Populations (OP), and Dipole Moments (μ) for $MOCl_4$, Where $M = Mo, W,$ and Sg (from Ref 62)

property	MoOCl ₄	WOCl ₄	SgOCl ₄
Q_M	1.00	1.04	0.90
ΔE , eV	1.01	1.90	2.40
OP(M=O)	0.52	0.70	0.77
OP(M-Cl)	0.33	0.42	0.43
μ , D	0.14	0.49	1.03

**Figure 14.** Energies of the HOMO and LUMO in $MOCl_4$ and MO_2Cl_2 , where $M = Mo, W,$ and Sg , obtained as a result of the DS DVM calculations. (Reproduced from ref 64. Copyright 1995 American Chemical Society.)

and calculated D_e of the oxides (Table 13). The difference is a smaller $D_e(\text{Ha}=\text{O})$ relative to $D_e(\text{Ta}=\text{O})$ in the DS-DVM results. This might be due to the fact, that in the scheme proposed in ref 52 for estimating ΔH_{diss} by using Q_M and OP, the ionic contribution is overestimated.

Results of the DS-DVM calculations⁵⁴ for the group 5 $MOBr_3$ have shown that trends within the group are similar to those for the corresponding $MOCl_3$, with the former compounds being more covalent.

B. Group 6 Oxytetrachlorides

Although the oxychlorides of Mo and W, $MOCl_4$, are known to be more stable than the corresponding hexachlorides, their stability with respect to thermal decomposition is different. $MoOCl_4$ decomposes readily at room temperature through loss of chlorine, while $WOCl_4$ is relatively stable.¹⁹⁶ The question about stability of $SgOCl_4$ is therefore of special importance for the gas chromatography experiments conducted at high temperatures.

Calculations of the electronic structure of $MOCl_4$ ($M = Mo, W,$ and Sg), which are monomers in the gas phase,^{217,218} have been performed in ref 62 using the DS-DV method. Results of these calculations are summarized in Table 15. They show that the trends (an increase in the energy gap ΔE and in covalency, see Figure 14) are similar to those found for the corresponding halides. Nevertheless, one can see that in going from $WOCl_4$ to $SgOCl_4$ the increase in covalency is mainly a result of an increasing metal-oxygen interaction, while the metal-chlorine covalent bonding is the same. (A similar situation was found for $SgCl_6$, where the total OP was lower than that of WCl_6). The dipole moments increase in going from $MoOCl_4$ to $SgOCl_4$.

In ref 62, $M=O$ and $M-Cl$ bond energies have been estimated using the calculated Q_M and OP. The metal-chlorine bond strength of $SgOCl_4$ was found

Table 16. Effective Charges (Q_M), Partial Overlap Populations (OP), Energy Gaps (ΔE), and Dipole Moments (μ) for MO_2Cl_2 , Where $M = Mo, W,$ and Sg (from Ref 64a)

property	CrO ₂ Cl ₂	MoO ₂ Cl ₂	WO ₂ Cl ₂	SgO ₂ Cl ₂
Q_M	0.96	1.03	1.08	0.97
OP(M=O)	0.46	0.54	0.69	0.74
OP(M-Cl)	0.31	0.32	0.43	0.43
ΔE , eV	2.64	3.47	3.79	3.51
μ , D	0.88	1.04	1.35	1.83

to be close to that of $MoOCl_4$. Thus, a decomposition



could take place by analogy with $MoOCl_4$.

Calculated via the Born-Haber cycle $\Delta H_f(SgOCl_4)$ of -114 ± 6 kcal/mol is less negative than those values for $MoOCl_4$ and $WOCl_4$ of -140 and -152 kcal/mol, respectively.²⁰⁴

C. Group 6 Dioxidichlorides

Since there is a risk of the decomposition of $MOCl_4$ at high temperatures, the group 6 MO_2Cl_2 compounds would be a better choice for the gas-phase chromatography experiments due to their higher thermochemical stability. Their formation enthalpies are also more negative than those of $MOCl_4$.²⁰⁴

Investigation of the electronic structure, spectra, bonding, and thermochemical stability of SgO_2Cl_2 relative to the lighter analogs, CrO_2Cl_2 , MoO_2Cl_2 , and WO_2Cl_2 , which are monomers in the gas phase,²¹⁹ has been done in ref 64a using the DS-DV method. Results are summarized in Table 16. In contrast to $MOCl_4$, the value of the energy gap between the occupied and vacant levels, ΔE , does not increase in going from WO_2Cl_2 to SgO_2Cl_2 (Figure 14). This means, that the +6 oxidation state of Sg in SgO_2Cl_2 will be less stable than the +6 state of W in WO_2Cl_2 . Trends in OP(M=O) and OP(M-Cl) are similar to those for the corresponding $MOCl_4$. Estimates of thermochemical bond energies are given in ref 64a. A higher stability of MO_2Cl_2 relative to $MOCl_4$ is explained by a much larger ΔE (see energy levels for $MoOCl_4$ and MoO_2Cl_2 in Figure 14). Since the estimated dissociation energy of the Sg-Cl bond in SgO_2Cl_2 is similar to that of W-Cl in WO_2Cl_2 , and since it has a very large ΔE , the compound will be rather stable.

IX. Other Compounds of the Transactinides

A. The Sg Carbonyl

In ref 68 the electronic structures of $M(\text{CO})_6$, where $M = Cr, W, U,$ and Sg , have been calculated using nonrelativistic and relativistic DV- X_α methods. The electronic structure of $Sg(\text{CO})_6$ was found to be very similar to that of Cr and W carbonyl complexes with the formation of synergic metal-carbonyl bonds with significant $\pi d(M)-\pi(\text{CO}_2)$ back-bonding. The electronic structure of the $U(\text{CO})_6$ complex proved to be different due to the presence of both valence 6d and 5f orbitals.

The influence of relativistic effects on the electronic structure data has been analyzed in this work.

Relativistic effects lower the energy of the HOMO t_{2g} orbital in $Sg(CO)_6$, which has a large contribution from the 6d orbital, by 2 eV, thus resulting in a HOMO energy very similar to that in $Cr(CO)_6$ and $W(CO)_6$. According to the electronic structure data (electron density distribution), the possible existence of $Sg(CO)_6$ (and $U(CO)_6$) as isolable molecular species has been predicted.

X. Volatility of the Halides and Oxyhalides

A. Experimental Investigations of Volatility

1. "One-Atom-at-a-Time" Chemistry

Volatility of the transactinide halides and oxyhalides is one of the few properties which can be quantitatively measured experimentally. Two groups of the gas-phase chromatography experiments differ by some principal techniques and by parameters measured. In the first group,⁶⁻⁸ the inner surface of the column serves as a track detector for fission fragments and the deposition temperature of compounds is correlated with sublimation enthalpies, ΔH_s . In the second group,⁹ the products pass through an empty isothermal chromatography column, and the temperature which gives 50% chemical yield ($T_{50\%}$) of products at the outlet is measured and then correlated with adsorption enthalpy, ΔH_a .

Various volatility measurements of the transactinide halides have given partially different results. Thus, in some experiments^{7b,8e,f,9g} the tetrachloride and tetrabromide of Rf were found to be more volatile than the tetrachloride and tetrabromide of Zr and Hf (the ΔH_s obtained for $RfCl_4$ of 90 ± 15 kJ/mol^{8g} can be compared with ΔH_s for $HfCl_4$ and $ZrCl_4$ of 107.6 ± 2 and 108.4 ± 2.0 kJ/mol,²⁰⁵ respectively). In the latest experiments,^{9d,e} however, volatilities of $RfCl_4$ and $ZrCl_4$ proved to be similar (their ΔH_a were estimated as -77 and -69 kJ/mol, respectively), while $HfCl_4$ turned out to be much less volatile ($\Delta H_a = -101$ kJ/mol).

$HaBr_5$ was believed to be less volatile than the pentabromides of Nb and Ta.^{9a} The upper limit of $\Delta H_s(HaCl_5)$ of 120 kJ/mol has been defined^{9h} which can be compared with $\Delta H_s(NbCl_5)$ of 95 ± 16 kJ/mol. Among oxyhalides, $HaOCl_3$ was found to be less volatile than $NbOCl_3$.^{9h}

2. Macrochemistry for the Lighter Homologs

Identification of properties of the transactinides by studying their volatility is a difficult task due to the fact that even for lighter compounds volatility is a property which is hardly correlated with one or even with a set of parameters, and available data are often contradictory. From macrochemistry it was established that (i) monomeric compounds are more volatile than polymeric, (ii) covalent compounds are more volatile than ionic, and (iii) volatility decreases with decreasing valency of a central atom.

The measure of volatility is known to be an equilibrium vapor pressure over a substance:

$$\ln P = A - (B/T) \quad (16a)$$

where coefficients A and B are determined experi-

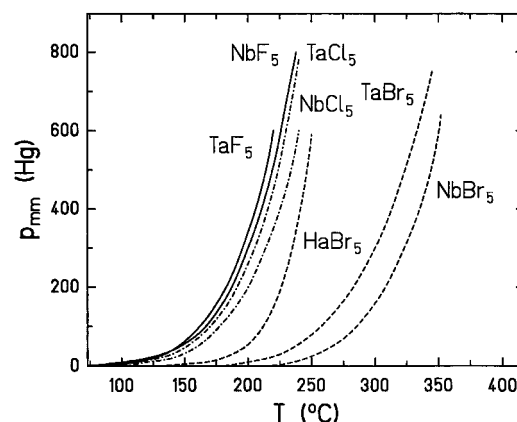


Figure 15. Volatility as a temperature dependence of P_{mm} for group 5 highest fluorides, chlorides, and bromides. The experimental data are from ref 206. The calculated data for $HaBr_5$ are from ref 53.

mentally and B corresponds to ΔH_s . The boiling points T_b basically correlate with P_{mm} . For the lighter analogs of Rf, Ha, and Sg the following trends have been observed:¹⁹⁶

1. Volatility of MX_n decreases in the sequence $F > Cl > Br > I$ (see Figure 15), although for group 4 $Cl > Br > I > F$.
2. 5d halides are more volatile than 4d halides.
3. 5d oxyhalides are less volatile than 4d oxyhalides.
4. All oxyhalides are less volatile than corresponding halides.
5. Volatility of halides decreases in going from group 6 to group 4.

In refs 53, 54, 59, and 62 it was suggested that the data for the equilibrium pressure $P_{mm} = f(T)$ of macroamounts should be used to estimate the volatility of substances measured on a "one-atom-at-a-time" scale. To predict the volatility of the transactinide compounds, such curves have been constructed for the highest halides (see Figure 15), using a model described in the next paragraph. In ref 9c,h, the usefulness of this approach was confirmed: differences in the temperature at a particular P_{mm} for different compounds (e.g., $NbCl_5$ relative to $NbOCl_3$) were shown to be equal to their differences in $T_{50\%}$ in the gas chromatography experiments.

B. Theoretical Interpretation of Volatility of the Transactinide-Containing Compounds

1. Empirical Extrapolations

A simple way to estimate the volatility of halides and oxyhalides was proposed by Eichler et al.^{112a-f} He calculated ΔH_s (as a measure of volatility) for a substance as the difference between formation enthalpies of the solid-state and gas-phase compounds, with ΔH_f being obtained by a linear function of the formation enthalpy of a corresponding element. (For comments on the validity of this approach see the preceding section.)

In this way, two values of ΔH_s of $HaBr_5$ have been obtained^{112a} (depending on different values of ΔH_f of Ha), resulting in one case in a higher volatility of $HaBr_5$ compared to $NbBr_5$ and $TaBr_5$, and in the other case in a lower volatility, thus leaving the

question open. In another work,^{112b} ΔH_s of group 6 chlorides and oxychlorides have been estimated in the same way, with the results being inconsistent. (Thus, e.g., although lower chlorides are known to be less volatile than the highest, the obtained ΔH_s of SgCl_4 and SgCl_6 are 78 and 108 kJ/mol, respectively, indicating that the former compound is more volatile.) According to these estimates volatility of both the halides and oxyhalides of the transactinides should be lower in comparison with the lighter analogs.

In a later work^{112e} ΔH_s for RfCl_4 , HaCl_5 , and HaOCl_3 of 122.1, 94.2, and 180.0 kJ/mol, respectively, have been obtained by using a linear correlation between ΔH_s of the halides or oxyhalides and ΔH_f of their corresponding elements. According to this approach, increasing ΔH_f of the 5d elements relative to the 4d ones would mean the same trends in the volatility of the highest halides and oxyhalides (their decrease), which, however, contradicts experimental data (see section IX.A.2).

2. Dependence on Geometry

It was found by Zvara^{8b,220} that for group IV tetrachlorides and tetrabromides, MX_4 , the inverse absolute normal boiling point temperature, $1/T_b$, is a linear function of the interatomic metal-halide distance in free molecules, or, finally, of the ionic radius. (The points for the actinides, UCl_4 and ThCl_4 were also included in the correlation.) Later it was stated,²²¹ that the dependence $Nx^2/T_b \approx l/x$, has a universal character for MX_4 , MX_5 , and MX_6 . (In this case, the points for U and Th were not included.) Here N is the number of facets of the polyhedron of a molecule, x is the halide radius extrapolated to $\text{CN} = 1$, and l is the closest possible distance between the surface of the metal atom (in the model) and the surface of X of an adjacent molecule.

By using $1/T_b = k(\text{IR})$ and MCDF $\text{IR}^{41,42}$ of Rf^{4+} and Ha^{5+} (which are too large and do not take into account the relativistic bond contraction), much lower volatilities (as $1/T_b$) of RfCl_4 relative to ZrCl_4 and HfCl_4 , and of HaBr_5 relative to NbBr_5 and TaBr_5 , have been predicted.^{8c} A similar linear correlation between ΔH_s and IR resulted in the same much lower volatility of RfCl_4 relative to the lighter analogs.^{112f}

Analyzing the data for all existing halides,^{214a} it was found out that the dependence $1/T_b = k(\text{IR})$ did not have a universal character. The following compounds do not obey this rule: (a) group 2 dichlorides; (b) actinide trichlorides; (c) actinide tetrahydroborates; (d) group 5 and 6 pentachlorides (they do not fit one plot); and (e) group 6 hexafluorides including those of the actinides. Thus, the data generally show that the situation is more complicated and depends on the group, solid-state structure, type of bonding in the solid state and gas phase (covalency), etc. Direct calculations of the energy of the intermolecular interaction (taking into account polarizabilities of molecules, etc.) are needed to estimate volatilities of compounds.

3. Estimates of Volatility on the Basis of the MO Calculations

a. Covalency as a Measure of Volatility. An attempt to find a relation between ΔH_a , measured

in gas-phase chromatography experiments and correlated to ΔH_s , and results of the electronic structure (DS-MS) calculations for the transactinides has been done in ref 49. There, a higher volatility of RfCl_4 compared to those of ZrCl_4 and HfCl_4 in the experiments^{8e,f} was explained by a lower effective charge of the Rf atom, and hence, more covalent bonding in RfCl_4 . (A plot $\Delta H_{\text{subl}} = f(Q_M)$ for MCl_4 , where $M = \text{Ti, Zr, Hf, and Rf}$, was shown to have a parabolic shape.) Analogously, a lower Q_M in RfBr_4 relative to ZrBr_4 and HfBr_4 would mean a higher volatility of the former compound.^{9g}

A larger series of the DS DVM calculations⁵²⁻⁶⁴ has enabled the establishment of a more universal character for the dependence "OP(covalency)-volatility". Thus, assuming that in a group, analogous compounds have similar structures in the solid state and in the gas phase, the following has been established: (a) higher values of OP(tot) for the 5d halides compared to the 4d ones correspond to their higher volatilities; (b) higher values of OP for group 5 halides compared to the group 4 halides correspond to their higher volatility; (c) smaller OP data for oxyhalides compared to the pure halides correspond to their lower volatility; (d) much lower OP data for the halides of actinides compared to those values for halides of the d elements are in line with their low volatility.

Thus, the higher values for the OP(tot) of the transactinide halides compared to the lighter analogs would be a reason to think their volatility should be higher.

b. Volatility as an Intermolecular Interaction. In ref 53 an attempt was made to calculate P_{mm} as an interaction of molecules in the gas phase. In a first approximation, such an interaction can be estimated on the basis of calculations of polarizabilities and dipole moments of separate molecules. A simpler approach, by using only polarizabilities of the ligand atoms (in case of symmetric molecules), was proposed in ref 53.

According to this model, a relationship between pressures of different compounds (see eq 16a) in a group can be expressed as a relationship between the energies of the dispersion interaction $\epsilon(x)$ of their molecules, which in turn are expressed via ionization potentials and polarizabilities of interacting ligand atoms. This resulted for HaBr_5 in

$$\log P_{\text{mm}} = 12.5 - (5088/T) \quad (16b)$$

which means that HaBr_5 should be more volatile than its analogs (see Figure 15).

The much lower volatility of this compound, obtained experimentally,^{9a} has been interpreted (also in ref 53) as the formation of HaOBr_3 , which was obviously a consequence of oxygen being present in the chromatography column. Calculated in the same way (as a parameter B in eq 16a) $\Delta H_s(\text{RfCl}_4)$ of 107.2 kJ/mol corresponding to $\Delta H_a = -88.2$ kJ/mol is in good agreement with the experimental result^{9e} of $\Delta H_a = -77$ kJ/mol. This indicates that volatility of RfCl_4 is nearly equal to that of ZrCl_4 , with ΔH_s of 110.5 kJ/mol.

Qualitatively, some differences in the volatilities of other compounds were also explained^{53,54} by dif-

ferences in their intermolecular interactions. Thus, the oxyhalides, in comparison with the corresponding pure halides, in addition to their lower covalency, have dipole moments strengthening their intermolecular interaction and, hence, decreasing volatility. Increasing dipole moments of the oxyhalides in the groups are a reason for a decrease in volatility of the 5d relative to the 4d compounds and for a further decrease in volatility in going to the transactinide oxyhalides.^{9e}

In ref 53 an interpretation of volatility as a process of adsorption–desorption of single molecules on the surface of a chromatography column has been given on the basis of results of the MO calculations.

Calculations of the intermolecular interaction using a statistical model of the electronic gas²²² are in progress.^{214b}

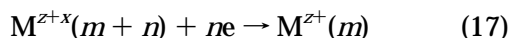
XI. Oxidation States of Rf, Ha, and Sg in Aqueous Solutions

Estimates of the stabilities of different oxidation states of the transactinides obtained on the basis of DF and DFS calculations of atomic IPs are summarized in reviews of Fricke.^{37,38} For Rf, oxidation state +4 was predicted as the most stable in solutions, while in the solid state the +2 and +3 states were believed to be also stable. (A $ds^2p_{1/2}$ ground state electronic configuration of Rf, obtained in the MCDF calculations^{40,41} was also a reason to think about stability of the +1 oxidation state due to the delocalization of the $7p_{1/2}$ electron. However, recent CCSD results⁸⁴ assign the ground state as d^2s^2 .) Ha is expected to be more stable in the +5 oxidation state, although the +4 and +3 states were supposed to be also exhibited. (The latter was assumed to have an enhanced stability due to the relativistic stabilization of the $7s^2$ pair.) Sg was expected to exist in solutions in the +6 and +4 oxidation states, with the latter being more stable. For the heavier transactinides lower oxidation states will be predominant.

MCDF calculations^{40–42} and recent CCSD ones^{84–86} have given new values of the IPs. These new MCDF values were used to estimate redox potentials in aqueous solutions (see refs 43, 55, 60, and 61) and to check the conclusions made earlier.

A. Characterization of Oxidation States

For characterizing an oxidation state, the oxidation–reduction potential E° is of crucial importance. For the reaction



a change in the free energy

$$\Delta G^\circ = -nFE^\circ \quad (18)$$

where F is the Faraday constant.

In ref 44 Bratsch and Lagowski proposed an estimate of the Gibbs free energy of formation of an ion M^{z+} using the Born–Haber cycle, so that

$$\Delta G^\circ(M^{z+}, \text{aq}) = z\Delta G^\circ(\text{H}^+, \text{aq}) + \Delta G^\circ(M^{z+}, \text{g}) + \Delta G_{\text{hyd}}^\circ(M^{z+}) - z[\Delta G^\circ(\text{H}^+, \text{g}) + \Delta G_{\text{hyd}}^\circ(\text{H}^+)] \quad (19)$$

where

$$\Delta G_{\text{hydr}}^\circ(M^{z+}) = A_y(z)/(r_{M^{z+}} + r_x(z)) \quad (20)$$

Here, $A_y(z)$ and $r_x(z)$ are parameters which are obtained by a least-square fitting to known experimental data. Using this scheme some redox potentials for Rf and Ha have been estimated.^{42–44}

In ref 55, group 5 redox potentials, including those for Ha and Pa, have been obtained using the following approach. The change in the free energy in the redox reaction 17 can be expressed as

$$\Delta G^\circ = -[\text{IP} + \Delta G_{\text{hyd}}^\circ] \quad (21)$$

with $\text{IP} = I \pm \Delta E$, where I is the ionization energy $M^{z+} \rightarrow M^{z+x}$, and ΔE is the energy which is necessary for the reconstruction of an electronic configuration of the metal ion when going from the (m) to the ($m+n$) valence state. Ionization potentials I and $\Delta G_{\text{hyd}}^\circ$ (eq 20) were shown^{94,95} to be a smooth function of the atomic number. Thus, ΔE correlates linearly with redox potentials and defines all the changes in their values. If IP includes the change in the electronic configuration, $E^\circ(M^{z+x}/M^{z+})$ is directly proportional to IP.

B. Redox Potentials in Aqueous Solutions

1. Group 4

In refs 43 and 44 redox potentials $E^\circ(\text{Rf}^{2+}/\text{Rf})$, $E^\circ(\text{Rf}^{3+}/\text{Rf})$, $E^\circ(\text{Rf}^{4+}/\text{Rf})$, $E^\circ(\text{Rf}^{3+}/\text{Rf}^{2+})$, and $E^\circ(\text{Rf}^{4+}/\text{Rf}^{3+})$ have been estimated using the model of Bratsch and Lagowski. In ref 44b a very approximate value of the atomic IP(0–4+) was used to obtain $\Delta G^\circ(M^{z+}, \text{g})$ and then E° . In ref 43 the procedure was repeated but with new MCDF IPs.⁴¹ Nevertheless, in both papers a very crude estimate of the $\Delta H_s(\text{Rf})$ of 129.06 kcal/mol was used (see the other values from Table 5). This resulted in a too large (absolute) value of the $E^\circ(M^{4+}/M^{3+})$ of -3.8 (-2.8 V). The main conclusion made in both papers is that Rf^{4+} is more stable than Rf^{3+} , and the latter is more stable than Rf^{2+} . The stability of the +1 oxidation state has not been analyzed.

In ref 61 a correlation between group 4 $E^\circ(M^{4+}/M)^{223}$ and MCDF IP(0–4+)⁴¹ was used (eqs 18 and 21) to obtain $E^\circ(\text{Rf}^{4+}/\text{Rf})$ of -1.85 V, showing that the earlier estimates (absolute values) of -0.8^{43} and -1.2 (-0.9) V⁴⁴ were too low. $E^\circ(\text{MO}_2/\text{M}) = -1.95$ V.⁶¹

2. Group 5 (Redox Reactions)

In ref 55 all redox reactions of group 5 elements including Pa in acid aqueous solutions have been considered. Unknown redox potentials have been determined on the basis of a linear correlation between $E^\circ(M^{z+x}/M^{z+})$ and the calculated⁴¹ MCDF IPs, which have been normalized and extrapolated to the experimentally known values.¹⁰¹ (The calculated IPs already included changes in the electronic configurations.) A linear correlation between IP(0–4+) and $E^\circ(\text{MO}_2/\text{M}^{3+})$ for V, Nb, Ta, Pa, and Ha is shown in Figure 16 as an example. The obtained value of the redox potential $E^\circ(\text{HaO}_2/\text{Ha}^{3+})$ of -1.38 V shows that the +3 oxidation state of Ha is even

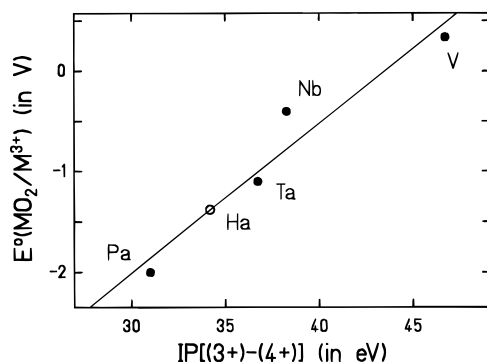


Figure 16. A correlation between ionization potentials $IP[(3+) \rightarrow 4+]$ and the standard potentials $E^\circ(MO_2/M^{3+})$ for group 5 elements. Filled circles are experimental data from ref 223. (Reproduced from ref 55. Copyright 1992 American Chemical Society.)

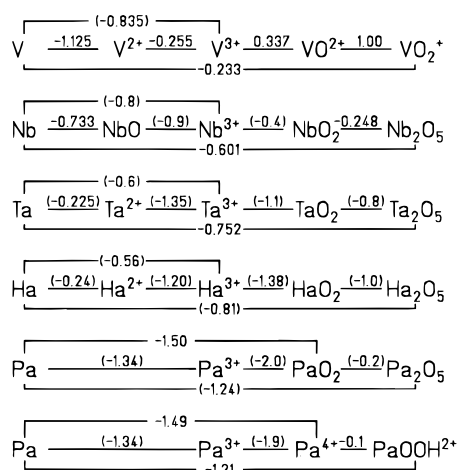
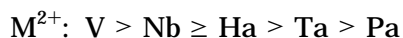
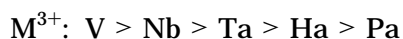
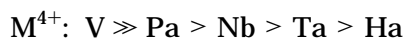
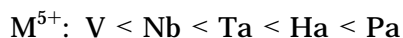


Figure 17. Standard redox potentials for group 5 elements. Figures in parentheses are the estimated values. (Reproduced from ref 55. Copyright 1992 American Chemical Society.)

less stable than the +3 oxidation state of Nb and Ta. (Pa^{3+} is not known in aqueous solutions.)

All the redox potentials, known and estimated in this way, are shown Figure 17. From these values the following trends in the stability of oxidation states for the group 5 elements have been established:



Thus, the stability of the pentavalent state increases in going from V to Ha, while that of the tetra- and trivalent states decreases in this direction. The divalent state of Ha will be as stable as that state of Nb, thus indicating a possible formation of its mixed-valence compounds by analogy with Nb.²²⁴ The present estimates show no enhanced stability of the trivalent state of Ha.

In ref 42 some standard potentials $E^\circ(M^{z+x}/M^{z+})$ for Ha were estimated using the Bratsch–Lagowski

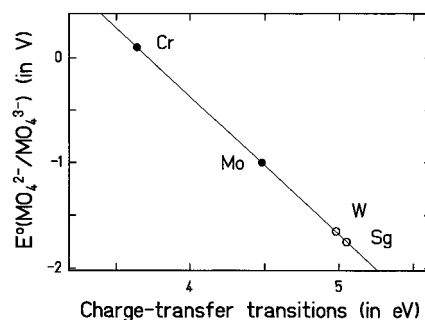


Figure 18. A correlation between standard redox potentials $E^\circ(MO_4^{2-}/MO_4^{3-})$ and energies of the calculated (by using the transition-state procedure in the DS DV method) lowest charge-transfer transitions in $[MO_4]^{2-}$, where $M = Cr, Mo, W,$ and Sg . The filled circles are experimental values from ref 223. (Reproduced with permission from ref 60. Copyright 1994 R. Oldenburg Verlag, München.)

approach and Born–Bierrum equation.²²⁵ The values obtained in these two ways differ drastically. A conclusion made in ref 42 is nevertheless the same as in ref 55: the +5 oxidation state will be the most stable in acid solutions, while the +2 and +3 are not. The +4 state may be also exhibited.

3. Group 6

In ref 60 calculations of the electronic structure of the oxyanionic complexes, $[MO_4]^{2-}$, which are formed in basic solutions, have been performed using the DS DV method. A linear correlation between calculated energies of the charge-transfer transitions, related to the reduction process M^{6+}/M^{5+} , and the reduction potentials $E^\circ(MO_4^{2-}/MO_4^{3-})$ were used to estimate $E^\circ(SgO_4^{2-}/SgO_4^{3-})$ (Figure 18). The obtained value of -1.60 V shows an increase in the stability of the +6 oxidation state in group 6 with increasing Z , although this increase is very small. This result was obtained for the shortest metal–oxygen bond lengths in $[SgO_4^{2-}]$. An increase in the bond lengths of 0.03 Å resulted in a decrease in the energy of the lowest charge-transfer transition, and hence, in a decrease in the absolute value of the reduction potential, so that $E^\circ(SgO_4^{2-}/SgO_4^{3-}) = -1.34$ V. This means that for these interatomic distances the +6 oxidation state of Sg is less stable than that of W.

MCDF calculations of the IPs for Sg which will be used to estimate other reduction potentials are in progress.⁹⁰

In summary, although the stability of the maximum oxidation state increases with increasing Z in groups 4–6, this increase becomes less pronounced in going from group 4 to group 6: for W and Sg the stability of the +6 state is nearly the same; the +7 oxidation state of Ns will probably not be stable. Thus, along the transactinide series the stability of the maximum oxidation state decreases in the following way: $Lr^{3+} > Rf^{4+} > Ha^{5+} > Sg^{6+}$ (see Table 17).

XII. Forms of the Transactinides in Aqueous Solutions

A. Experimental Study of Solvent Extraction

The transition metals of groups 4–6 are known to form neutral species or anionic oxy, hydroxy, or

Table 17. Standard Reduction Potentials $E^0(M^{z+}/M^{z+})$ (in V) for Heavy Elements

element	$E^0(M^{3+}/M^{2+})^a$	$E^0(M^{4+}/M^{3+})^a$	$E^0(M^{5+}/M^{4+})^b$	$E^0(M^{6+}/M^{5+})^c$
Lr	-2.6	8.1		
Rf	-1.7	-1.5		
Ha	-1.20	-1.38	-1.0	
Sg				-0.93

^a Reference 44b. ^b Reference 55. ^c Reference 61.

oxyhalide complexes in acidic aqueous solutions, depending on the acid concentration.^{201,226,227} The ability for complex formation is known to increase in the groups with increasing atomic number of the element: the 3d elements exist in aqueous solutions mainly in the form of cations, while the 4d and 5d elements are known to form stable anionic complexes of different composition (depending on the concentration of a halogenating agent) with the metal in its maximum oxidation state. The question whether the transactinides continue this trend can be answered by studying their solvent extraction properties, thus providing information about extracted chemical species, complexing ability, and ionic radii. Techniques which are particularly useful here are liquid-liquid extraction or ion-exchange resin separations.

First on-line experiments for the liquid extraction of Rf and Ha confirmed that they belong to groups 4 and 5. Silva et al.^{10a} and then Hulet et al.,^{10b} investigating the chloride complexing and extraction of the anionic species on chromatographic columns of trioctylmethylammonium chloride, found that Rf behaves like Zr and Hf and not like the actinides. (Zr, Hf, and Rf were extracted from 12 M HCl while trivalent actinides were not sorbed on the chromatographic column. Rf, together with Hf tracer, was then eluted with 6 M HCl.)

In earlier experiments,^{11a} Ha was shown to adhere to a glass surface upon fuming with concentrated nitric acid, a property characteristic of group 5 elements, Nb and Ta. Later it was not extracted into methyl isobutyl ketone (MIBK) under conditions in which Ta was extracted but Nb was not. This was attributed to the formation of the nonextractable $[HaF_7]^{2-}$ species or other polynegative fluoride complexes in contrast to $[TaF_6]^-$.

In recent detailed studies^{11b,c,12} the behavior of Rf and Ha was found to deviate from the trends found within the 4d and 5d analogs. Thus, experiments^{11c} on the extraction of Zr, Hf, and Rf along with pseudoanalogs Th and Pu from HCl solutions into TBP (depending on the HCl, Cl^- , and H^+ concentrations) have shown that (1) Rf and Pu form anionic chloride species $[RfCl_6]^{2-}$ with increasing $[Cl^-]$, which are not extracted into TBP, while Zr, Hf, and Th are well extracted (they do not form anionic complexes with TBP); (2) extraction of Rf increases with increasing $[H^+]$ while that for Zr and Hf does not. This was explained by formation of the neutral salt $RfCl_4 \cdot xHCl \cdot yTBP$.

In the experiments^{12a-c} on the extraction of group 5 elements from HCl + HF solutions into triisooctylamine (TIOA), Ha was found to be extracted together with Nb and Pa and not together with Ta. In the process of elution of these elements with HCl from the TIOA columns, very strong halide complexes of

Ta were not eluted and had to be stripped with 6 M $HNO_3/0.015$ M HF. Ha was eluted between Nb and Pa, showing that its anionic halide complexes are different from those of Ta, and more like those of Nb and Pa. This difference between Ta and Ha is indicative of a deviation from the trend which could not be predicted by simple extrapolation within the group 5.

Results of the experiments^{12c} on the extraction of Ha, Nb, and Pa from aqueous HBr and HCl solutions into diisobutylcarbinol (DIBC) indicated that the tendency of Ha to form polynegative complexes at high halide concentration is stronger than that of Nb and much stronger than that of Pa.

In the preliminary on-line experiments^{13d-g} to study the complex formation of Sg, various systems were tried in order to find proper conditions to separate the lighter analogs, Mo and W. The best conditions were found for the mixture of very dilute HF and HCl acids as an aqueous phase, which allows separation of Mo and W from group 4 ions and trivalent actinides by using the cation exchange resins.^{13d} A separation of W from Mo can also be achieved by applying this mixture as a diluent.^{13e} Some other good conditions were found for the separation of W from Mo in the extraction^{13f} from aqueous HCl and HNO_3 solutions by different organic extractants.

B. Theoretical Study of the Complex Formation and Extraction

Analyzing results of the DS atomic calculations, Fricke^{37,38} predicted that the transactinides would exhibit a rich chemistry of complex ions in solution in analogy with the 5d elements. Results of later DS-DVM calculations⁵⁸⁻⁶⁰ of the electronic structure of the experimentally studied group 5 and 6 compounds in solutions shed light on the complex formation and bonding and proved helpful in the interpretation and prediction of the experimental results.

1. Anionic Halide and Oxyhalide Complexes of Group 5 Elements in Acid Solutions

a. Complex Formation. In aqueous HCl solutions Nb and Pa are known²²⁶⁻²²⁷ to form oxyhalide complexes $[MOCl_4]^-$, $[M(OH)_2Cl_4]^-$, or $[MOCl_5]^{2-}$ at intermediate HCl concentrations, and the formation of pure $[MCl_6]^-$ starts only at very high HCl concentrations (of the order of 10 M). Tantalum, in contrast, forms very stable halide complexes $[TaCl_6]^-$ and $[TaCl_7]^{2-}$ at nearly all HCl concentrations. Since Ha was extracted together with Nb and Pa, in ref 12a the formation of $[HaOCl_4]^-$, $[Ha(OH)_2Cl_4]^-$, or $[HaOCl_5]^{2-}$ was suggested by analogy with Nb and Pa.

Results of the MO calculations⁵⁸ of the electronic structure of different complexes of Nb, Ta, Ha, and Pa were used to analyze the role of different orbitals in bond formation and a tendency of a metal to form covalent bonds with different ligands and their related (coordination) number (CN). As an example, the OP data for complexes with CN = 6, which are formed in the concentrated HCl solutions, are given in Table 18.

Table 18. Partial and Total Overlap Population Data for the $[\text{MCl}_6]^-$ and $[\text{MOCl}_5]^{2-}$ Complexes (from Ref 58)

OP (M–L)	$[\text{NbCl}_6]^-$	$[\text{TaCl}_6]^-$	$[\text{HaCl}_6]^-$	$[\text{PaCl}_6]^-$
M–Cl	0.42	0.50	0.49	0.42
M–6Cl (tot)	2.52	2.97	2.95	2.51
OP (M–L)	$[\text{NbOCl}_5]^{2-}$	$[\text{TaOCl}_5]^{2-}$	$[\text{HaOCl}_5]^{2-}$	$[\text{PaOCl}_5]^{2-}$
M=O	0.78	0.88	0.92	0.83
M–Cl _{eq}	0.34	0.39	0.42	0.36
M–Cl _{ax}	0.36	0.40	0.36	0.28
M–L (tot)	2.51	2.85	2.96	2.57

The data show that the total OP for $[\text{MOCl}_5]^{2-}$ increases in going from the Nb to the Ha complex, while for the $[\text{MCl}_6]^-$ series there is no increase in OP in going from $[\text{TaCl}_6]^-$ to $[\text{HaCl}_6]^-$. (A much smaller overlap of the $7p_{3/2}$ orbitals with valence orbitals of the chlorines leads the total metal–ligand overlap in the Ha complex to be smaller than that in the tantalum complex.) Comparing OP in $[\text{MCl}_6]^-$ and $[\text{MOCl}_5]^{2-}$, one can see that tantalum shows a clear preference to form the pure halide complex, while for niobium and Ha a tendency to form the oxyhalide or halide complex is nearly the same (for Ha there is an even more pronounced trend to form oxyhalide species.) Protactinium would also form oxyhalide complexes rather than the hexahalide ones.

In addition, an analysis of the *trans* effect in the oxypentahalide complexes has shown, that the substitution of oxygen by chlorine is much easier in $[\text{TaOCl}_5]^{2-}$ than in any other compound. In $[\text{HaOCl}_5]^{2-}$ the oxygen is strongly bound.

Thus, the results of the calculations reflected the experimental trends qualitatively: a specific position of Ta in the group and a tendency of Pa and Ha (and Nb at lower concentrations) to form oxyhalide complexes. Ha, having a large IR, was thought also to form complexes with CN higher than 6 in strong HCl solutions by analogy with Pa.

b. Extraction of the Complexes by Anion Exchange with Aliphatic Amines. To describe the extraction behavior of the complexes under discussion from aqueous HCl solutions by aliphatic amines, in ref 58 Born's theory of ionic solvation²²⁸ has been applied to a transfer (ΔG_t) of a complex ion from the aqueous to organic phase, the Bjerrum's theory of an ionic association²²⁹ for the association in the organic phase (ΔG_{ass}). According to the Born theory, the partition coefficient of a complex between an organic and aqueous phase is expressed as

$$P = \frac{C_{\text{org}}}{C_{\text{aq}}} = \frac{\gamma_{\text{aq}}}{\gamma_{\text{org}}} \exp \left[\frac{Ne^2 Z_i^2}{2RT r_i} \left(\frac{1}{\epsilon_{\text{org}}} - \frac{1}{\epsilon_{\text{aq}}} \right) \right] \quad (22)$$

Here r_i is a radius of the extracted ion, Z_i is its charge, and γ_{org} and γ_{aq} are activity coefficients of the solute in the organic and aqueous phases ($\gamma_{\text{aq}}/\gamma_{\text{org}} \approx 1$).²³⁰

DS-DVM results⁵⁸ explain the specific position of Ta in the group (formation of the most covalent $[\text{TaCl}_6]^-$ complex) and its superior extractability from the HCl (back-extraction) or HCl + HF solutions into the organic phase.

For a series of analogous oxyhalide complex ions of Nb, Pa, and Ha, $[\text{MOCl}_5]^{2-}$, $[\text{MOCl}_4]^-$, or $[\text{M(OH)}_2\text{Cl}_4]^-$

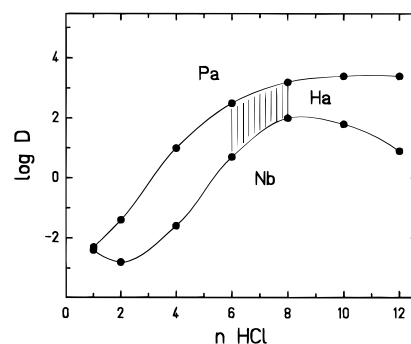


Figure 19. Distribution coefficients of Nb, Pa, and Ha between the triisooctylamin and HCl as a function of the HCl concentration. The experimental data for Nb and Pa are from ref 231. The data for Ha are estimated. (Reproduced from ref 58. Copyright 1994 R. Oldenburg Verlag, München).

$\text{Cl}_4]^-$, ΔG_t and P are finally defined by a size of the extracted anion (eq 22). After the sizes of the anions under discussion were estimated by using the MCDF IR,^{41,42} the following sequence for P has been predicted for them when extracted from pure HCl solutions: $P(\text{Pa}) > P(\text{Ha}) > P(\text{Nb})$ (Figure 19). The strengths of the associated complexes at medium and high HCl concentrations were shown to change in the following way: $K_{\text{ass}}(\text{Nb}) > K_{\text{ass}}(\text{Ha}) > K_{\text{ass}}(\text{Pa})$, where K_{ass} is the association constant. Hydrogen bonding and charge transfer have also been analyzed for these systems.

Although the results obtained by the application of these theories are generally simplified, they still can be reliable, since in practice the electrostatic interaction of the ion association, their size and degree of hydration, allows one to make the right estimates of the extraction.²³¹

Application of the Born theory to back-extraction enabled one to predict the following sequence in the elution of the $[\text{MOCl}_5]^{2-}$, $[\text{MOCl}_4]^-$, or $[\text{M(OH)}_2\text{Cl}_4]^-$ anions:⁵⁸ the smallest anion of Nb should be eluted first, while the largest anion of Pa, the last. The Ha anion will be eluted between those of Nb and Pa.

An interpretation of the extraction from mixed aqueous HCl + HF solutions encounters some difficulties due to the formation of a great variety of complexes, and hence, problems for their identification. In the experiments^{12a} the position of the distribution coefficient of Ha below Nb might be explained by the formation of multicharged mixed chlorofluoro ions, like, e.g. $[\text{HaOF}_x\text{Cl}_y]^{x+y-3}$ or $[\text{HaF}_x\text{Cl}_y]^{x+y-5}$. In the clearer case of the pure aqueous HCl solutions, new experiments²³² are on the way to shed light on the extraction behavior of Ha.

2. Complexes of Group 6 Elements

a. Anionic Complexes in Basic Solutions. In aqueous basic solutions, group 6 elements in macroamounts and on the "one-atom-at-a-time" scale form monomeric oxyanions $[\text{MO}_4]^{2-}$, where M = Cr, Mo, and W. These anions are also structural units of many crystalline compounds, which have been studied experimentally^{233–236} and theoretically.^{237–240} In ref 60 the DS DVM electronic structure calculations have been performed for the solid-state and aqueous-phase tetraoxyanions of Cr, Mo, W, and Sg.

Table 19. Interatomic Distances (R_{M-O}), Effective Charges (Q_M), Total Overlap Populations (OP), Energies of the Charge-Transfer Transitions ($E_{\pi-d}$), Symmetric Stretching Frequencies (ν_1), and Reduction Potentials $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$ for Group 6 Oxyanions (from Ref 60)

anion	R_{M-O} , Å ^a	Q_M	OP	$E_{\pi-d}$, eV	ν_1 , cm ⁻¹ ^a	$E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$, V ^b
CrO ₄ ²⁻	1.609	0.73	2.10	3.64	—	0.10
MoO ₄ ²⁻	1.759	0.71	2.28	4.48	879	-1.00
WO ₄ ²⁻	1.780	0.71	2.81	4.98	922	(-1.55)
SgO ₄ ²⁻	1.840	0.58	2.84	5.05	—	(-1.60)

^a Reference 233–234. ^b Reference 223 (in the parentheses are the estimated values from ref 60).

The information obtained on bonding and stability is useful to understand the extraction behavior of Sg in the future experiments.

In Table 19 some results of the calculations are presented. The trends in the electronic structure data are similar to those found for the group 5 oxyhalide complexes: there is an increase in the covalency (OP) and an increase in the values of the energy gap ΔE between the occupied ligand levels and vacant metal levels in the group and in the energies of the charge-transfer transitions.

The latter are known to be responsible for the luminescence absorption and emission of the solid-state compounds.^{235,236} (Many molybdates and tungstates have strong luminescence with a green and blue emission, respectively.) Since the energies of the charge-transfer transitions of the Sg complex are even higher than those of W, the luminescence of [SgO₄]²⁻ (provided this complex were obtained in a crystalline form) would be even stronger, with the emission being in the blue-violet region. The same might be valid for [HaO₄]³⁻, or [HaO₆]⁷⁻, or [HaO₈]¹¹⁻ which will probably have higher charge-transfer transition energies than those of the corresponding Ta complexes.

In solution, the stability of the [SgO₄]²⁻ complex will be decreased by a hydration energy contribution which is the smallest in the series due to the largest IR(Sg⁶⁺).

However, in this complex, Sg has the maximum stability of the +6 oxidation state in the group (provided the shortest bond lengths are realized). Reduction potentials $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$ for W and Sg have been estimated (see Table 19) by using a linear correlation between the E^0 and the calculated energies of the charge-transfer transitions, corresponding to the process of the reduction (Figure 18).

b. Neutral and Anionic Complexes in Aqueous Acid Solutions. A lot of effort has been devoted to the identification of the Mo and W species in aqueous solutions at various acid concentrations. Using different techniques (e.g. extraction²⁴¹ or spectrophotometry²⁴²) most authors agreed that in aqueous HCl solutions between 2 and 6 M the predominant species are monomeric MoO₂Cl₂, between 6 and 12 M, MoO₂Cl₃⁻, and at the concentrations above 12 M the formation of MoO₂Cl₄²⁻ starts.

Raman and infrared spectra²⁴³ of the solutions containing complexes of Mo and W have confirmed the existence of MoO₂Cl₄²⁻ and WO₂Cl₄²⁻ above 12 M HCl, with MO₂²⁺ having a *cis* configuration. These

investigations have also shown that at 6 M HCl MoO₂Cl₂ exists in the form of the adduct, MoO₂Cl₂(H₂O)₂, favoring the octahedral structure with *cis*-oxy ligands. In organic solutions the adducts have the same form, having organic molecules in the coordination sphere instead of water molecules,²⁴⁴ e.g. *cis*-MoO₂Cl₂(OEt)₂ or MoO₂Cl₂[OPPh₃]₂. For compounds of this type π -donating chloride ligands were found^{244,245} to be in the *trans* position to each other and *cis* to the Mo–O_t bond. This is explained by the fact that the weaker π -bonding donor atoms (*trans* to Mo–O_t) do not compete for the empty p and d orbitals along the same axis. The same is valid for the tungsten compounds.^{244b} Knowing this, one can assume formation of the same types of complexes for Sg.

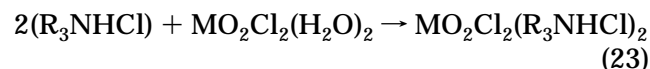
In the process of extraction of these complexes from an aqueous HCl into an organic phase, their dipole moments will be a decisive factor in defining the distribution coefficient. The DS DVM calculations⁶⁴ have shown an increase in the values of dipole moments for group 6 MO₂Cl₂ with increasing Z. Preliminary calculations²⁴⁶ have shown that this will be also the case for MO₂Cl₂(H₂O)₂.

A pseudoanalog within the actinides, uranium, in aqueous HCl solutions at intermediate concentrations is known to form UO₂Cl₂(H₂O)₂. In contrast to the d-element compounds, the uranyl ion UO₂²⁺ has a linear structure thus having no dipole moment. A linear structure is defined by a fd hybridization (U f^{2.6}d^{0.8}s^{0.003} in UO₂²⁺²⁴⁷ or f^{3.01}d^{1.71}s^{0.09} in UO₂Cl₄²⁻²⁴⁸), while a ds hybridization in SgO₂²⁺ (Sg d^{4.1}s^{0.5}⁶⁴) results in an angle structure. The differences in the geometrical configurations and electron density distributions of the U and Sg complexes will be reflected in their extraction into an organic phase.

In aqueous HF solutions group 6 elements are supposed to form the MO₂F₃⁻ complexes around 1 M and MOF₅⁻ at higher molarities. Uranium forms various UO₂F_n^{z-n} complexes, depending on the HF concentration.²⁴⁹

In mixed HF + HCl solutions, at low HCl concentrations (and/or higher HF) the predominant species are oxyfluoride complexes, while at higher HCl molarities neutral and oxychloride complexes are predominant.

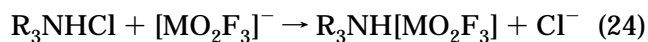
c. Extraction of the Complexes. Results of the extraction of the Mo, W, and U species from aqueous HF solutions on the one hand and from HCl solutions on the other hand by different organic media have shown opposite trends in the distribution coefficients: $D(\text{U}) > D(\text{Mo}) > D(\text{W})$ in HCl solutions^{250–251} and $D(\text{U}) < D(\text{Mo}) < D(\text{W})$ in HF.^{250–252} This is obviously connected with two different extraction mechanisms. In the case of the extraction of the neutral species from the 2–8 M HCl solutions, the mechanism of adduct formation is valid²⁵³



The process of the transfer (ΔG_t) in this case is defined by the strengths of the dipole–dipole interaction of the MO₂Cl₂(H₂O) species with water molecules. Since the dipole moments increase in the group from Mo to Sg, the distribution coefficient will

decrease in this direction. This is in agreement with the experimental data for Mo and W. The absence of a dipole moment for the uranium compound explains its superior extractability.

In the HF solutions or mixed HF + HCl solutions, the anion exchange takes place



Here, the work of transfer will be determined by the sizes of the extracted species (see eq 22). Investigations of the electronic structure and stability of the anionic complexes existing in HF solutions and HF + HCl solutions with the final aim to predict experimental behavior, will be the subject of future work.

XVIII. Summary

Investigations of properties of the transactinide-containing compounds by using modern relativistic molecular codes have brought research to a new level of understanding of the physics and chemistry of the transactinides. The questions about bonding interactions, stability, and influence of relativistic effects on them have become more clear after having performed the MO calculations.

Among applied methods, the LDF methods proved to be very useful. The DS calculations represent the case, where fully relativistic schemes can be applied at present to chemically interesting, complicated systems and still provide sufficient computational accuracy. Such calculations for a large number of the gas-phase molecules and complexes of the transactinides and their analogs in aqueous solutions has enabled one to establish important trends within the transition-element groups and along the transactinide series for such molecular properties as ionicity, covalency, stability toward oxidation or reduction, crystal-field and spin-orbit effects, bonding, and the influence of relativistic effects on them. Thus, e.g., relativistic effects were shown to be responsible for a continuation of the trends in properties in the groups with increasing Z . Consequently, they are a reason for an increase in covalency and bonding. For the highest halides and oxyhalides they are responsible for an increase in ionization potentials, a decrease in electron affinity, larger energy gaps and energies of the charge-transfer transitions, spin-orbit and crystal-field splittings. They are also a reason for an increase in the stability of the maximum oxidation states in the groups.

The bonding was also shown to be dependent on group, type of ligand, and coordination. Thus, along the transactinide series a decrease was found in metal-ligand bonding for the highest halides, in the formation enthalpies and in the stability of the maximum oxidation state. There are also some peculiarities in the electronic structure of individual compounds which are accounted for by strong relativistic effects.

Recent improvements in the LDF codes for the exchange-correlation potentials and integration schemes allow their use for accurate calculations of binding energies and optimization of geometry.

Application of the RCP methods is without doubt very useful in defining ground and excited states of

open-shell compounds, electronic excited state spectra, and potential energy surfaces. In combination with accurate correlation schemes they give at present reliable predictions for diatomic molecules of the very heavy elements, although the computational efforts are very high. In addition, use of sophisticated correlation schemes comes at the expense of ease in the interpretation of the wave function.

More sophisticated all electron *ab initio* methods are just beginning to be applied to transactinide systems. Nevertheless for chemically interesting compounds they still encounter methodical (correlation part) and computational difficulties and can be prohibitively expensive. Thus, we share the opinion of Pepper and Bursten¹¹⁸ that a combination of LDF and all-electron *ab initio* calculations is the best approach to study the actinide and transactinide systems whose chemistry still has quite a number of open questions.

These questions are the following: regularities in properties along the entire transactinide series and the influence of relativistic effects on them; the stability of oxidation states for Sg, Ns, and heavier elements; redox potentials in aqueous solutions (since starting with these elements lower oxidation states become predominant); stereochemistry of Ns compounds (since compounds of its lighter analogs, Tc and Re, having the same chemical formula, can exhibit different geometrical configurations); stability of transactinide compounds in lower oxidation states; and some others.

All these questions need to be solved by a complex approach, including accurate atomic and molecular calculations, as well as a use of different qualitative and quantitative models. Thus, e.g., interpretation of experimental results from the gas-phase chromatography needs a further step to the calculation of physisorption in order to make a quantitative prediction of the adsorption enthalpy of the studied compounds. For the very heavy relativistic systems this work still represents a challenge for modern quantum chemistry.

Acknowledgments

The author gratefully acknowledges the financial support of the Deutsche Forschungsgemeinschaft and Gesellschaft für Schwerionenforschung, Darmstadt. She is grateful for the support from and useful discussions with Professor B. Fricke and colleagues at the Physics Department of the University of Kassel (especially Dr. T. Bastug), as well as with Professor G. Ionova. She thanks Dr. E. Eliav for the comments on the relativistic *ab initio* methods and Professor G. Malli for providing preliminary results.

XIV. References

- (1) Hoffmann, S.; Ninov, V.; Hessberger, F. P.; Armbruster, P.; Folger, H.; Münzenberg, G.; Schött, H. J.; Popeko, A. G.; Yereimin, A. V.; Saro, S.; Janik, R.; Leino, M. *Z. Phys. A* **1996**, *354*, 229.
- (2) (a) Hoffmann, S.; Ninov, V.; Hessberger, F. P.; Armbruster, P.; Folger, H.; Münzenberg, G.; Schött, H. J.; Popeko, A. G.; Yereimin, A. V.; Andreev, A. N.; Saro, S.; Janik, R.; Leino, M. *Z. Phys. A* **1995**, *350*, p 277. (b) Hoffmann, S.; Ninov, V.; Hessberger, F. P.; Armbruster, P.; Folger, H.; Münzenberg, G.; Schött, H. J.; Popeko, A. G.; Yereimin, A. V.; Andreev, A. N.; Saro, S.; Janik, R.; Leino, M. *Z. Phys. A* **1995**, *350*, 281.

- (3) (a) Loughheed, R. W.; Moody, K. J.; Wild, J. F.; Hulet, E. K.; McQuiad, J. H.; Lazarev, Yu. A.; Lobanov, Yu. V.; Oganessian, Yu. Ts.; Utyonkov, V. K.; Abdullin, F. Sh.; Buklanov, G. V.; Gikal, B. N.; Iliev, S.; Mezentsev, A. N.; Polyakov, A. N.; Sedykh, I. M.; Shirokovsky, I. V.; Subbotin, V. G.; Sukhov, A. M.; Tsyganov, Yu. S.; Zhuchko, V. E. *J. Alloys Compd.* **1994**, *213/214*, 61. (b) Schädel, M. and Hoffman, S. *J. Radioanal. Nucl. Chem.* **1996**, *203*, 283.
- (4) Jost, D. T.; Gäggeler, H. W.; Vogel, Ch.; Schädel, M.; Jäger, E.; Eichler, B.; Gregorich, K. E.; Hoffman, D. C. *Inorg. Chim. Acta* **1988**, *146*, 255.
- (5) (a) Scherer, U. W.; Kratz, J. V.; Schädel, M.; Brüchle, W.; Gregorich, K. E.; Henderson, R. A.; Lee, D.; Nurmia, M.; Hoffman, D. C. *Inorg. Chim. Acta* **1988**, *146*, 249. (b) Loughheed, R. W.; Moody, K. J.; Dougan, R. J.; Wild, J. F.; Hulet, E. K. LLNL Nuclear Chemistry Division Annual Report, UCAR 10062-88; 1988, p 130.
- (6) Chuburkov, Yu. T.; Belov, V. Z.; Tsaletka, R.; Shalaevskii, M. R.; Zvara, I. *Radiokhimiya* **1969**, *11*, 394.
- (7) (a) Zvara, I.; Chuburkov, Y. T.; Belov, V. Z.; Buklanov, G. V.; Zakhvataev, B. B.; Zvarova, T. S.; Maslov, O. D.; Caletka, R.; Shalaevsky, M. R. *J. Inorg. Chem.* **1970**, *32*, 1885. (b) Zvara, I.; Belov, V. Z.; Chelnokov, L. B.; Domanov, V. P.; Hussonois, M.; Korotkin, Yu. S.; Schegolev, V. A.; Shalayeviskii, M. R. *Inorg. Nucl. Chem.* **1971**, *7*, 1109.
- (8) (a) Zvara, I.; Eichler, B.; Belov, V. Z.; Zvarova, T. S.; Korotkin, Yu. S.; Shalaevskii, M. R.; Schegolev, V. A.; Hussonois, M. *Radiokhimiya* **1974**, *16*, 720. (b) Zvara, I. In *Transplutonium Elements*; Müller, W., Lindner, R., Eds.; North-Holland: Amsterdam, 1976; pp 11–20. (c) Zvara, I.; Belov, V. Z.; Domanov, V. P.; Shalaevskii, M. R. *Radiokhimiya* **1976**, *18*, 371. (d) Zvara, I. In *Proceedings of the International School-Seminar on Heavy Ion Physics*, JINR D7-87-68 Dubna, 1987; p 145; (e) Zvara, I. In *Abstracts of Int. Conf. "Actinides-89"*, Tashkent, Sept 24–29, 1989; Nauka: Moscow, 1989; p 989. (f) Timokhin, S. N.; Kim U. Jin, Domanov, V. P.; Chuburkov, Yu. T.; Zhuikov, B. L.; Gavrilov, K. A.; Zvara, I. In *Abstracts of Int. Conf. "Actinides-89"*, Tashkent, Sept. 24–29, 1989; Nauka: Moscow, 1989; p 227. (g) Eichler, B.; Domanov, V. P.; Zvara, I. Report JINR 12-9454, Dubna, 1976.
- (9) (a) Gäggeler, H. W.; Jost, D. T.; Kovacs, J.; Scherer, U. W.; Weber, A.; Vermeulen, D.; Kratz, J. V.; Gober, M. K.; Zimmermann, H. P.; Schädel, M.; Brüchle, W.; Zvara, I.; Türler, A.; Gregorich, K. E.; Henderson, R. A.; Czerwinski, K. R.; Kadkhodayan, B.; Lee, D. M.; Nurmia, M.; Hoffman, D. C. *Radiochim. Acta* **1992**, *57*, 93. (b) Türler, A.; Gäggeler, H. W. Private communication, 1994. (c) Türler, A.; Eichler, B.; Jost, D. T.; Piguet, D.; Gäggeler, H. W.; Gregorich, K. E.; Kadkhodayan, B.; Kreek, S. A.; Lee, D. M.; Mohar, M.; Sylwester, E.; Hoffman, D. C.; Hübener, S. *Radiochim. Acta* **1996**, *73*, 55. (d) Kadkhodayan, B. On line gas chromatographic studies of rutherfordium (element 104), hahnium (element 105), and homologs. Doctoral dissertation, Lawrence Berkeley Laboratory, May 1993. (e) Kadkhodayan, B.; Türler, A.; Gregorich, K. E.; Baisden, P. A.; Czerwinski, K. R.; Eichler, B.; Gäggeler, H. W.; Hamilton, T. M.; Jost, D. T.; Kacher, C. D.; Kovacs, A.; Kreek, S. A.; Lane, M. R.; Mohar, M. F.; Neu, M. P.; Stoyer, N. J.; Sylwester, E. R.; Lee, D. M.; Nurmia, M. J.; Seaborg, G. T.; Hoffman, D. C. *Radiochim. Acta* **1996**, *72*, 169. (f) Gäggeler, H. W. *J. Radioanal. Nucl. Chem., Art.* **1994**, *183*, 261. (g) Türler, A.; Gäggeler, H. W.; Gregorich, K. E.; Barth, H.; Brüchle, W.; Czerwinski, K. R.; Gober, M. K.; Hannik, N. J.; Henderson, R. A.; Hoffman, D. C.; Jost, D. T.; Kacher, C. D.; Kadkhodayan, B.; Kovacs, J.; Kratz, J. V.; Kreek, S. A.; Lee, D. M.; Leyba, J. D.; Nurmia, M. J.; Schädel, M.; Scherer, U. W.; Schimpf, E.; Vermeulen, D.; Weber, A.; Zimmermann, H. P.; Zvara, I. *Radioanal. Nucl. Chem.* **1992**, *160*, 327. (h) Türler, A. *Radiochim. Acta* **1996**, *72*, 7.
- (10) (a) Silva, R. J.; Harris, J.; Nurmia, M.; Eskola, K.; Ghiorso, A. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 871. (b) Hulet, E. K.; Loughheed, R. W.; Wild, J. F.; Landrum, J. H.; Nitschke, J. M.; Ghiorso, A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 79. (c) Hulet, E. K. *Radiochim. Acta* **1983**, *32*, 7. (d) Brüchle, W.; Scherer, U. W.; Kratz, J. V.; Gregorich, K. E.; Lee, D. M.; Nurmia, M.; Chasterler, R. M.; Hall, H. L.; Henderson, R. A.; Hoffman, D. C. *Inorg. Chim. Acta* **1988**, *146*, 267.
- (11) (a) Gregorich, K. E.; Henderson, R. A.; Lee, D. M.; Nurmia, M. J.; Chasterler, R. M.; Hall, H. L.; Bennett, D. A.; Gannett, C. M.; Chadwick, R. B.; Leyba, J. D.; Hoffman, D. C.; Herrmann, G. *Radiochim. Acta* **1988**, *43*, 223. (b) Czerwinski, K. R.; Gregorich, K. E.; Hannik, N. J.; Kacher, C. D.; Kadkhodayan, B. A.; Kreek, S. A.; Lee, D. M.; Nurmia, M. J.; Türler, A.; Seaborg, G. T.; Hoffman, D. C. *Radiochim. Acta* **1994**, *64*, 23. (c) Czerwinski, K. R.; Gregorich, K. E.; Hannik, N. J.; Kacher, C. D.; Kadkhodayan, B. A.; Kreek, S. A.; Lee, D. M.; Nurmia, M. J.; Türler, A.; Seaborg, G. T.; Hoffman, D. C. *Radiochim. Acta* **1994**, *64*, 29.
- (12) (a) Kratz, J. V.; Zimmermann, H. P.; Scherer, U. W.; Schädel, M.; Brüchle, W.; Gregorich, K. E.; Gannett, C. M.; Hall, H. L.; Henderson, R. A.; Lee, D. M.; Leyba, J. D.; Nurmia, M.; Hoffman, D. C.; Gäggeler, H. W.; Jost, D.; Baltensperger, U.; Ya Nai-Qi, Türler, A.; Lienert, Ch. *Radiochim. Acta* **1989**, *48*, 121. (b) Zimmermann, H. P.; Gober, M. K.; Kratz, J. V.; Schädel, M.; Brüchle, W.; Schimpf, E.; Gregorich, K. E.; Türler, A.; Czerwinski, K. R.; Hannik, N. J.; Kadkhodayan, B.; Lee, D. M.; Nurmia, M. J.; Hoffman, D. C.; Gäggeler, H.; Jost, D.; Kovacs, J.; Scherer, U. W.; Weber, A. *Radiochim. Acta* **1993**, *60*, 11. (c) Gober, M. K.; Kratz, J. V.; Zimmermann, H. P.; Schädel, M.; Brüchle, W.; Schimpf, E.; Gregorich, K. E.; Türler, A.; Hannik, N. J.; Czerwinski, K. R.; Kadkhodayan, B.; Lee, D. M.; Nurmia, M. N.; Hoffman, D. C.; Gäggeler, H.; Jost, D.; Kovacs, J.; Scherer, U. W.; Weber, A. GSI Report, GSI-91-57, October, 1991.
- (13) (a) Türler, A.; Yakushev, A. B.; Eichler, B.; Gäggeler, H. W.; Jost, D. T.; Scherrer, U. W. PSI Annual Report 1993, March 1994, p 43. (b) Hoff, A.; Hübener, S.; Eichler, B.; Gäggeler, H. W.; Türler, A.; Jost, D. T.; Yakushev, A. B. PSI Annual Report 1993, March 1994, p 44. (c) Eberhardt, K.; Herrmann, G.; Nähler, A.; Pense-Maskow, M.; Trautmann, N.; Wierczinski, B.; Skarnemark, G.; Alstadt, J.; Eichler, B.; Gäggeler, H.; Jost, D.; Türler, A.; Reddy, A. V. R. GSI Scientific Report 1993, March 1994; p 239. (d) Schumann, D.; Fischer, S.; Taut, St.; Dressler, R.; Novgorodov, A. F.; Misiak, R.; Trautmann, N.; Schädel, M.; Brucherseifer, H. GSI Scientific Report 1993, March 1994; p 241. (e) Schumann, D.; Fischer, S.; Taut, St.; Dressler, R.; Binder, R.; Brucherseifer, H.; Eichler, B.; Gäggeler, H. W.; Jost, D. T.; Türler, A. PSI Annual Report 1993, March 1994, p 51. (f) Becker, H. U.; Kratz, J. V.; Brüchle, W.; Schädel, M. GSI Scientific Report 1993, March 1994, p 242. (g) Eberhardt, K.; Herrmann, G.; Nähler, A.; Pense-Maskow, M.; Trautmann, N.; Wierczinski, B.; Skarnemark, G.; Alstadt, J.; Eichler, B.; Gäggeler, H.; Jost, D.; Türler, A.; Reddy, A. V. R. PSI Annual Report 1993, March 1994, p 52.
- (14) Seaborg, G. T. *Annu. Rev. Nucl. Sci.* **1968**, *18*, 53.
- (15) Keller, O. L.; Seaborg, G. T. *Annu. Rev. Nucl. Sci.* **1977**, *27*, 139.
- (16) Keller, O. L. *Radiochim. Acta* **1984**, *37*, 169.
- (17) Silva, R. J. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morrs, L. R., Eds.; Chapman and Hall: London, 1986; Vol. 2, p 1103.
- (18) Hoffman, D. C. XXXIV Fifty Years With Transuranium Elements. In *Proceedings of The Robert A. Welch Foundation Conference on Chemical Research*, R. Welch Foundation: Houston, TX, 1990, p 255.
- (19) Hoffman, D. C. In *Transuranium Elements: A Half Century*; Morss, L. R., Fuger, J., Eds.; Washington: American Chemical Society, 1992; p 104.
- (20) Hoffman, D. C. *Radiochim. Acta* **1983**, *32*, 7.
- (21) Hoffman, D. C. *Chem. Eng. News* **1994**, May, 24.
- (22) Hulet, E. K. *Radiochim. Acta* **1983**, *32*, 7.
- (23) Seaborg, G. T. *J. Chem. Educ.* **1985**, *62*, 463.
- (24) Seaborg, G. T.; Walter, D. L. *The Elements Beyond Uranium*; John Wiley & Sons, Inc.: New York, 1990.
- (25) (a) Schädel, M. Nuclei Far From Stability. In *Proceedings of the 6th Int. Conf., Bernkastel-Kues*, 1992, Neugart, R., Wöhr, A., Eds.; Institute of Physics Conference Series Number 132, Institute of Physics Publishing: Bristol, 1993; pp 413–422. (b) Schädel, M. A. *Radiochim. Acta* **1995**, *70/71*, 207. (c) Kratz, J. V. *Chem. Unserer Zeit* **1995**, *4*, 194.
- (26) Fricke, B.; Waber, J. T. *J. Chem. Phys.* **1972**, *57*, 351.
- (27) Waber, J. T.; Cromer, D. T.; Lieberman, D. J. *Chem. Phys.* **1969**, *51*, 664.
- (28) Fricke, B.; Greiner, W.; Waber, J. T. *Theoret. Chim. Acta (Berlin)* **1971**, *21*, 235.
- (29) Mann, J. B. *J. Chem. Phys.* **1969**, *51*, 841. (b) Mann, J. B.; Waber, J. T. *J. Chem. Phys.* **1970**, *53*, 2397. (c) Mann, J. B.; Waber, J. T. *At. Data* **1973**, *5*, 201. (d) Mann, J. B.; Waber, J. T. *J. Chem. Phys.* **1975**, *53*, 2397.
- (30) Keller, O. L.; Nestor, C. W.; Carlson, T. A.; Fricke, B. *J. Phys. Chem.* **1973**, *77*, 1806.
- (31) Keller, O. L., Jr.; Nestor, C. W., Jr.; Fricke, B. *J. Phys. Chem.* **1974**, *78*, 1945.
- (32) Coulthard, M. A. *Proc. Phys. Soc.* **1967**, *91*, 44.
- (33) (a) Hässinsky, M. *Radiochem. Radioanal. Lett.* **1971**, *8*, 107. (b) Hässinsky, M. *J. Chim. Phys.* **1972**, *5*, 845.
- (34) Penneman, R. A.; Mann, J. B. *J. Inorg. Nucl. Chem., Suppl.* **1976**, 257.
- (35) Cunningham, B. B. The Transuranium Elements. In *Proceedings of the Robert A. Welch Foundation Conference on Chemical Research XIII*. Milligan, W. O., Ed.; R. Welch Foundation: Houston, TX, 1970; Chapter XI.
- (36) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311.
- (37) Fricke, B.; Waber, J. T. *Actinides Rev.* **1971**, *1*, 433.
- (38) Fricke, B. *Struct. Bond.* **1975**, *21*, 89.
- (39) Desclaux, J.-P.; Fricke, B. *J. Phys.* **1980**, *41*, 943.
- (40) Glebov, V. A.; Kasztura, L.; Nefedov, V. S.; Zhuikov, B. L. *Radiochim. Acta* **1989**, *46*, 117.
- (41) Johnson, E.; Fricke, B.; Keller, O. L., Jr.; Nestor, C. W., Jr.; Tucker, T. C. *J. Chem. Phys.* **1990**, *93*, 8041.
- (42) Fricke, B.; Johnson, E.; Rivera, G. M. *Radiochim. Acta* **1993**, *62*, 17.
- (43) Johnson, E.; Fricke, B. *J. Phys. Chem.* **1991**, *95*, 7082.

- (44) (a) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1985**, *89*, 3310. (b) Bratsch, S. G.; Lagowski, J. J. *J. Phys. Chem.* **1986**, *90*, 307.
- (45) (a) Rosen, A.; Fricke, B.; Morovic, T. *Phys. Rev. Lett.* **1978**, *40*, 856. (b) Waber, J. T.; Averill, F. M. *J. Chem. Phys.* **1974**, *60*, 4466.
- (46) Rosen, A.; Fricke, B.; Morovic, T.; Ellis, D. E. *J. Phys. C-4, Suppl.* **1979**, *40*, C-4/218.
- (47) (a) Pyykkö, P.; Desclaux, J.-P. *Chem. Phys. Lett.* **1977**, *50*, 503. (b) Pyykkö, P.; Desclaux, J.-P. *Nature (London)* **1977**, *226*, 336.
- (48) Pyykkö, P.; Desclaux, J.-P. *Chem. Phys.* **1978**, *34*, 261.
- (49) Zhuikov, B. L.; Glebov, V. A.; Nefedov, V. S.; Zvara, I. *J. Radioanal. Nucl. Chem.* **1990**, *143*, 103.
- (50) Ryzhkov, M. V.; Gubanov, V. A.; Zvara, I. *Radiochim. Acta* **1992**, *57*, 11.
- (51) Pershina, V. G.; Ionova, G. V.; Suraeva, N. I. *Croat. Chim. Acta* **1989**, *62*, 763.
- (52) Pershina, V.; Sepp, W.-D.; Fricke, B.; Rosen, A. *J. Chem. Phys.* **1992**, *96*, 8367.
- (53) Pershina, V.; Sepp, W.-D.; Fricke, B.; Kolb, D.; Schädel, M.; Ionova, G. V. *J. Chem. Phys.* **1992**, *97*, 1116.
- (54) Pershina, V.; Sepp, W.-D.; Bastug, T.; Fricke, B.; Ionova, G. V. *J. Chem. Phys.* **1992**, *97*, 1123.
- (55) Ionova, G. V.; Pershina, V.; Johnson, E.; Fricke, B.; Schädel, M. *J. Phys. Chem.* **1992**, *96*, 11096.
- (56) Pershina, V.; Fricke, B.; Ionova, G. V.; Johnson, E. *J. Phys. Chem.* **1994**, *98*, 1482.
- (57) Pershina, V.; Fricke, B. *J. Chem. Phys.* **1993**, *99*, 9720.
- (58) Pershina, V.; Fricke, B.; Kratz, J. V.; Ionova, G. V. *Radiochim. Acta* **1994**, *64*, 37.
- (59) Pershina, V.; Fricke, B.; Ionova, G. V. *J. Alloys Compd.* **1994**, *213/214*, 33.
- (60) Pershina, V.; Fricke, B. *Radiochim. Acta* **1994**, *65*, 13.
- (61) Pershina, V.; Fricke, B. *J. Phys. Chem.* **1994**, *98*, 6468.
- (62) Pershina, V.; Fricke, B. *J. Phys. Chem.* **1995**, *99*, 144.
- (63) (a) Ionova, G. V.; Pershina, V.; Zuraeva, I. T.; Suraeva, N. I. *Russ. J. Inorg. Chem.* **1995**, *40*, 1019. (b) Ionova, G. V.; Pershina, V.; Zuraeva, I. T.; Suraeva, N. I. *Russ. J. Inorg. Chem.* **1995**, *40*, 1023. (c) Ionova, G. V.; Pershina, V.; Zuraeva, I. T.; Suraeva, N. I. *Russ. J. Inorg. Chem.* **1996**, *41*, 167. (d) Ionova, G. V.; Pershina, V.; Zuraeva, I. T.; Suraeva, N. I. *Radiochem.* **1995**, *37*, 282.
- (64) (a) Pershina, V.; Fricke, B. *J. Phys. Chem.* **1996**, *100*, 8748. (b) Pershina, V.; Bastug, T.; Fricke, B. Manuscript in preparation.
- (65) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J. Phys. Chem.* **1993**, *97*, 5852.
- (66) (a) Malli, G. L. In *Relativistic and Electron Correlation Effects in Molecules and Solids*. Malli, G. L., Ed.; NATO ASI Series, B: Physics; Plenum Press: New York, 1994; Vol. 318, p 1. (b) Malli, G. L. Presented at an invited talk "Ab-initio All-Electron Fully Relativistic Dirac-Fock Calculations for Compounds of the Trans-Lawrencium Elements", Lawrence Berkeley National Laboratory, August 14, 1995. (c) Malli, G. L.; Silva, A. B. F.; Ishikawa, Y. *Phys. Rev. A* **1993**, *47*, 143. (d) Malli, G. L.; Styszynski, J. *J. Chem. Phys.* **1994**, *101*, 10736. (e) Malli, G. L.; Styszynski, J. *J. Chem. Phys.* **1996**, *104*, 1012. (f) Lau, K. H.; Brittain, R. D.; Hildenbrand, D. L. *J. Chem. Phys.* **1989**, *90*, 1158. Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1982**, *76*, 2646; **1984**, *80*, 1312; **1987**, *86*, 2949.
- (67) (a) Seth, M.; Dolg, M.; Faegri, K.; Hess, B. A.; Kaldor, U.; Schwerdtfeger, P. *Chem. Phys. Lett.* **1996**, *250*, 461. (b) Seth, M.; Schwerdtfeger, P. *J. Phys. Chem.* **1996**, submitted for publication.
- (68) Nash, C. S.; Bursten, B. E. *New J. Chem.* **1995**, *19*, 669.
- (69) Coulthard, M. A. *Proc. Phys. Soc.* **1967**, *91*, 44.
- (70) Fricke, B.; Greiner, W. *Phys. Lett.* **1969**, *30B*, 317.
- (71) Pyykkö, P. *Relativistic Theory of Atoms and Molecules*. A. Bibliography 1916–1985. *Lect. Notes Chem.* **1986**, 41.
- (72) (a) Grant, I. P. *Adv. Phys.* **1970**, *19*, 747. (b) Grant, I. P.; Quiney, H. M. *Adv. At. Mol. Phys.* **1988**, *23*, 37. (c) Desclaux, J.-P. *Comput. Phys. Commun.* **1975**, *9*, 31.
- (73) (a) Quiney, H. M. In *The Effects of Relativity in Atoms, Molecules and the Solid State*; Wilson, S., Grant, P., Gyorffy, B. L., Eds.; Plenum: New York, 1991; p 83. (b) Wilson, S. In *The Effects of Relativity in Atoms, Molecules and the Solid State*; Wilson, S., Grant, P., Gyorffy, B. L., Eds.; Plenum: New York, 1991; p 149.
- (74) Blundell, S. A.; Johnson, W. R.; Sapirsten, J. *Phys. Rev. A* **1988**, *37*, 2764.
- (75) Shukla, A.; Das, B. P.; Andriessen, J. *Phys. Rev. A* **1994**, *50*, 1155.
- (76) Ishikawa, I.; Koc, K. *Phys. Rev. A* **1994**, *50*, 4733.
- (77) Hartley, A. C.; Martensson-Pendrill, A. M. *J. Phys. B* **1991**, *24*, 1193.
- (78) (a) Salomonsson, S.; Lindgren, I.; Martensson, A.-M. *Phys. Scr.* **1980**, *21*, 351. (b) Lindgren, I.; Morrison, J. *Atomic Many-Body Theory*, 2nd ed.; Springer-Verlag: Berlin, 1986. (c) Lindgren, I. *Phys. Scr.* **1991**, *34*, 36.
- (79) Mukherjee, D.; Pal, S. *Adv. Quantum Chem.* **1989**, *20*, 292.
- (80) (a) Ishikawa, Y.; Quiney, H. M. *Int. J. Quantum Chem., Symp.* **1987**, *21*, 523. (b) Ishikawa, Y. *Chem. Phys. Lett.* **1990**, *165*, 243.
- (81) Matsuoka, O.; Okada, S. *Chem. Phys. Lett.* **1989**, *155*, 547.
- (82) (a) Ilyabaev, E.; Kaldor, U. *Chem. Phys. Lett.* **1992**, *194*, 95. (b) Ilyabaev, E.; Kaldor, U. *Phys. Rev.* **1993**, *A 47*, 137. (c) Ilyabaev, E.; Kaldor, J. *Chem. Phys.* **1992**, *97*, 8455.
- (83) (a) Eliav, E.; Kaldor, U.; Ishikawa, Y. *Phys. Rev. A* **1994**, *49*, 1724. (b) Eliav, E.; Kaldor, U.; Ishikawa, Y. *Phys. Rev. A* **1994**, *50*, 1121.
- (84) Eliav, E.; Kaldor, U.; Ishikawa, Y. *Phys. Rev. Lett.* **1995**, *74*, 1079.
- (85) (a) Eliav, E.; Kaldor, U.; Schwerdtfeger, P.; Hess, B. A.; Ishikawa, Y. *Phys. Rev. Lett.* **1994**, *73*, 3203. (b) Eliav, E.; Kaldor, U.; Ishikawa, Y. *Phys. Rev. A* **1995**, *52*, 2765. (c) Eliav, E.; Kaldor, U.; Ishikawa, Y.; Seth, M.; Pyykkö, P. *Phys. Rev. A* **1996**, *53*, 3926.
- (86) Eliav, E.; Kaldor, U.; Ishikawa, Y. *Phys. Rev. A* **1995**, *52*, 291.
- (87) Liu, Z. W.; Kelly, H. P. *Phys. Rev. A* **1991**, *43*, 3305.
- (88) (a) Blindell, S. A.; Johnson, W. R.; Sapirstein, J. *Phys. Rev. A* **1991**, *43*, 3407. (b) Blindell, S. A.; Hartley, A. C.; Liu, Z.; Martensson-Pendrill, A.-H.; Sapirstein, J. *Theor. Chim. Acta* **1991**, *80*, 257. (c) Lindroth, E.; Ynnerman, A. *Phys. Rev. A* **1993**, *47*, 961.
- (89) Brewer, L. *J. Opt. Soc. Am.* **1971**, *61*, 1102.
- (90) Johnson, E. Private Communication, 1994.
- (91) Bylander, D. M.; Kleinman, L. *Phys. Rev. Lett.* **1983**, *51*, 889.
- (92) (a) Pyykkö, P. *Adv. Quantum Chem.* **1978**, *11*, 353. (b) Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276.
- (93) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271.
- (94) Ionova, G. V.; Pershina, V. G.; Spitsyn, V. I. *Zh. Neorg. Khim. (Sov.)* **1983**, *28*, 3107.
- (95) Ionova, G. V.; Pershina, V. G.; Spitsyn, V. I. *Electronic Structure of the Actinides*; Moscow: Nauka, 1976 (in Russian).
- (96) *Relativistic Effects in Atoms, Molecules, and Solids*; Malli, G. L., Ed.; Plenum Press: New York, 1983.
- (97) Christiansen, P. A.; Ermler, W. C.; Pitzer, K. S. *Annu. Rev. Phys. Chem.* **1985**, *36*, 407.
- (98) Balasubramanian, K.; Pitzer, K. S. *Adv. Chem. Phys.* **1987**, *67*, 287.
- (99) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.
- (100) Seth, M.; Dolg, M.; Fulde, P.; Schwerdtfeger, P. *J. Am. Chem. Soc.* **1995**, *117*, 6597.
- (101) (a) Moore, C. E. *Atomic Energy Levels*; Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.: Washington, DC, 1971; NSRDS-NBS 35, SD Catalog No. C13.48:35. (b) Moore, C. E. *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra*; Natl. Stand. Ref. Data Ser., Natl. Stand.: Washington, DC, 1970; NSRDS-NBS 34, SD Catalog No. C 13.48:34.
- (102) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
- (103) (a) Hübener, S.; Zvara, I. *Radiochim. Acta* **1982**, *31*, 89. (b) Hübener, S. *Radiochim. Radioanal. Lett.* **1980**, *44*, 79.
- (104) Eichler, B.; Domanov, V. P.; Zvara, I. JINR Dubna Report, P12-9454, 1976.
- (105) Eichler, B.; Hübener, S.; Gäggeler, H. W.; Jost, D. T. *Inorg. Chim. Acta* **1988**, *146*, 261.
- (106) Brewer, L. *J. Opt. Soc. Am.* **1971**, *61*, 1101.
- (107) Nugent, I. J.; Burnett, J. L.; Morss, L. R. *J. Chem. Thermodyn.* **1973**, *5*, 665.
- (108) Johansson, B. *Phys. Rev. B* **1975**, *11*, 1367.
- (109) David, F.; Samhoun, K.; Guillaumont, R.; Edelstein, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 69.
- (110) Kleinschmidt, P. D.; Ward, J. W.; Haire, R. G. *Proc. of Symposium on High Temperature Materials*; Munir, Z. A., Cubicciotti, D., Eds.; The Electrochemical Society, Inc.: Pennington, NJ, 1983; Chem. II; Vol. 83, pp 23–31.
- (111) Zhuikov, B. L.; Chuburkov, Yu. T.; Timokhin, S. N.; Kim U Jin, Zvara, I. *Radiochim. Acta* **1989**, *46*, 113.
- (112) (a) Eichler, B. PSI Annual Report 1993, March 1994, p 38; (b) PSI Annual Report 1993, March 1994, p 40; (c) Eichler, B.; Rossbach, H. *Radiochim. Acta* **1983**, *33*, 121. (d) Eichler, B.; Hübener, S. GSI Scientific Report 1991, GSI 92-1, March 1992, p 323. (e) Eichler, B.; Türler, A.; Gäggeler, H. W. PSI Annual Report 1994, March 1995, p 34. (f) Eichler, B.; Türler, A.; Gäggeler, H. W. PSI Annual Report 1994, March 1995, p 35.
- (113) Brewer, L. In *Phase Stability in Metals and Alloys*; McGraw-Hill: New York, 1967; p 39.
- (114) Samsonov, G. V.; Pryadko, I. F.; Pryadko, L. F. *A Configurational Model of Matter*; Consultants Bureau, Plenum Publishing Co.: New York, 1973.
- (115) (a) Pecora, L.; Ficalora, P. J. *Solid State Chem.* **1979**, *27*, 239. (b) Brooks, M. S. S.; Johansson, B.; Skriver, H. L. In *Handbook on the Physics and Chemistry of the Actinides*; Freeman, A. J., Lander, J. H., Eds.; Elsevier: Amsterdam, 1984; Vol. 1, p 153.
- (116) Glushko, V. P. *Thermodynamic Properties of Individual Substances*; Nauka: Moscow, 1982; Vol. 4 (in Russian).
- (117) (a) Pyykkö, P., Ed. *Int. J. Quantum Chem.* **1984**, *25*(1), 1. (b) Pyykkö, P. *Adv. Quantum Chem.* **1978**, *11*, 353.
- (118) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719.
- (119) *Relativistic and Correlation Effects in Molecules and Solids*; Malli, G. L., Ed.; NATO ASI Series, Series B: Physics; Plenum Press: New York, 1994; Vol. 318.

- (120) Makrodt, W. C. *Mol. Phys.* **1970**, *18*, 697.
- (121) Desclaux, J. P. ref 96; pp 213–225.
- (122) (a) Desclaux, J. P.; Pyykkö, P. *Chem. Phys. Lett.* **1974**, *29*, 534. (b) Desclaux, J. P.; Pyykkö, P. *Chem. Phys. Lett.* **1976**, *39*, 300. (c) Pyykkö, P.; Desclaux, J. P. *Chem. Phys. Lett.* **1976**, *42*, 545.
- (123) Snijders, J. G.; Pyykkö, P. *Chem. Phys. Lett.* **1980**, *75*, 5.
- (124) Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050.
- (125) (a) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1978**, *36*, 1789. (b) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.
- (126) Ellis, D. E. *Int. J. Quantum Chem. Symp.* **1968**, *2*, 35.
- (127) Ziegler, T.; Snijders, J. G.; Baerends, E. J. *Chem. Phys. Lett.* **1980**, *75*, 1.
- (128) Ziegler, T.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1981**, *74*, 1271.
- (129) Koelling, D. D.; Harmon, B. N. *J. Phys. C* **1977**, *10*, 3107.
- (130) Boring, M.; Wood, J. H. *J. Chem. Phys.* **1979**, *71*, 392.
- (131) Thornton, G.; Edelstein, N.; Rösch, N.; Egdel, R. G.; Woodwark, D. R. *J. Chem. Phys.* **1979**, *70*, 5218.
- (132) (a) Topol, I. A.; Kovba, V. M.; Osina, E. L. *Theor. Chim. Acta* **1986**, *64*, 217. (b) Kovba, V. M.; Topol, I. A. *J. Mol. Struct. (Theochem.)* **1986**, *137*, 65.
- (133) (a) Yang, C. Y.; Rabii, S. *Phys. Rev. A* **1975**, *12*, 362. (b) Yang, C. V. *J. Chem. Phys.* **1978**, *68*, 2626.
- (134) Case, D. A.; Yang, C. Y. *J. Chem. Phys.* **1980**, *72*, 3443.
- (135) Soldatov, A. A. *Zh. Strukt. Khim.* **1985**, *26*, 3.
- (136) Case, D. A. *Annu. Rev. Phys. Chem.* **1982**, *33*, 151.
- (137) (a) Rosen, A.; Ellis, D. E. *Chem. Phys. Lett.* **1974**, *27*, 595. (b) Rosen, A.; Ellis, D. E. *J. Chem. Phys.* **1975**, *62*, 3039.
- (138) (a) Ellis, D. E.; Goodman, G. L. *Int. J. Quantum Chem.* **1984**, *25*, 185. Ellis, D. E. In *Handbook on the Physics and Chemistry of the Actinides*; Freeman, A. J., Lander, G. H., Eds.; Elsevier: Amsterdam, 1985; Vol. 2, pp 1–27.
- (139) (a) Rosen, A. *Int. J. Quantum Chem.* **1978**, *13*, 509. (b) Meyer, J. *Int. J. Quantum Chem.* **1988**, *33*, 445.
- (140) Meyer, J.; Sepp, W.-D.; Fricke, B. *Comput. Phys. Commun.* **1989**, *54*, 55.
- (141) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1846.
- (142) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (b) Delly, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949.
- (143) (a) Sepp, W.-D.; Sengler, W.; Kolb, D.; Hartung, H.; Fricke, B. *Chem. Phys. Lett.* **1984**, *109*, 233. (b) Sepp, W.-D.; Kolb, D.; Sengler, W.; Hartung, H.; Fricke, B. *Phys. Rev. A* **1986**, *33*, 3679.
- (144) Bastug, T. Exact Calculations of Total Energies for Small Molecules and Atomic Clusters using the Dirac-Fock-Slater Method. Doctor Thesis, University of Kassel, 1994. (b) Bastug, T.; Heinemann, D.; Sepp, W.-D.; Kolb, D.; Fricke, B. *Chem. Phys. Lett.* **1993**, *211*, 119.
- (145) Bastug, T.; Sepp, W.-D.; Kolb, D.; Fricke, B.; Rashid, K. *Phys. Rev. A* **1996**, submitted for publication.
- (146) (a) Boerringer, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87. (b) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.
- (147) (a) Bastug, T.; Sepp, W.-D.; Kolb, D.; Fricke, B.; Baerends, E. J.; te Velde, G. *J. Phys. B* **1994**, *28*, 2325. (b) Bastug, T.; Sepp, W.-D.; Fricke, B.; Johnson, E.; Barshick, C. H. *Phys. Rev. A* **1995**, *52*, 2734.
- (148) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (149) (a) Engel, E.; Vosko, S. H. *Phys. Rev. A* **1993**, *47*, 2800. (b) Engel, E.; Vosko, S. H. *Phys. Rev. A* **1993**, *47*, 13164. (c) Engel, E.; Keller, S.; Facco Bonetti, A.; Müller, H.; Dreizler, R. M. *Phys. Rev. A* **1995**, *52*, 2750.
- (150) (a) Krauss, M.; Stevens, W. J. *Annu. Rev. Phys. Chem.* **1984**, *35*, 357. (b) Kahn, L. R. *Int. J. Quantum Chem.* **1984**, *25*, 149.
- (151) Kahn, L. R.; Hay, P. J.; Cowan, R. D. *J. Chem. Phys.* **1978**, *68*, 2386.
- (152) (a) Hay, P. J.; Wadt, W. R.; Kahn, L. R.; Bobrowicz, F. W. *J. Chem. Phys.* **1978**, *69*, 984. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284.
- (153) (a) Kahn, L. R.; Hay, P. J.; Cowan, R. D. *J. Chem. Phys.* **1978**, *68*, 2386. (b) Hay, P. J.; Wadt, W. R.; Kahn, L. R.; Raffanetti, R. C.; Phillips, D. H. *J. Chem. Phys.* **1979**, *71*, 1767. (c) Hay, P. J. *J. Chem. Phys.* **1983**, *79*, 5469.
- (154) *JANAF Thermochemical Tables*; Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.: Washington, DC, 1971; Vol. 37.
- (155) (a) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866. (b) Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1980**, *90*, 1730. (c) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.
- (156) (a) Pitzer, K. S. ref 96; pp 403–420. (b) Christiansen, P. A.; Lee, Y. S.; Pitzer, K. S. *J. Chem. Phys.* **1979**, *71*, 4445.
- (157) Ermler, W. C.; Lee, Y. S.; Christiansen, P. A.; Pitzer, K. S. *Chem. Phys. Lett.* **1981**, *81*, 70.
- (158) Pitzer, R. M.; Winter, N. W. *J. Phys. Chem.* **1988**, *92*, 3061.
- (159) Collins, C. L.; Dyall, K. G.; Schaefer, H. F. *J. Chem. Phys.* **1995**, *102*, 2024.
- (160) (a) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Adv. Quantum Chem.* **1988**, *19*, 139. (b) Ermler, W. C.; Ross, R. B.; Christiansen, P. A. *Int. J. Quantum Chem.* **1991**, *40*, 829. (c) Ross, R. B.; Ermler, W. C. *J. Phys. Chem.* **1985**, *89*, 5202. (d) Hurley, M. M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840.
- (161) (a) Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500. (b) Pepper, M.; Bursten, B. E. *J. Am. Chem. Soc.* **1990**, *112*, 7803. (c) Chang, A. H. H.; Zhao, K.; Ermler, W. C.; Pitzer, R. H. *J. Alloys Compd.* **1994**, *213/214*, 191.
- (162) Nash, C. Private communication.
- (163) (a) Quiney, H. M. In *Methods in Computational Chemistry*; Wilson, S., Ed.; Plenum: New York, 1988; Vol. 2, p 227; (b) Lee, Y. S.; McLean, A. D. In *Current Aspects of Quantum Chemistry 1981*; Carbo, R., Ed.; Elsevier: Amsterdam, 1982; p 219. (c) Stanton, R. E.; Havriliak, S. *J. Chem. Phys.* **1984**, *81*, 1910. (d) Dyall, K. G.; Grant, I. P.; Wilson, S. *J. Phys. B* **1984**, *17*, 493. (e) Quiney, H. M.; Grant, I. P.; Wilson, S. *Lect. Notes Chem.* **1989**, *52*, 307.
- (164) Lee, Y. S.; McLean, A. D. *Current Aspects of Quantum Chemistry 1981*; Carbo, R., Ed.; Elsevier: Amsterdam, 1982; p 219.
- (165) McLean, A. D.; Lee, Y. S. *J. Chem. Phys.* **1982**, *76*, 735.
- (166) Baeck, K. K.; Lee, Y. S. *Chem. Phys. Lett.* **1988**, *147*, 367.
- (167) Baeck, K. K.; Lee, Y. S. *Chem. Phys.* **1990**, *93*, 5775.
- (168) Laaksonen, L.; Grant, I. P.; Wilson, S. *J. Phys.* **1988**, *B 21*, 1969.
- (169) Aerts, P. J. C.; Nieuwpoort, W. C. *Int. J. Quantum Chem. Symp.* **1986**, *19*, 267.
- (170) Aerts, P. J. C. Towards Relativistic Quantum Chemistry. Thesis, University of Groningen, 1986.
- (171) (a) Olsen, J.; Roos, B. O.; Jorgensen, P.; Jensen, H. J. Aa. *J. Chem. Phys.* **1988**, *89*, 2185. (b) Visscher, L. Relativity and Electron Correlation in Quantum Chemistry. Thesis, University of Groningen, 1993.
- (172) Hegarty, D.; Aerts, P. J. C. *Phys. Scr.* **1987**, *36*, 432.
- (173) Visser, O.; Aerts, P. J. C.; Visscher, L. In *The Effects of Relativity in Atoms, Molecules and Solid State*; Grant, I. P., Gyroff, B., Wilson, S., Eds.; Plenum: New York, 1991; pp 185, 197.
- (174) (a) Visser, O.; Visscher, L.; Aerts, P. J. C.; Nieuwpoort, W. C. *Theor. Chim. Acta* **1992**, *81*, 405. (b) Visser, O.; Visscher, L.; Aerts, P. J. C.; Nieuwpoort, W. C. *J. Chem. Phys.* **1992**, *96*, 2910.
- (175) Visser, O.; Visscher, L.; Aerts, P. J. C.; Nieuwpoort, W. C. *J. Chem. Phys.* **1992**, *96*, 2910.
- (176) Visscher, L.; Nieuwpoort, W. C. *Theor. Chim. Acta* **1994**, *88*, 447.
- (177) (a) Visscher, L.; Saue, T.; Nieuwpoort, W. C.; Faegri, K.; Gropen, O. *J. Chem. Phys.* **1993**, *99*, 6704. (b) Visser, O.; et al. *Comp. Phys. Commun.* **1994**, *81*, 120.
- (178) Visscher, L.; Dyall, K. G.; Lee, T. J. *Int. J. Quantum Chem. Quant. Chem. Symp.* **1995**, *29*, 411.
- (179) Nieuwpoort, W. C.; Aerts, P. J. C.; Visscher, L. In *Relativistic and Correlation Effects in Molecules and Solids*; Malli, G. L., Ed.; NATO ASI Series, Series B: Physics; Plenum Press: New York, 1994, Vol. 318, p 59.
- (180) De Jong, W. A.; Nieuwpoort, W. C. *Int. J. Quantum Chem.* **1996**, *58*, 203.
- (181) Matsuoka, O. *J. Chem. Phys.* **1992**, *97*, 2271.
- (182) (a) Dyall, K. G.; Faegri, K., Jr.; Taylor, P. R. In *The Effects of relativity in atoms, molecules and solid state*; Grant, I. P.; Gyroff, B.; Wilson, S., Eds.; Plenum: New York, 1990; p 167. (b) Dyall, K. G. *J. Chem. Phys.* **1992**, *96*, 1210. (c) Dyall, K. G. *J. Chem. Phys.* **1993**, *98*, 2191. (d) Dyall, K. G. *Chem. Phys. Lett.* **1992**, *196*, 178.
- (183) Dyall, K. G.; Faegri, K., Jr.; Taylor, P. R.; Partridge, H. *J. Chem. Phys.* **1991**, *95*, 2583.
- (184) Dyall, K. G. *J. Chem. Phys.* **1993**, *98*, 9678.
- (185) Dyall, K. G. In *Relativistic and Correlation Effects in Molecules and Solids*; Malli, G. L., Ed.; NATO ASI Series, Series B: Physics; Plenum Press: New York, 1994; Vol. 318; p 17.
- (186) (a) Saue, T. Thesis, Oslo, 1991. (b) Saue, T.; Faegri, K.; Gropen, O. Dirac Program for Atomic and Molecular Direct Iterative Relativistic All-electron Calculations, 1995. (c) Saue, T. *Chem. Phys. Lett.* **1996**, submitted for publication.
- (187) (a) Malli, G. L.; Pyper, N. C. *Proc. R. Soc. London, A* **1986**, *407*, 377. (b) Ramos, A. F.; Pyper, N. C.; Malli, G. L. *Phys. Rev. A* **1988**, *38*, 2729. (c) Malli, G. L. In *Self-Consistent Field: Theory and Applications*; Carbo, R., Klobukowski, M., Eds.; Elsevier: Amsterdam, 1990; pp 447–530. (d) Malli, G. L. In *Molecules in Physics, Chemistry and Biology*. Maruani, J., Ed.; Kluwer Academic Publishers: The Netherlands, 1988; Vol. II, pp 85–144. (e) Malli, G. L. *Can. J. Chem.* **1992**, *70*, 421.
- (188) Ishikawa, Y.; Malli, G. L.; Pyper, N. C. *Chem. Phys. Lett.* **1992**, *194*, 481.
- (189) Kaldor, U.; Hess, B. A. *Chem. Phys. Lett.* **1994**, *230*, 1.
- (190) Hess, B. A. *Phys. Rev.* **1986**, *A33*, 3742.
- (191) Scullman, R.; Cederbalk, P. *J. Phys. B* **1977**, *10*, 3659.
- (192) Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4385.
- (193) (a) Seip, H. M. *Acta Chem. Scand.* **1965**, *19*, 1955. (b) Galkin, N. P.; Toumanov, Y. N. *Russ. Chem. Rev.* **1971**, *40*, 154.
- (194) (a) Douglas, M.; Kroll, N. M. *Ann. Phys. NY* **1974**, *82*, 89. (b) Hess, B. A. *Phys. Rev. A* **1985**, *32*, 756; **1986**, *33*, 3742. (c) Jansen, G.; Hess, B. A. *Phys. Rev. A* **1989**, *39*, 6016. (d) Samsow,

- R.; Hess, B. A.; Jansen, G. *J. Chem. Phys.* **1992**, *96*, 1227. (e) Jansen, G.; Hess, B. A. *Z. Phys. D* **1989**, *13*, 363.
- (195) Pyykkö, P.; Shijders, J. G.; Baerends, E. *J. Chem. Phys. Lett.* **1981**, *93*, 432.
- (196) Canterford, J. H.; Colton, R. *Halides of the Second and Third Row Transition Metals*, John Wiley and Sons Ltd.: London, 1968.
- (197) Waber, J. T.; Averill, F. W. *J. Chem. Phys.* **1974**, *60*, 4466.
- (198) Hurst, G. S.; Nayfeh, M. H.; Young, J. P. *Appl. Phys. Lett.* **1977**, *30*, 229.
- (199) Fairbank, W. M.; Hänsch, T. W.; Schawlow, A. L. *J. Opt. Soc. Am.* **1975**, *65*, 199.
- (200) (a) Girichev, V.; Petrov, V. M.; Giricheva, N. I.; Utkin, A. N.; Petrova, V. N. *Zh. Strukt. Khim.* **1981**, *22*, 65. (b) Ischenko, A. A.; Strand, T. G.; Demidov, A. V.; Spiridonov, V. P. *J. Mol. Struct.* **1978**, *43*, 227.
- (201) (a) Brown, D. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Ed.; Pergamon Press: Oxford, 1973; Vol. 3, pp 553–622. (b) Fergusson, M. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Ed.; Pergamon Press: Oxford, 1973; Vol. 3, p 760.
- (202) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.
- (203) (a) Brewer, L. *At. Energy Rev.* **1980**, *N 7*, p 5. (b) Novikov, G. T.; Galitskij, N. V. *Russ. J. Inorg. Chem.* **1965**, *10*, 313. (c) Mercer, M. *J. Chem. Soc., Chem. Commun.* **1967**, *2*, 119.
- (204) (a) Chase, M. V., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1. (b) Dellien, I.; Hall, F. M.; Hepler, L. G. *Chem. Rev.* **1976**, *76*, 283.
- (205) *Molecular Constants of Inorganic Compounds*; Krasnov, K. S., Ed.; Leningrad: Khimiya, 1989 (in Russian).
- (206) *Thermochemical Properties of Inorganic Substances II*; Knacke, O., Kubaschewski, O., Hesselmann, K., Eds.; Springer-Verlag: Berlin, 1991.
- (207) Pershina, V. Unpublished data.
- (208) Smoes, S.; Drowart, J.; Myers, C. E. *J. Chem. Thermodyn.* **1976**, *8*, 255.
- (209) *Energies of Chemical Bonding. Ionization Potentials and Electron Affinity*; Kondratiev, V. N., Ed.; Moscow: Nauka, 1974 (in Russian).
- (210) Ionova, G. V. Unpublished data, 1992.
- (211) Ionova, G. V.; Spitsyn, V. I. *Effective Charges in Actinide Compounds*; Moscow: Nauka, 1989 (in Russian).
- (212) (a) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.
- (213) (a) Hübener, S.; Eichler, B.; Becker, U.; Kratz, J. V.; Gäggeler, H. W.; Jost, D. T.; Kovacs, J. *GSI Sci. Rep.* **1991**, p 320. (b) Hübener, S.; Ross, A.; Eichler, B.; Gäggeler, H. W.; Kovacs, J.; Timokhin, S. N.; Yakuchev, A. B. PSI Annual Report 1992, March 1993, p 102. (c) Eichler, B.; Gäggeler, H. W.; Hübener, S. PSI Annual Report 1992, March 1993, p 105. (d) Ross, A.; Hübener, S.; Eichler, B.; Gäggeler, H. W.; Türler, A.; Jost, D. T. PSI Annual Report 1993, March 1994, p 46.
- (214) (a) Pershina, V. Unpublished data. (b) Pershina, V.; Bastug, T.; Fricke, B. Manuscript in preparation.
- (215) Domanov, V. P.; Kim U. Zin. *Sov. Radiochem.* **1989**, *31*, 160.
- (216) Ozin, G. A.; Reynolds, D. J. *J. Chem. Soc., Chem. Commun.* **1969**, *884*.
- (217) Lijima, K.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 666.
- (218) (a) Lijima, K.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1393. (b) Hagen, K.; Hobson, R. J.; Holwill, C. J.; Rice, D. A. *Inorg. Chem.* **1986**, *25*, 3659.
- (219) (a) Ward, B. G.; Stafford, F. E. *Inorg. Chem.* **1968**, *7*, 2569. (b) Iorns, T. V.; Stafford, F. E. *J. Am. Chem. Soc.* **1966**, *88*, 4819. (c) Zharskii, I. M.; Zsorin, E. Z.; Spiridonov, V. P.; Novikov, G. I.; Kupreev, V. N. *Koord. Khim.* **1975**, *1*, 574.
- (220) Zvara, I. In *Problems of Prognosis in the Structure of Matter Science*; Moscow: Nauka, 1976; p 92.
- (221) Zvara, I. Scientific Report of JINR 1991–1992, Dubna, 1992; p 170.
- (222) (a) Cohen, J. S.; Pack, R. T. *J. Chem. Phys.* **1974**, *61*, 2373. (b) Schneider, B.; Boring, A. M.; Cohen, J. C. *Chem. Phys. Lett.* **1974**, *27*, 577.
- (223) Bratsch, S. G. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1.
- (224) Turkova, N. Ya. *Tables on Inorganic Chemistry*; Khimiya: Leningrad, 1977; p 52 (in Russian).
- (225) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd ed.; Cambridge University Press: New York, 1982.
- (226) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley and Sons: New York, 1970.
- (227) Korkisch, J. *Handbook on Ion Exchange Resins*, CRC Press, Inc.: Boca Raton, Florida, 1974; Vol. II, p 5.
- (228) Born, M. *Z. Phys.* **1920**, *1*, 45.
- (229) Bjerrum, N. K. *Danske Vidensk. Selsk. Mat.-fys. Medd.* **1926**, *7*, N 9.
- (230) Valloton, M.; Merbach, A. E. *Helv. Chim. Acta* **1974**, *57*, 2345.
- (231) *Solvent Extraction Reviews*; Marcus, Y., Ed.; Marcel Dekker: New York, 1971; Vol. 5, p 133.
- (232) Paulus, W.; Zimmermann, H. P.; Zauner, S.; Kratz, J. V. GSI Scientific Report 1993, March 1994, p 245.
- (233) (a) Gurmen, E.; Daniels, E.; King, J. S. *J. Chem. Phys.* **1971**, *55*, 1093. (b) Leciejewicz, J. *Z. Krist.* **1965**, *121*, 158. (c) Zalkin, A.; Templeton, D. H. *J. Chem. Phys.* **1964**, *40*, 501. (d) Kalman, A. *J. Chem. Soc. (A)* **1971**, 1857. (e) Müller, A.; Dieman, E. *Chem. Phys. Lett.* **1971**, *9*, 369.
- (234) Shannon, R. D.; Vincent, H. *Struct. Bond.* **1974**, *19*, 1.
- (235) Blasse, G. *Struct. Bond.* **1986**, *42*, 1.
- (236) (a) Freiberg, A.; Rebane, L. A. *J. Lumin.* **1979**, *18/19*, 702. (b) Groenink, J. A.; Hakfoort, C.; Blasse, G. *Phys. Stat. Sol. (a)* **1979**, *54*, 477. (c) Beard, G. B.; Kelly, W. H.; Malloy, M. L. *J. Appl. Phys.* **1962**, *33*, 144. (d) Blasse, G.; Schipper, W. J. *Phys. Stat. Sol. (a)* **1974**, *25*, 63.
- (237) Ziegler, T.; Rank, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *43*, 261.
- (238) Kebabcioğlu, R.; Müller, A. *Chem. Phys. Lett.* **1971**, *8*, 59.
- (239) Ziegler, T.; Rank, A.; Baerends, E. J. *Chem. Phys.* **1976**, *16*, 209.
- (240) (a) van Oosterhoud, A. B. *J. Chem. Phys.* **1977**, *67*, 2412. (b) van Oosterhoud, A. B. *Phys. Stat. Sol. (a)* **1977**, *41*, 607.
- (241) Kitaeva, L. P.; Volinets, M. P.; Suvorova, S. N. *Zh. Neorg. Khim.* **1980**, *XXXV*, 301.
- (242) Rohwer, E. F. C. H.; Cruywagen, J. J. *J. S. Afr. Chem. Inst.* **1966**, *XIX*, 11.
- (243) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. (A)* **1967**, 188.
- (244) (a) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Oxford: Pergamon Press, 1987; Vol. 3. (b) Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.
- (245) Florian, L. R.; Corey, E. R. *Inorg. Chem.* **1968**, *7*, 722.
- (246) Pershina, V.; Fricke, B. To be published.
- (247) Walch, P. E.; Ellis, D. E. *J. Chem. Phys.* **1976**, *65*, 2387.
- (248) Pershina, V.; Ionova, G. V.; Suraeva, N. I. *Russ. J. Inorg. Chem.* **1990**, *35*, 1178.
- (249) Ahrland, S. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Ed.; Pergamon Press: Oxford, 1973; Vol. 5, p 519.
- (250) Caletka, R.; Krivan, V. *J. Radioanal. Nucl. Chem.* **1990**, *142*, 359.
- (251) Caletka, R.; Krivan, V. *J. Radioanal. Nucl. Chem.* **1990**, *142*, 373.
- (252) Kraus, K. A.; Nelson, F.; Moore, G. E. *J. Am. Chem. Soc.* **1955**, *77*, 3972.
- (253) Vieux, A. S.; Amand, J. *Bull. Soc. Chim. Fr.* **1969**, *N 9*, 3366.