

# The chemistry of superheavy elements. III. Theoretical studies on element 113 compounds

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The chemistry of element 113 is investigated by theoretical methods. The results of fully relativistic calculations for (113)H and (113)F are compared with those derived by other techniques to obtain an indication of the accuracy of the more approximate models as well as the importance of including scalar and/or spin-orbit relativistic effects. Both of these effects are found to be important. The spin-orbit coupled pseudopotential approximation yields results of satisfactory accuracy, but the two relativistic methods that do not include spin-orbit coupling (Douglas-Kroll and scalar relativistic pseudopotential method) do not agree so well with each other. The calculated properties of (113)H and (113)F and a number of other hydrides and halides of element 113 are compared with the properties of the equivalent compounds of the lighter group 13 elements. In general, element 113 exhibits behavior that is consistent with its placement in group 13 of the periodic table. Some of its properties are found to be somewhat unusual however, e.g., the element is relatively electronegative, the molecules (113)H<sub>3</sub>, (113)F<sub>3</sub>, and (113)Cl<sub>3</sub> are predicted to be T-shaped rather than trigonal planar, and the 6*d* electrons of element 113 participate to a significant extent in chemical bonding. Compounds where element 113 is present in the +5 oxidation state are considered as well but are predicted to be thermodynamically unstable. © 1999 American Institute of Physics.

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## I. INTRODUCTION

In the last few years there has been renewed interest in the chemistry and physics of the transactinides. Experiments in both nuclear physics and nuclear chemistry have been responsible for this revival. Three new elements, those with 110, 111, and 112 protons were synthesized for the first time at the GSI in Darmstadt between 1994 and 1996<sup>1-3</sup> and very recently, evidence for the creation of element 114 was announced by the Dubna group.<sup>4</sup> Element 113 has not yet been observed, but nuclear structure theory predicts that certain isotopes of element 113 will be particularly stable, e.g., <sup>285</sup>113 is calculated to have an  $\alpha$ -decay half-life of 2 h.<sup>5</sup> Subsequent chemical investigations involving superheavy elements are extremely difficult because of the short lifetimes and yields of a few atoms.<sup>6</sup> The element with the greatest nuclear charge that has been examined experimentally so far is element 106.<sup>7,8</sup>

Because of the difficulties in atom-at-a-time chemistry, theoretical calculations can provide useful information for such experiments, and in many cases may be the only way a particular aspect of an element's chemistry can be investigated. However, these calculations are far from trivial due to the large numbers of electrons involved and the dominance of special relativity in systems including superheavy elements. As a consequence, the chemistry and physics of su-

perheavy elements is not well understood. Recent advances in relativistic quantum theory and computer hardware have now made it feasible to study the chemical and physical properties of superheavy elements in more detail. In particular, fully relativistic correlated Dirac-Fock-Coulomb (DFC) calculations are possible for simple molecules and should be capable of producing accurate molecular properties. These calculations then provide benchmark data for computationally less expensive methods which may, or may not, be applicable to this region of the periodic table. In this article, we take advantage of these developments to discuss the chemistry of the element with 113 protons, eka-Tl or element 113. Aspects of element 111, 112, and 114 chemistry have been examined in recent articles.<sup>9-12</sup>

Element 113 is predicted to have a [Rn]5*f*<sub>5/2</sub><sup>6</sup>5*f*<sub>7/2</sub><sup>8</sup>6*d*<sub>3/2</sub><sup>4</sup>6*d*<sub>5/2</sub><sup>6</sup>7*s*<sup>2</sup>7*p*<sub>1/2</sub><sup>1</sup> electron configuration,<sup>13,14</sup> isoelectronic with Tl. Because of the large spin-orbit splitting of the 7*p* shell, which is 2.79 eV at the fully relativistic coupled-cluster (RCC) level<sup>15</sup> (compared to 0.97 eV for Tl),<sup>16</sup> molecular properties will be strongly influenced by spin-orbit coupling.

From a theoretical point of view, molecular spin-orbit effects are difficult to determine accurately and it is therefore necessary to analyze the accuracy of the methods used. This is especially the case for the pseudopotential method used extensively in calculations involving heavy elements. We therefore compare molecular properties of the two diatomic molecules (113)H and (113)F derived by applying the pseudopotential approximation with those calculated using

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the more computationally demanding all-electron methods, in particular the Dirac–Hartree–Fock–Coulomb (DFC), the Douglas–Kroll (DK), and the standard Hartree–Fock (HF) method. For comparison the properties of TIH were also calculated at the DFC level.

The valence  $s$  electrons of element 113 are lower in energy than those of any of the other group 13 elements except B; the second ionization potential of element 113 is predicted to be 23.94 eV (Ref. 15) compared to Tl (20.43 eV), In (18.89 eV), Ga (20.51 eV), Al (18.82 eV), and B (25.15 eV).<sup>16,17</sup> However, the outermost shell of  $d$  electrons of element 113 is higher in energy than the equivalent shells of Tl or In; the  ${}^2S_{1/2} \rightarrow {}^2D_{5/2}$  energy of element  $113^{2+}$  is predicted to be only 0.12 eV (Ref. 15) compared to  $\text{Tl}^{2+}$  (8.21 eV) and  $\text{In}^{2+}$  (14.32 eV).<sup>16</sup> This low  $d/s$  gap may give rise to unusual high oxidation states of element 113.

Given the known chemistry of the lighter group 13 congeners and the experiments on superheavy elements carried out so far,<sup>18–20</sup> we decided to study the hydrides and halides of element 113. The hydrides (113)H and (113)H<sub>3</sub> are of particular interest because they can be compared with previous spin–orbit coupled calculations on the structure and bonding in TIH and  $\text{TIH}_3$ .<sup>21–28</sup> The relative stability of the 0, +1, +3, and +5 oxidation states of element 113 were considered in detail since this property is interesting both from a fundamental chemistry point of view as well as providing information to future atom-at-a-time chemistry.

Previous studies involving element 113 utilize atomic calculations and trends deduced empirically from the periodic system. A summary of early work was published some years ago<sup>29</sup> and later work has been reviewed more recently.<sup>30,31</sup> Only a small number of calculations of element 113 compounds have been published so far. Wood and Pyper have examined (113)<sub>2</sub> and element 113 halides using simple valence-bond type methods.<sup>32,33</sup> More recently, Nash has discussed calculations of a number of element 113 compounds in his thesis<sup>34</sup> and Han and co-workers have published two-component calculations of the properties of (113)H and (113)F.<sup>35</sup> We will compare the relevant data from these works with our results.

## II. COMPUTATIONAL DETAILS

In order to investigate the accuracy of the pseudopotential approximation for element 113, the bond lengths ( $R_e$ ), dissociation energies ( $D_e$ ), force constants ( $k_e$ ), and dipole moments ( $\mu_e$ ) of (113)H and (113)F were calculated using the DFC, DK, nonrelativistic Hartree–Fock (HF), spin–orbit averaged relativistic pseudopotential (ARPP), spin–orbit averaged relativistic pseudopotential plus a spin–orbit correction (ARPP+SO) derived using a two component pseudopotential (SOPP), and nonrelativistic pseudopotential (NRPP) methods. To compare the properties of (113)H with its lighter congeners we also carried out DFC calculations for TIH using basis sets of similar quality.

All the DFC calculations were performed using the MOLDIR suite of programs.<sup>36</sup> The basis sets used were of the family type.<sup>37</sup> All small component sets were derived by kinetic balance.<sup>38</sup> The actual values of the optimized large component  $s$  and  $p$  exponents along with a complete descrip-

tion of the derivation of the DFC element 113 and TI basis sets are given in the supplementary material that accompanies this article.<sup>39</sup> The exponents and further details for all other heavy atom all-electron basis sets used in this paper are also given in the supplementary material.<sup>39</sup> The exponents used in the large component basis set for H are those of the cc-pVTZ basis set of Dunning<sup>40</sup> omitting the  $d$  functions. The exponents used for the large component basis of F were taken from the cc-pVDZ basis of Dunning<sup>40</sup> with the additional hard  $p$  exponent of 128.185 40 recommended by Visscher *et al.*<sup>41</sup> In order to achieve kinetic balance for the F basis we chose 1.316 as the  $d$  exponent. The small and large component basis sets for each atom were contracted using the atomic balance scheme.<sup>38</sup> Separate contracted functions were used for each of the  $l+1/2$  and  $l-1/2$  orbitals. The final basis sets derived by carefully avoiding linear dependencies are as follows: element 113:  $25s25p18d12f/10s16p11d5f$  (large),  $25s25p25d18f12g/10s14p18d11f5g$  (small); Tl:  $22s22p15d10f/9s14p9d3f$  (large),  $22s22p22d15f10g/9s12p15d9f3g$  (small); F:  $9s5p1d/3s3p1d$  (large),  $5s9p5d1f/3s4p3d1f$  (small); and H:  $5s2p/3s2p$  (large),  $2s5p2d/2s3p2d$  (small).

In all DFC calculations the finite extension of the nucleus was modeled by a Gaussian function with exponents  $1.147 \times 10^8$  (113),  $1.389 \times 10^8$  (Tl),  $5.335 \times 10^8$  (F), and  $2.125 \times 10^9$  (H). Due to large requirements of disc space and CPU time in these DFC calculations we chose the two-electron integral (SS|LL) cutoff to be  $1.0 \times 10^{-10}$ .

The (SS|SS) integrals are by far the largest subset of the two-electron integrals and can be neglected in cases where only one heavy element is involved in the chemical bonding.<sup>42–44,30</sup> The Coulomb correction proposed by Visscher<sup>43</sup> was used to model the small–small interaction. The necessary point charges were derived from atomic small component populations dependent on the nuclear charge  $Z$  of the neutral atom,  $q(Z)$ . To simplify this procedure, the small component population was expressed as a sixth-order polynomial in  $Z$ ,  $q(Z) = \sum a_i Z^i$ , with coefficients

$$\begin{aligned} a_0 &= +1.192\,70 \times 10^{-5}, & a_1 &= -2.709\,30 \times 10^{-5}, \\ a_2 &= +2.735\,26 \times 10^{-5}, & a_3 &= +1.122\,96 \times 10^{-6}, \\ a_4 &= -9.529\,91 \times 10^{-9}, & a_5 &= +5.762\,29 \times 10^{-11}, \\ a_6 &= -9.008\,36 \times 10^{-14}. \end{aligned}$$

$q(Z)$  was determined from numerical DFC calculations for neutral elements up to  $Z = 120$ .<sup>45</sup> For  $Z > 50$  the deviation of the polynomial fit from the calculated small component population is less than 0.1%.

The DK and all-electron HF calculations were carried out using a modified version of the MOLCAS-3 program.<sup>46</sup> This implementation includes the option of using the spin-free DK Hamiltonian<sup>47</sup> with the simple Coulomb electron–electron interaction.

The H basis set used in the DK and HF calculations is based upon the  $9s2p$  set by Lie and Clementi<sup>48</sup> adding a  $1s1p1d$  set with exponents 0.01, 0.08, and 1.0, respectively. The F exponents used were taken from the aug-cc-pVTZ basis.<sup>40</sup> As was mentioned earlier, details of the element 113

DK and HF basis sets can be found in the supplementary material accompanying this article.<sup>39</sup> All basis sets were generally contracted using contraction coefficients derived from either an atomic DK or HF calculation. The final basis sets used were  $31s25p18d13f/14s13p10d5f$  for element 113 at the DK level,  $26s22p18d12f/14s13p10d5f$  for element 113 at the HF level,  $11s6p3d2f/5s4p3d2f$  for F, and  $10s3p1d/8s3p1d$  for H.

The pseudopotential parameters and basis sets for element 113 (ARPP, SOPP, and NRPP) were taken from Ref. 49. The basis sets for H and F used in the pseudopotential calculations were identical to those from the nonrelativistic HF calculations.

The influence of spin-orbit coupling was included in the ARPP calculations through a spin-orbit configuration interaction procedure (SOC) using two-component pseudopotentials (SOPP) as described in Refs. 9,50. The SOC calculations were performed using a modified version of the COLUMBUS program suite.<sup>51-53</sup>

In all cases the properties of (113)H and (113)F were calculated at the uncorrelated, MP2 and CCSD(T) levels. In the correlated DFC calculations the  $[Rn]5f$  core of element 113 and the F  $1s$  electrons were kept frozen and all virtual orbitals with energy greater than 50 a.u. were deleted. In the DK and all-electron HF calculations only the  $[Xe]4f5d$  core of element 113 was frozen and in the pseudopotential calculations all electrons and virtuals were included in the correlation treatment. Wherever possible,  $\mu_e$  was evaluated through the expectation value, otherwise the dipole moment was obtained from a finite field method using charges of  $\pm 5.0$  a.u. at  $\pm 1000$  a.u. along the molecular axis. The molecular orientation was chosen such that  $(113^+)X^-$  corresponds to a positive dipole moment.

The calculations of the polyatomic hydrides and halides of element 113 were performed with pseudopotentials only. Spin-orbit effects were included in the ARPP calculations in the same way as for (113)H and (113)F. Due to the larger sizes of the systems treated it was necessary to reduce the basis sets. In the basis sets for element 113 the softest  $d$  function is omitted and two rather than four  $f$  functions are included. Those  $f$  functions have exponents 0.582 854 and 0.246 436 in the case of the ARPP and 1.506 926, 0.652 046 in the case of the NRPP. The H basis set used in the polyatomic calculations was identical to that used in the all-electron HF calculations of (113)H. For F and Cl aug-cc-pVTZ basis sets with the  $f$  functions and the diffuse  $d$  function deleted were chosen. The original Br and I basis sets given in Ref. 54 were modified in the following way: a diffuse  $p$  function was added (exponent 0.02 in both cases) and the three hardest functions of both the  $s$  and  $p$  set were contracted. The single  $d$  function was replaced with a  $2d$  set (exponents 1.0 and 0.35 for Br and 0.80 and 0.266 for I). These modifications were carried out in order to obtain Br and I valence basis sets similar in quality to F and Cl. In the case of (113)F<sub>5</sub>, these basis sets were still too large for the electron correlation treatment and the smaller aug-cc-pVDZ fluorine basis set (with the diffuse  $d$  deleted) was used instead.<sup>40</sup> The larger (113)F<sub>x</sub> basis set is referred to as B1

TABLE I. Calculated properties of TIH.<sup>a</sup>

Level of Theory	$R_e$	$D_e$	$k_e$	$\mu_e$
Exp <sup>b</sup>	1.870	2.06	1.14	
DFC CCSD(T)	1.885	2.07	1.11	-1.22
DFC MP2	1.862	1.83	1.21	-1.39
DFC	1.869	1.17	1.24	-0.94

<sup>a</sup> $R_e$  in Å,  $D_e$  in eV,  $k_e$  in mdyn/Å,  $\mu_e$  in D.

<sup>b</sup>Reference 59.

and the smaller is referred to as B2 in the following discussion.

The structures of (113)H, (113)H<sub>3</sub>, (113)H<sub>5</sub>, (113)F, (113)F<sub>3</sub>, (113)F<sub>5</sub>, (113)Cl, (113)Cl<sub>3</sub>, (113)Br, (113)Br<sub>3</sub>, (113)I, and (113)I<sub>3</sub>, H<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, and I<sub>2</sub> were optimized at the NRPP and ARPP MP2 level. All electrons were correlated with the exception of the Cl  $1s2s2p$  core. F<sub>2</sub>, (113)F, and (113)F<sub>3</sub> were also recalculated using the smaller aug-cc-pVDZ-fluorine basis set so that all the energy differences needed could be obtained. Unfortunately, but not completely unexpectedly, we found no minimum on the 113+5F nonrelativistic potential energy hypersurface corresponding to the (113)F<sub>5</sub> molecule. The nonrelativistic properties of (113)F<sub>5</sub> were therefore not considered further. Test calculations involving (113)H<sub>3</sub>, (113)F<sub>3</sub>, and (113)I<sub>3</sub> show that spin-orbit effects in molecular properties are quenched if the number of ligands on the heavy atom increases. This effect is well known and has been discussed before.<sup>55,56</sup> However, spin-orbit effects on the geometry of (113)H<sub>3</sub> were still found to be important and was therefore included in the geometry optimization. In the case of the trihalides spin-orbit coupling had only a negligible influence on structures (of the order of 0.002 Å in bond lengths and 0.1 deg in bond angles) and can therefore be neglected. CCSD(T) calculations for (113)X<sub>3</sub> and (113)F<sub>5</sub> were performed only at the optimized MP2 equilibrium geometries. Again, with the exception of the Cl  $1s2s2p$  cores all electrons and virtual orbitals were included in these correlation treatments.

All MP2 geometry optimizations were performed using GAUSSIAN94<sup>57</sup> while the program ACESII<sup>58</sup> was used for all single point CCSD(T) calculations.

### III. RESULTS AND DISCUSSION

#### A. TIH, (113)H, and (113)F

In order to assess the accuracy of our basis sets and electron correlation procedures applied in the DFC calculations, we discuss briefly the lighter congener of (113)H, TIH, since experimental results are available.<sup>59</sup> As mentioned in the previous section, the Tl and H basis sets used in the DFC calculations were chosen to be as equivalent as possible to those used in the (113)H calculations. TIH has been examined theoretically many times,<sup>22,24,26-28,56,60-72</sup> but to our knowledge the calculations described here constitute the first fully self-consistent MP2 and CCSD(T) DFC calculations. The results are summarized in Table I. The DFC CCSD(T) method yields accurate properties of TIH except for the Tl-H bond distance, which is 0.015 Å above the experimental value most likely due to basis set deficiencies. Therefore,

the basis sets and level of electron correlation used in the (113)H DFC calculations should be sufficient to produce reliable predictions of the properties of that molecule. As we shall see later, the same statement cannot be made about the DFC (113)F  $D_e$  and  $\mu_e$  due to deficiencies in the F basis set.

The calculated properties of (113)H and (113)F are summarized in Table II. Also included in Table II are the results for (113)H and (113)F given by Nash<sup>34</sup> and Han *et al.*<sup>35</sup> It is more difficult to discuss *a priori* whether scalar relativistic DK or ARPP approximations will yield reasonable results for (113)H or (113)F or other molecules including super-heavy elements. Recent calculations for (111)H are encouraging<sup>50,73</sup> but spin-orbit effects are expected to be considerably larger for element 113 compared to element 111. We mention that the DK, HF, and pseudopotential basis sets used are very similar in quality in the valence region. However, due to the high disk space requirements of four-component calculations, it was necessary to use less accurate basis sets and a direct comparison may not give accurate values for spin-orbit effects. For example, comparing the DFC and ARPP +SO results, the most obvious disagreement is in the dissociation energy of (113)F where the uncorrelated ARPP +SO, ARPP +SO MP2, and ARPP +SO CCSD(T) are, respectively, 0.29, 0.39, and 0.59 eV greater than the equivalent DFC result. An indication that basis set effects are responsible for this deficiency comes from a further uncorrelated DFC calculation using an extended F basis set with the *sp* diffuse functions recommended by Dunning<sup>40</sup> included. The dissociation of (113)F calculated using this basis set is 0.83 eV, in significantly better agreement with the uncorrelated ARPP +SO value of 0.93 eV.

The DFC basis set lacking diffuse functions on the F atom was judged to be inappropriate for the evaluation of the dipole moment of (113)F and therefore no such calculations were attempted. The dipole moment was evaluated using the larger basis set and was found to be 5.03 D in good agreement with the uncorrelated ARPP +SO value. Unfortunately, correlated DFC calculations of (113)F using this basis set are beyond our computational resources at this time.

All the other properties of (113)H and (113)F calculated at the ARPP +SO level are in good agreement with the equivalent DFC values which suggests that the element 113 pseudopotential used<sup>49</sup> is of reasonable accuracy. In fact, given the lack of diffuse functions on F in the DFC calculations of (113)F, the properties of this molecule calculated at the ARPP +SO CCSD(T) level probably represent the best predictions for (113)F given here despite the use of a more approximate method. We note that the agreement between the ARPP +SO and DFC results observed for (113)H and (113)F is slightly inferior to that seen in similar calculations for (111)H.<sup>73</sup> This suggests that the method of adding spin-orbit effects to pseudopotential results may become less accurate when these effects are very large and further work on this point is required.

Comparing now the two scalar relativistic methods, the DK and ARPP results, we see that the agreement is only average in most cases. In contrast, at the nonrelativistic level the pseudopotential results are in excellent agreement with the nonrelativistic all-electron calculations. Hence, the devia-

tion in the scalar relativistic case cannot be attributed to basis set effects. Moreover, previous calculations involving (111)H found the ARPP and DK results are in excellent agreement.<sup>50,73</sup> We believe that the major difference between DK and ARPP lies in the different definition of “spin-orbit averaged” used. The scalar DK approximation is spin-orbit averaged in the sense that all terms in the DK-Hamiltonian that depend on spin are neglected. In our ARPP approximation spin-orbit averaged means that *j*-averaged energies are used in the fitting procedure for the pseudopotential parameters (energy consistent pseudopotentials). Other groups define spin-orbit averaged by averaging over  $j = l \pm 1/2$  orbitals for each angular symmetry *l* (shape consistent pseudopotentials). It is easily verified that these different types of spin-orbit averaged methods do not lead to the same results, particularly in systems where spin-orbit effects are very large. This may lead to the false conclusion that pseudopotentials are not reliable.

(113)H and (113)F have also been considered by Nash<sup>34</sup> and Han and co-workers.<sup>35</sup> The results derived by these workers are included in Table II. Han has compared in detail their results and the present numbers<sup>35</sup> and no further discussion is necessary here except to point out that in general the agreement between the ARPP +SO and the DHF data is similar in quality as to the agreement between the relativistic effective potential (REP) results and the same all-electron data. This is encouraging as it provides further evidence that the spin-orbit CI correction used here, a method which can easily be applied with any standard one-component method at little extra computational cost, may often be sufficiently accurate even for systems with large spin-orbit coupling. The ARPP SOCISD equilibrium bond lengths<sup>34</sup> are in good agreement with our spin-orbit coupled calculations. However, the ARPP SOCI dissociation energies of (113)H and (113)F are not in such good agreement. The differences in  $D_e$  are probably due to the relatively small basis sets and CI expansions used in this work.<sup>34,74</sup>

The calculated properties of (113)H and (113)F are compared with experimental data for the lighter group 13 monohydrides and monofluorides in Fig. 1 [the DFC CCSD(T) properties for (113)H are used, while for (113)F we used the ARPP +SO CCSD(T) results instead]. These properties follow the well-known trends of the group 13 hydrides and fluorides with the exception of the equilibrium bond length and the dipole moment of (113)H. The change in trend for these two properties is due to the large spin-orbit effects present which are strongly influenced by SO effects, i.e., if one substitutes the ARPP CCSD(T) or DK CCSD(T) results for (113)H for the DFC CCSD(T) points in Fig. 1(a) and 1(d) both graphs continue the trends shown by the lighter elements.

Spin-orbit effects on properties other than dissociation energies are generally regarded as small. This is certainly not the case for (113)H. In fact, spin-orbit effects on the properties of (113)H are similar in magnitude to the scalar relativistic effects calculated for properties of AuH.<sup>75,54</sup> With the exception of the equilibrium bond length and perhaps the force constant, spin-orbit effects on properties of (113)F are also significant.

TABLE II. Calculated properties of (113)H and (113)F<sup>a</sup>.

Method	(113)H				(113)F			
	$R_e$	$D_e$	$k_e$	$\mu_e$	$R_e$	$D_e$	$k_e$	$\mu_e$
Relativistic, spin-orbit coupled								
DFC CCSD(T)	1.789	1.44	1.09	0.19	2.187	2.52	2.25	
DFC MP2	1.757	1.20	1.29	0.28	2.180	2.77	2.40	
DFC	1.704	0.50	1.69	-0.17	2.167	0.64	2.23	
ARPP+SO CCSD(T)	1.782	1.62	1.37	0.20	2.173	3.11	2.25	4.23
ARPP+SO MP2	1.768	1.36	1.49	0.33	2.169	3.16	2.30	4.38
ARPP+SO HF	1.767	0.70	1.67	0.14	2.162	0.93	2.21	4.93
ARPP SOCISD <sup>b</sup>	1.75	2.4			2.18	2.2		
REP KRCCSD(T) <sup>c</sup>	1.762	1.37	1.15		2.239	2.66	1.82	
REP KRMP2 <sup>c</sup>	1.736	1.16	1.38		2.232	2.92	1.92	
REP KRHF <sup>c</sup>	1.707	0.46	1.61		2.222	0.77	1.80	
Relativistic, scalar								
DK CCSD(T)	2.006	2.43	0.87	2.73	2.244	4.61	1.85	5.80
DK MP2	1.974	2.14	0.99	2.73	2.238	4.98	1.90	5.82
DK	2.014	1.49	0.89	3.03	2.252	3.08	1.73	6.29
ARPP CCSD(T)	1.942	2.60	1.00	1.98	2.202	4.96	2.10	5.15
ARPP MP2	1.919	2.32	1.11	2.06	2.199	5.00	2.14	5.24
ARPP HF	1.935	1.70	1.08	2.02	2.205	3.05	2.01	5.58
AREP CCSD(T) <sup>c</sup>	1.970	2.30	0.92		2.273	4.51	1.75	
AREP MP2 <sup>c</sup>	1.940	2.10	1.05		2.266	4.73	1.78	
AREP HF <sup>c</sup>	1.984	1.50	0.95		2.274	2.95	1.68	
Nonrelativistic								
HF CCSD(T)	2.077	2.52	1.07	0.99	2.215	5.36	2.30	3.81
HF MP2	2.059	2.19	1.14	1.24	2.219	5.37	2.24	4.14
HF	2.082	1.77	1.18	0.53	2.203	3.73	2.47	3.34
NRPP CCSD(T)	2.072	2.52	1.06	0.95	2.197	5.34	2.33	3.67
NRPP MP2	2.055	2.18	1.13	1.23	2.202	5.35	2.22	4.04
NRPP HF	2.076	1.77	1.18	0.44	2.185	3.71	2.61	3.15

<sup>a</sup> $R_e$  in Å,  $D_e$  in eV,  $k_e$  in mdyne/Å,  $\mu_e$  in D.<sup>b</sup>Reference 34.<sup>c</sup>Reference 35.

It has been noted previously that the ratio in the  $6p_{3/2}$  to  $6p_{1/2}$  populations in the  $\sigma$  highest occupied molecular orbital (HOMO) of TIH is approximately 0.6 rather than the nonrelativistic limit of 2.0.<sup>60-62</sup> Using the orbital projection method outlined by Saue and co-workers,<sup>76,77</sup> the  $6p_{3/2}$  to  $6p_{1/2}$  ratio in the  $\sigma$  HOMO of the DFC wavefunction of TIH was found to be 0.6 in agreement with these earlier results. Other calculations have found that the principal bonding MO of TIH is of almost  $\sigma$  symmetry in apparent contradiction to the 0.6 ratio obtained from a population analysis (a Tl-H  $\sigma$  bond is formed from the overlap of the H  $1s$  and Tl  $p_z$  orbital, a  $p_z$  orbital is  $2/3 p_{3/2}$  and  $1/3 p_{1/2}$ , i.e., ratio of 2.0).<sup>78</sup> Our calculated DFC population for TIH using an LS coupled basis also predicts that the HOMO is of  $\sigma$  character (populations:  $6s$ : 1.87,  $6p_\sigma$ : 0.77,  $6p_\pi$ : 0.04). As pointed out recently by Saue *et al.* and analyzed in detail for (117)H,<sup>76</sup> the combination of  $p_{1/2}$  and  $p_{3/2}$  orbitals in a ratio 1:2 gives a  $p_z$  orbital only if both  $jj$  coupled orbitals have the same radial functions. This is not the case when spin-orbit coupling is large, e.g.,  $\langle R \rangle$  of the  $6p_{1/2}$  and  $6p_{3/2}$  orbitals of Tl are 3.51 a.u. and 4.01 a.u., respectively. Hence, given the differing radial extents of the  $6p_{3/2}$  and  $6p_{1/2}$  orbitals of Tl, a ratio of 0.6 is sufficient to produce a bond that is almost purely  $\sigma$ .

The calculated DFC populations for (113)H and (113)F are summarized in Tables III and IV. The atomic orbital

(AO) coefficients for (113)H derived by the projection method are given in Table V. It is clear from Table III that, in contrast to TIH, the principal bonding orbital of (113)H [30(1/2)] has significant  $\pi$  character. Furthermore, the  $7p_{1/2}$  contribution to this MO is much greater than expected in the absence of spin-orbit coupling: the ratio of the square of the  $7p_{3/2}$  and  $7p_{1/2}$  coefficients from Table V is 0.06, considerably less than the nonrelativistic value of 2.00: Thus, spin-orbit coupling has a significant effect on the nature of the (113)-H bond. Given the relatively small  $7p_{3/2}$  contribution to the principal bonding MO of (113)H the bond has significantly more  $\sigma$  character than would be expected for a pure

TABLE III. Mulliken population analysis of (113)H<sup>a</sup>.

MO	$\epsilon$	$6d$	$7s$	$7p_\sigma$	$7p_\pi$	H
27(1/2)	-0.777	1.786	0.060	0.004	0.000	0.144
16(3/2)	-0.735	2.000	0.000	0.000	0.000	0.000
28(1/2)	-0.641	0.802	0.852	0.020	0.002	0.318
8(5/2)	-0.586	2.000	0.000	0.000	0.000	0.000
17(3/2)	-0.586	1.996	0.000	0.000	0.000	0.004
29(1/2)	-0.579	1.242	0.750	0.000	0.002	0.004
30(1/2)	-0.327	0.086	0.212	0.712	0.430	0.554
total		9.912	1.874	0.736	0.434	1.024
$q$	+0.03					

<sup>a</sup> $\epsilon$  denotes the orbital energy and  $q$  represents the net charge of element 113.

TABLE IV. Mulliken population analyses of (113)F<sup>a</sup>.

MO	113					F		
	$\epsilon$	6d	7s	7p <sub><math>\sigma</math></sub>	7p <sub><math>\pi</math></sub>	2s	2p <sub><math>\sigma</math></sub>	2p <sub><math>\pi</math></sub>
28(1/2)	-1.417	0.008	0.003	-0.002	0.001	1.984	0.005	0.000
29(1/2)	-0.772	1.921	0.000	0.000	0.000	0.007	0.058	0.011
16(3/2)	-0.774	1.995	0.000	0.000	0.000	0.000	0.000	0.004
30(1/2)	-0.649	1.211	0.260	0.000	0.000	0.013	0.447	0.063
8(5/2)	-0.634	2.000	0.000	0.000	0.000	0.000	0.000	0.000
17(3/2)	-0.633	1.846	0.000	0.000	0.000	0.009	0.000	0.113
31(1/2)	-0.615	0.562	1.281	0.000	0.000	0.005	0.141	0.009
18(3/2)	-0.500	0.123	0.000	0.000	0.011	0.000	0.000	1.861
32(1/2)	-0.500	0.100	0.005	0.000	0.018	0.000	0.000	1.869
33(1/2)	-0.434	0.180	0.421	0.183	0.058	-0.011	1.159	0.007
total		9.946	1.970	0.181	0.088	2.007	1.810	3.937
q	+0.75							

<sup>a</sup> $\epsilon$  denotes the orbital energy and q represents the net charge of element 113.

113(7p<sub>1/2</sub>)–H(1s) bond which would be only 1/3  $\sigma$ . As was the case for TIH, this is due to the differing radial behavior of the 7p<sub>3/2</sub> and 7p<sub>1/2</sub> orbitals.

The net charge of element 113 in (113)H (Table III) is relatively small in comparison to TIH (+0.30 at TI, from the DFC calculations). Furthermore, the dipole moment of (113)H is much smaller than that of TIH, InH, and GaH [see Fig. 1(d)]. This suggests that element 113 is somewhat more electronegative than Tl, In, or even Ga. However, the (113)F dipole moment is predicted to be the largest in the series of the group 13 monofluorides [see Fig. 1(d)]. The difference for (113)F is due to the more ionic nature of this molecule (see Table IV).

The 6d and the 7s electrons of element 113 participate little in the bonding; the populations of both of these orbitals are close to 2.0 and 10.0, respectively in both (113)H and (113)F (Tables III and IV). Therefore, spin-orbit effects on the properties of these molecules can be explained simply by consideration of the 7p shell. The large spin-orbit contraction of the (113)–H bond is due to the spin-orbit contraction of the 7p<sub>1/2</sub> orbital. The (113)–F bond does not undergo a similarly large decrease because it is mostly ionic (the ionic radius of 113<sup>+</sup> is not reduced by spin-orbit coupling). The dipole moments of (113)H and (113)F are decreased by spin-orbit coupling because of the SO stabilization of the 7p<sub>1/2</sub> orbital. The SO decrease of  $\mu_e$ [(113)H] is approximately twice that of (113)F because of the larger spin-orbit bond contraction in (113)H.

As expected, spin-orbit effects are particularly large for the dissociation energy destabilizing (113)H by 0.98 eV. The atomic SO contribution to  $D_e$  of (113)H is large (2.33 eV)

TABLE V. AO coefficients in the valence MOs of (113)H<sup>a</sup>

Orbital	Coefficient of				
	6d <sub>3/2</sub>	6d <sub>5/2</sub>	7s	7p <sub>1/2</sub>	7p <sub>3/2</sub>
27(1/2)	0.924	-0.116	-0.141	-0.013	-0.014
28(1/2)	0.324	0.530	0.604	0.016	0.045
29(1/2)	-0.031	0.786	-0.606	-0.016	0.013
30(1/2)	-0.130	0.207	0.385	-0.648	-0.152

<sup>a</sup>Only AOs and MOs with  $m_j = 1/2$  are included.

but partly compensated by the molecular stabilization of 1.35 eV. In comparison, the spin-orbit destabilization of TIH is 0.50 eV.<sup>28</sup> Since (113)F is an ionic compound the molecular spin-orbit contribution is quenched and the calculated CCSD(T) SO increase of the first ionization potential of element 113 (1.86 eV)<sup>15</sup> is very close to the spin-orbit decrease in  $D_e$  of (113)F (1.85 eV).

Scalar relativistic effects on the properties of (113)H and (113)F are much smaller than those calculated previously for (111)H or (112)H<sup>+</sup>.<sup>10,50</sup> This is analogous to the behavior observed in the previous rows of the periodic table where

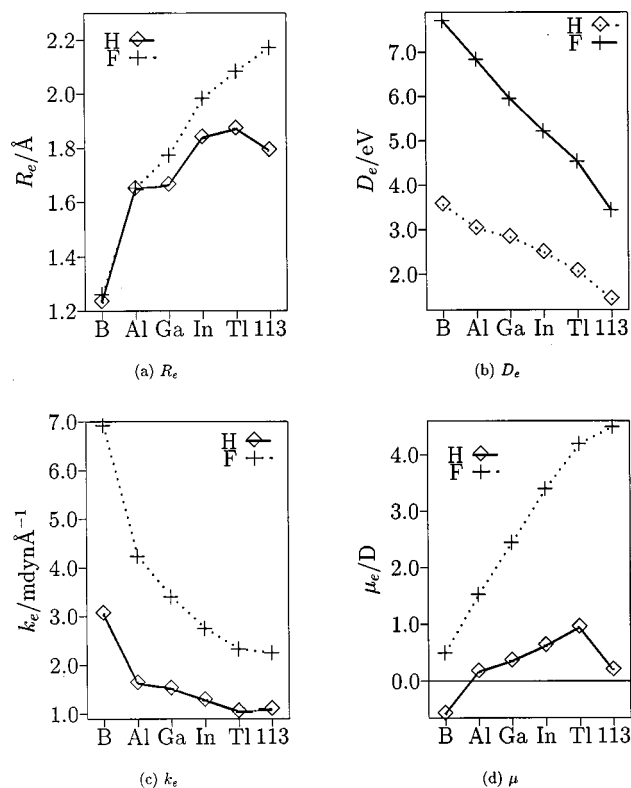


FIG. 1. The properties of the group 13 hydrides and fluorides. The (113)H properties are DFC CCSD(T) results. ARPP+SO CCSD(T) results are used for (113)F. The AlH, GaH, InH, and TIH dipole moments are theoretical results (Refs. 97, 98) as are the dissociation energies of the AlH and GaH. All other data were experimentally determined (Ref. 59).

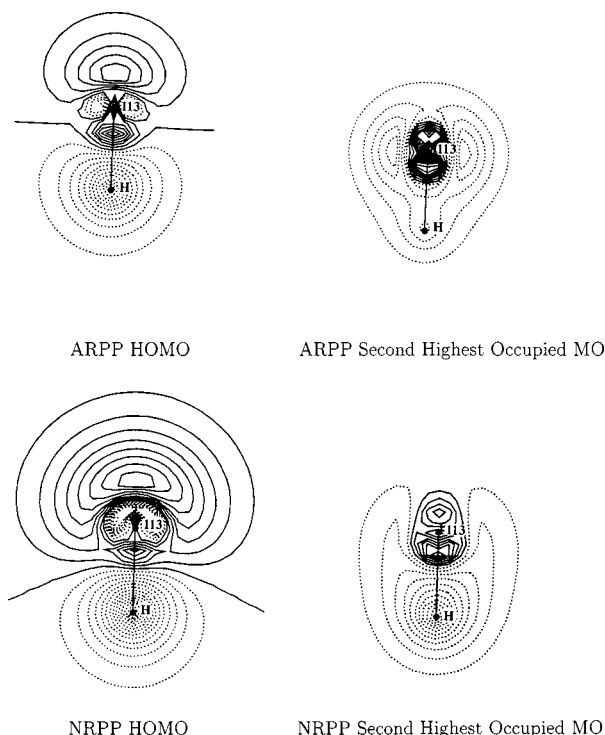


FIG. 2. MOs of (113)H from ARPP and NRPP calculations.

scalar relativistic effects have been found to reach a maximum at group 11 (Ref. 79) (but see also Ref. 80). The scalar relativistic effects on the properties of (113)H and (113)F follow a similar pattern to those observed for TIH and TIF.<sup>56,68</sup>

One relativistic effect on the properties of group 13 hydrides and fluorides that has not been explained in detail is the unusual increase in the dipole moment observed when scalar relativistic effects are included. Although the bond length of (113)H and net charge at element 113 in that molecule are decreased by about 0.1 Å and 0.12 electrons, respectively by scalar relativistic effects,<sup>80</sup> the dipole moment is approximately doubled, the opposite effect to what one expects. The unusual change in the dipole moment of (113)H upon the inclusion of scalar relativistic effects can be explained by reference to MO diagrams plotted using the orbitals derived from the PP calculations (Fig. 2). The MOs of interest, the HOMO, and next highest energy MO, consist primarily of the element 113  $7s$  and  $7p$  orbitals and the H  $1s$  orbital. In the relativistic case, the HOMO is a simple bonding combination of a  $p$  and an  $s$  orbital. The MO energetically below this HOMO consists mostly of element 113  $7s$  contributions but is slightly perturbed by the presence of the H nucleus. All the other MOs of (113)H (not shown) are basically corelike orbitals centered on the element 113 nucleus. Therefore, the dipole moment of (113)H calculated at the relativistic level is mostly due to the polarity of the bond described by the HOMO.

The NRPP MOs are rather different from the equivalent ARPP MOs. For nonrelativistic element 113 the  $7s$  and  $7p$  shells are closer in energy than they are in the relativistic case. The nonrelativistic  $7s$  and  $7p$  can therefore more easily achieve  $sp$  hybridization. The second highest occupied MO

TABLE VI. Equilibrium geometries of the element 113 hydrides and halides<sup>a</sup>.

	ARPP		$\alpha$	NRPP	
	$R_1$	$R_2$		$R_3$	$R_4$
(113)H	1.758			2.051	
(113)H <sub>3</sub>	1.798	1.621	98.6	1.941	
(113)H <sub>5</sub>	1.816	1.628	95.6	1.868	1.957
(113)F	2.212			2.197	
(113)F <sub>3</sub> B1 <sup>b</sup>	2.183	1.933	93.2	2.160	
(113)F <sub>3</sub> B2 <sup>c</sup>	2.191	1.956	93.9	2.174	
(113)F <sub>5</sub>	2.173	1.984	93.8		
(113)Cl	2.570			2.662	
(113)Cl <sub>3</sub>	2.515	2.361	103.2	2.542	
(113)Br	2.679			2.802	
(113)Br <sub>3</sub>	2.564	2.564	120.0	2.676	
(113)I	2.853			3.027	
(113)I <sub>3</sub>	2.782	2.782	120.0	2.885	

<sup>a</sup>All bond lengths are in Å and all angles are in degrees. The  $R_i$  and  $\alpha$  are defined in Fig. 2 and 3. The relativistic trihydride and trihalides are considered to have  $C_{2v}$  symmetry. All the nonrelativistic (113)X<sub>3</sub> molecules have  $D_{3h}$  symmetry as does the nonrelativistic geometry of (113)H<sub>5</sub>. The relativistic geometries of (113)H<sub>5</sub> and (113)F<sub>5</sub> have  $C_{4v}$  symmetry.

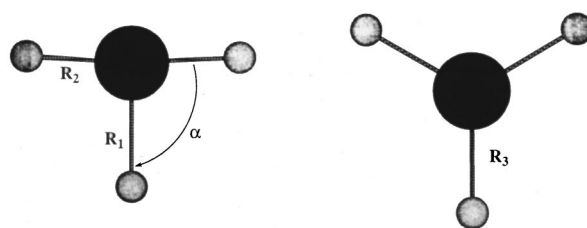
<sup>b</sup>Larger basis set results.

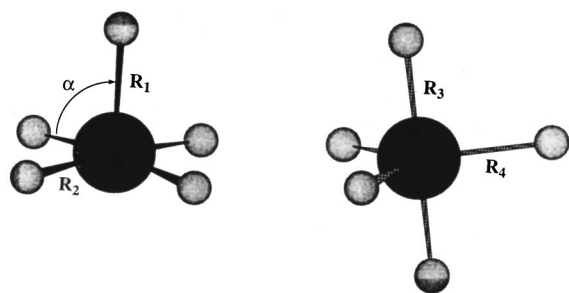
<sup>c</sup>Smaller basis set results.

in the NRPP calculation is strongly bonding and is formed from the H  $1s$  orbital and the  $sp$ -hybridized AO pointing towards the H atom. The NRPP HOMO describes a lone pair of electrons on the element 113 nucleus which occupies the other  $sp$ -hybridized AO. Most of the electron density described by this orbital is on the far side of element 113 nucleus away from the H atom. Thus, while the nonrelativistic second highest occupied MO is polarized towards H and therefore makes a large positive contribution to the dipole moment, the HOMO makes a significant negative contribution. As a result, the overall nonrelativistic dipole moment of (113)H is smaller than the SO-averaged relativistic dipole moment despite the relativistic bond length and net charge being smaller. A similar argument can be applied to other TI and element 113 diatomic molecules to rationalize the large relativistic decrease in their dipole moments.

## B. The polyatomic hydrides and halides of element 113

The calculated geometries of the hydrides and halides of element 113 are listed in Table VI. Two structures of different symmetry were considered for both the element 113(III) (see Fig. 3) and 113(V) compounds (Fig. 4). We mention that the bondlengths of (113)H and (113)F given in Table VI

FIG. 3.  $C_{2v}$  and  $D_{3h}$  structures of (113)X<sub>3</sub>.

FIG. 4.  $C_{4v}$  and  $D_{3h}$  structures of  $(113)X_5$ .

differ by only about 0.01 Å from those calculated at the same level of approximation with the larger basis sets (Table II).

The most striking feature of the geometries of the 113(III) compounds is that the global minima of  $(113)H_3$ ,  $(113)F_3$ , and  $(113)Cl_3$  correspond to a T-shaped geometry with  $C_{2v}$  symmetry. This is in contrast to the trihalides or trihydrides of the lighter group 13 elements which have been found to have trigonal planar structures in all cases.<sup>81,56,25</sup>  $(113)Br_3$  and  $(113)I_3$  are predicted to have the usual trigonal planar arrangements (no stable T-shaped structure was found for these compounds). No local minima corresponding to the trigonal planar structure was found on the potential energy surfaces (PES) of  $(113)H_3$ ,  $(113)F_3$ , and  $(113)Cl_3$  and these geometries in fact are second-order transition states with  $e'$  distortion modes. This corresponds to a second-order Jahn–Teller distortion leading to a Mexican hat PES with three T-shaped minima and three Y-shaped first-order transition states connecting the T-shaped structures.<sup>82</sup> In order to get an idea of the main features of the reaction pathways between two minima a few points in relevant regions of the potential energy surface were calculated at the HF level. The calculated potential energy barriers for the Y-shaped transition state between different minima were approximately 3, 63, and 2 kJ mol<sup>-1</sup> for  $(113)H_3$ ,  $(113)F_3$ , and  $(113)Cl_3$ , respectively. Given these barrier heights the calculated distortion of  $(113)F_3$  can be regarded as accurate, while the distortion for

$(113)H_3$  and  $(113)Cl_3$  may correspond to a dynamic Jahn–Teller effect [the zero-point energies (ZPVE) of  $(113)F_3$  and  $(113)Cl_3$  derived from frequency analyses are of the order of 10 kJ mol<sup>-1</sup>, the ZPVE of  $(113)H_3$  is somewhat larger]. The reaction pathway between two of the three minima is very flat and larger basis sets or a more complete treatment of electron correlation could easily result in a very different geometry.

The relativistic  $6d$  populations calculated for  $(113)H_3$ ,  $(113)F_3$ , and  $(113)Cl_3$  given in Table VII are all significantly less than 10.0. At the same time, the  $6d$  populations of  $(113)Br_3$  and  $(113)I_3$  are both close to 10.0. No evidence has been found for large  $d$  participations in Tl, In, or Ga compounds.<sup>83</sup> We therefore expect that the influence of the  $6d$  electrons causes the symmetry breaking in  $(113)H_3$ ,  $(113)F_3$ , and  $(113)Cl_3$ . To confirm this hypothesis, the geometry of  $(113)F_3$  was reoptimized using a 3-electron PP for element 113.<sup>84</sup> Calculations carried out using this PP treat the  $6d$  electrons as chemically inert since only the  $7s$  and  $7p$  electrons of element 113 are treated explicitly. Using a 3-electron PP the geometry of  $(113)F_3$  is calculated to be trigonal planar. We also note that the large energy gap between the  $7s$  and  $7p$  orbitals in element 113 results in a reduced  $sp^2$  hybridization. In the absence of  $sp^2$  hybridization, main-group elements tend to form bond angles of 90 deg.<sup>55</sup> However, if  $(113)Br_3$  and  $(113)I_3$  were  $sp^2$  hybridized then the  $7s$  and  $7p$  populations of these molecules should be significantly lower and higher, respectively, than those of the other  $(113)X_3$  molecules. The  $7p$  populations of  $(113)Br_3$  and  $(113)I_3$  are indeed higher but their  $7s$  populations do not decrease and in fact increase relative to that of  $(113)Cl_3$ . The steric repulsion between the larger Br and I atoms also increase the tendency to form trigonal planar structures.

The T-shaped geometry of certain  $(113)X_3$  molecules is rather reminiscent of the structure of  $ClF_3$ . The situations in the two molecules are somewhat different however. In the latter case, a possible explanation for the observed structure

TABLE VII. Mulliken population analyses for  $(113)H_3$ ,  $(113)H_5$ ,  $(113)F_3$ ,  $(113)F_5$ , and  $(113)Cl_3$ .<sup>a</sup>

		$6d$	$7s$	$7p$	$q(113)$	$q(a)$	$q(b)$
$(113)H_3$	ARPP	9.67	1.31	1.39	+0.62	-0.26	-0.18
	NRPP	9.99	0.83	1.01	+1.19	-0.40	-0.40
$(113)H_5$	ARPP	9.23	0.65	1.95	+1.15	-0.24	-0.23
	NRPP	9.80	0.93	1.78	+0.78	-0.22	-0.06
$(113)F_3$	ARPP	9.61	1.18	0.50	+1.58	-0.69	-0.45
	NRPP	10.10	0.28	0.31	+2.29	-0.76	-0.76
$(113)F_5$	ARPP	9.12	0.84	0.74	+2.05	-0.65	-0.35
$(113)Cl_3$	ARPP	9.84	1.27	0.64	+1.25	-0.56	-0.34
	NRPP	10.15	0.45	0.62	+1.79	-0.60	-0.60
$(113)Br_3$	ARPP	9.99	1.38	0.91	+0.72	-0.24	-0.24
	NRPP	10.22	0.59	0.78	+1.42	-0.47	-0.47
$(113)I_3$	ARPP	10.05	1.49	1.42	+0.04	-0.01	-0.01
	NRPP	10.23	0.63	1.19	+0.97	-0.32	-0.32

<sup>a</sup> $q(113)$  is the net charge at element 113. For the  $(113)X_3$  molecules,  $q(a)$  is the net charge on the axial atom and  $q(b)$  is the net charge on each of the equatorial atoms. For the  $(113)X_5$  molecules with  $C_{4v}$  symmetry,  $q(a)$  is the net charge on the atom forming the apex of the square pyramid and  $q(b)$  is the net charge on each of the other four atoms bonded to element 113. For the  $(113)X_5$  molecules with  $D_{3h}$  symmetry,  $q(a)$  is the net charge on the axial atoms and  $q(b)$  is the net charge on the equatorial atoms.



TABLE VIII. CCSD(T) dissociation energies and reaction energies of the hydrides and halides of element 113<sup>a</sup>.

	$D_e$			$\Delta U_e$		
	ARPP+SO	ARPP	NRPP	ARPP+SO	ARPP	NRPP
(113)H	159.4	253.3	246.2			
(113)H <sub>3</sub>	463.4	579.6	673.1	-149.2	-126.8	-26.3
(113)H <sub>5</sub>	737.4	888.1	754.3	-178.9	-144.8	-372.0
(113)F	276.2	456.1	486.3			
(113)F <sub>3</sub>	443.8	616.7	1134.4	31.7	25.7	513.3
(113)F <sub>5</sub>	429.9	587.8		-105.6	-86.9	
(113)Cl	242.3	411.0	400.5			
(113)Cl <sub>3</sub>	406.6	571.4	906.5	-31.6	-35.5	310.2
(113)Br	210.5	382.9	360.8			
(113)Br <sub>3</sub>	348.1	544.0	802.0	-14.2	-11.9	268.2
(113)I	175.6	350.1	315.7			
(113)I <sub>3</sub>	314.1	497.8	685.2	6.1	12.0	221.9

<sup>a</sup>All energies in kJ mol<sup>-1</sup>.

is the presence of five sterically important electron pairs (two lone pairs and three bonding pairs) or, alternatively, a second-order Jahn–Teller distortion arising from the interaction of the  $A'_1$  HOMO and  $E'$  LUMO. For the (113)X<sub>3</sub> molecules, there are eight potentially sterically important electron pairs (13 electrons from 113,  $6d^{10}7s^27p^1$ , and three from the three ligands) which is unlikely to give a T-shaped structure. Possibly the simplest way to consider these molecules is to think of them as linear (113)X<sub>2</sub><sup>+</sup> species analogous to HgF<sub>2</sub> or AuF<sub>2</sub><sup>-</sup> with an additional 113–X bond that involves just the element 113  $7p$  orbital perpendicular to the (113)X<sub>2</sub><sup>+</sup> part and the appropriate ligand orbitals.

All nonrelativistic (113)X<sub>3</sub> structures are trigonal planar. Thus, the fact that (113)H<sub>3</sub>, (113)F<sub>3</sub>, and (113)Cl<sub>3</sub> are T-shaped rather than trigonal planar is mainly due to the relativistic lowering of the  $6d/7s$  gap. The relativistic bond length contraction of the two equatorial 113–H bonds in the T-shaped structure of (113)H<sub>3</sub> is 0.32 Å and the largest contraction for a group 13 compound calculated so far. Furthermore, the relativistic contraction of 0.23 Å of the two equatorial 113–F bonds in (113)F<sub>3</sub> is at least three times as large as any known Tl–X (X is any halide atom) relativistic contraction.<sup>85</sup> The effect of relativity on bond angles is known to be generally small<sup>79</sup> (it has been pointed out recently however, that relativistic effects on bond angles can be large if second-order Jahn–Teller effects are involved).<sup>86</sup> The three bond angles of (113)H<sub>3</sub>, (113)F<sub>3</sub>, and (113)Cl<sub>3</sub> undergo significant relativistic changes. The largest of these changes are +40.2, +53.6, and +33.6 deg for (113)H<sub>3</sub>, (113)F<sub>3</sub>, and (113)Cl<sub>3</sub>, respectively. To our knowledge, these represent the largest relativistic bond angle changes calculated so far for any molecule.

Spin–orbit effects on the geometries of element 113 trihalides are very small. The effects on the geometry of (113)H<sub>3</sub> are larger but are still much smaller than the scalar relativistic changes. The geometrical parameters of (113)H<sub>3</sub> listed in Table VI were calculated including the effects of spin–orbit coupling. In the absence of SO coupling they are as follows:  $R_1 = 1.836$  Å,  $R_2 = 1.629$  Å, and  $\alpha = 97.7$  deg. Therefore  $R_1$  and  $R_2$  are decreased by only 0.038 and 0.008 Å, respectively by SO coupling and  $\alpha$  is increased by only

0.9 deg. The changes in  $R_1$  and  $R_2$  may be compared with the SO decrease of 0.170 Å in the bond length of (113)H.

Like (113)H<sub>3</sub>, the relativistic and nonrelativistic structures of (113)H<sub>5</sub> are very different. The relativistic structure of (113)H<sub>5</sub> [and (113)F<sub>5</sub>] is square pyramidal while nonrelativistically it is trigonal bipyramidal (see Fig. 3). Not surprisingly, the  $6d$  populations of (113)H<sub>5</sub> and (113)F<sub>5</sub> calculated at the ARPP levels are much less than 10.0, indicating that these electrons also participate significantly in the bonding of (113)H<sub>5</sub> and (113)F<sub>5</sub>.

It is well known that for group 13 elements the stability of the +3 relative to the +1 oxidation state decreases from B to Tl. It has been predicted that the +3 oxidation state will be even less important in element 113 chemistry.<sup>29,87</sup> The relatively high energy of the  $6d$  electrons was also noted leading to the prediction that element 113 might be observed in the +5 oxidation state, a state unknown in any of the lighter group 13 elements.<sup>29,87</sup> To examine the relative thermodynamic stability of the +1 and +3 oxidation states of element 113, the reaction energy of the following gas phase elimination reaction was calculated



where X=H,F,Cl,Br,I. The reaction energy of Eq. (1) [denoted  $\Delta U_e(1)$ ] is defined as

$$\Delta U_e(1) = (E((113)X) + E(X_2) - E((113)X_3)). \quad (2)$$

Similarly, the relative stability of the +3 and +5 oxidation states will be examined using the reaction energy of the elimination reaction defined in Eq. (3),



where X=H,F. The reaction energy of Eq. (3) [denoted  $\Delta U_e(2)$ ] is defined as

$$\Delta U_e(2) = (E((113)X_3) + E(X_2) - E((113)X_5)). \quad (4)$$

$\Delta U_e(1)$  and  $\Delta U_e(2)$  were calculated at the ARPP+SO CCSD(T), ARPP CCSD(T), and NRPP CCSD(T) levels using the optimized MP2 geometries. The calculated reaction energies are listed in Table VIII. Also included in Table VIII are the dissociation energies of all the

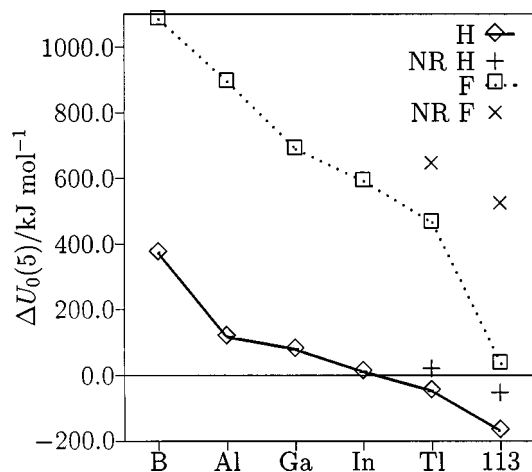


FIG. 5. Calculated MP2 reaction energies for the reaction  $\text{MX}_3 \rightarrow \text{MX} + \text{X}_2$  ( $\text{M} = \text{B}, \text{Al}, \text{Ga}, \text{In}, \text{Tl}, 113$ ;  $\text{X} = \text{H}, \text{F}$ ). All energies in  $\text{kJ mol}^{-1}$ . Data for B to Tl are from Ref. 56.

element 113 compounds considered. In Fig. 5 the elimination energies of  $\text{H}_2$  from  $(113)\text{H}_3$  and  $\text{F}_2$  from  $(113)\text{F}_3$  are compared with the equivalent energies for the B, Al, Ga, In, and Tl compounds.<sup>56</sup> Figure 5 shows that the trend towards increasing exothermicity of the  $\text{H}_2$  (or  $\text{F}_2$ ) elimination reaction of  $\text{MH}_3(\text{MF}_3)$  is continued with element 113. Furthermore, the ARPP+SO values of  $\Delta U_e(5)$  for  $(113)\text{Cl}_3$ ,  $(113)\text{Br}_3$ , and  $(113)\text{I}_3$  are all more than  $100 \text{ kJ mol}^{-1}$  less than the reaction energy for the equivalent Tl compounds.<sup>56,68</sup> These results are in agreement with the prediction that for element 113 the +3 oxidation state is even less stable relative to the +1 oxidation state than is the case for Tl. We mention that despite some claims,<sup>88</sup> the synthesis of  $\text{TlH}_3$  remains a challenge.<sup>89,90</sup>  $\text{InH}_3$  has been studied recently<sup>91</sup> but is extremely unstable. Thus, it appears that  $(113)\text{H}_3$  will not be a stable compound. Considering the halides,  $\text{TlF}_3$  is thermodynamically stable but  $\text{TlCl}_3$  and  $\text{TlBr}_3$  are strong oxidants and  $\text{TlI}_3$  with Tl in the +3 oxidation state is unknown.<sup>81,92,93</sup> All of the element 113 halides considered here will therefore probably be unstable as their reaction energies are all more negative than that calculated for  $\text{TlI}_3$ .<sup>56</sup> This analysis, of course, neglects kinetic effects. Anionic complexes of Tl with F, Cl, Br, and I have all been made and equivalent complexes such as  $(113)\text{Cl}_4^-$  should be more stable than the neutral compounds, especially since the T-shaped structure predicted for several of the  $113(\text{III})$  compounds opens up a vacant coordination site.

In the absence of relativity, the +3 oxidation state would still be important in the chemistry of element 113. This is demonstrated by a comparison of the NRPP elimination energies from Table VIII with previously published results<sup>56</sup> which shows that in the absence of relativity, the redox behavior of element 113 would fall somewhere in between that observed for In and Tl. SO effects, as expected, are large for the dissociation energies of all molecules but cancel almost completely in all the elimination energies.

From the calculated values of  $\Delta U_e(2)$  in Table VIII it appears that neither  $(113)\text{H}_5$  nor  $(113)\text{F}_5$  are thermodynamically stable relative to the equivalent  $113(\text{III})$  molecules. In

both cases  $\Delta U_e(2)$  is less than  $-100 \text{ kJ mol}^{-1}$ . The compound  $(113)\text{F}_6^-$  may be stable however. Further work is still needed to decide whether it could be possible to synthesize  $113(\text{V})$  species.

#### IV. CONCLUSION

Many of the results discussed in this article suggest that element 113 is a typical group 13 element. In most cases the properties calculated for molecules containing element 113 show a continuation of the periodic trends within the group 13 compounds. However, the dipole moment of  $(113)\text{H}$  is predicted to be very small due to spin-orbit effects, suggesting that element 113 may be somewhat more electronegative than Ga, In, Tl, or even Al. Three of the  $(113)\text{X}_3$  molecules are predicted to have T-shaped rather than trigonal planar geometries as a consequence of significant participation of the  $6d$  electrons in the bonding of these molecules. Element 113 may therefore be described as showing some "pseudotransition element character." The +3 oxidation state is very unstable for element 113 and only the anionic complexes such as  $(113)\text{F}_4^-$  may be stable and should be investigated in future. Finally, it seems unlikely that the +5 oxidation will be stable for element 113.

Comparison with four-component results for  $(113)\text{H}$  and  $(113)\text{F}$  and those calculated with a number of other methods showed that two-component relativistic pseudopotentials are capable of yielding reasonable predictions of the properties of molecules including element 113. ARPP, scalar DK, NRPP, and HF results did not agree so well with those from four component calculations due to their very different nature of their relativistic perturbation operators. Therefore, in general both spin-orbit and scalar relativistic effects are needed and more work on the adjustment of pseudopotentials is necessary for superheavy elements.

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