

We have carried out high-level ab initio calculations, by using relativistic pseudopotentials, on the structure, stability, and vibrational frequencies of gaseous  $\text{HgF}_4$ . Our results strongly suggest it to be a viable molecular species. For comparison we have also studied  $\text{KrF}_2$ , one of the few known and well-characterized<sup>[7]</sup> endothermic fluorine compounds.

The structure of  $\text{HgF}_4$  (in  $D_{4h}$  symmetry), optimized at the Hartree-Fock (HF),<sup>[8a]</sup> MP2,<sup>[8a, b]</sup> and QCISD levels<sup>[9, 10]</sup> of theory is shown in Figure 1. Harmonic vibrational frequency analysis at the HF level<sup>[8a]</sup> (see below) confirms the square-planar structure to be a minimum on the potential energy surface, in agreement with the expectations for a tetracoordinate low-spin  $5d^8$  species,<sup>[11]</sup> and with previous results for the isoelectronic  $\text{AuF}_4^-$ .<sup>[6c]</sup>

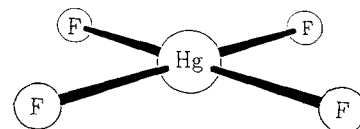


Fig. 1. Structure of  $\text{HgF}_4$ . Calculated Hg-F distances [ $\text{\AA}$ ] ( $D_{4h}$  symmetry): 1.886 (HF, cf. refs. [8a,b]); 1.962 (MP2, cf. refs. [8a,b]); 1.923 (MP2, with one additional f function at the metal); 1.904 (ANO-MP2, cf. refs. [8a,b, 9, 10]); 1.884 (ANO-QCISD, cf. refs. [9, 10]).

The results of large-scale ANO-QCISD and ANO-QCISD(T) calculations<sup>[9, 10]</sup> of the energies of several important reactions involving  $\text{HgF}_4$  or  $\text{KrF}_2$ <sup>[11]</sup> are shown in Table 2. Experimental data for  $\text{KrF}_2$  are also included. The most probable decomposition pathway for  $\text{HgF}_4$  in the gas phase (at least at low concentrations) is the reductive elimination of  $\text{F}_2$  [Table 2, Eq. (a)]. This reaction is slightly exothermic at the QCISD level ( $\Delta E = -12.5 \text{ kJ mol}^{-1}$ ) but slightly endothermic ( $\Delta H_0 = +11.6 \text{ kJ mol}^{-1}$ ) when contributions from connected triple excitations to the wavefunction (QCISD(T)) and zero point vibrational energy corrections (ZPE) are included. In contrast, loss of  $\text{F}_2$  from  $\text{KrF}_2$  [Table 2, Eq. (b)] is considerably exothermic ( $\Delta H = -75.5 \text{ kJ mol}^{-1}$ ). Hence, the oxidation of (gaseous monomeric)  $\text{HgF}_2$  by  $\text{KrF}_2$  [Eq. (c)] also is remarkably exothermic ( $\Delta H_0 = -94.2 \text{ kJ mol}^{-1}$ ).

## Gaseous Mercury(IV) Fluoride, $\text{HgF}_4$ : An Ab Initio Study\*\*

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The group 12 elements are usually considered to be main group rather than transition elements, since the completely filled ( $n-1$ )d shell does not participate in chemical bonding.<sup>[1, 2]</sup> Hence, the known chemistry of these elements is restricted to the  $M^{\text{II}}$  or lower oxidation states.<sup>[2]</sup> In general, the maximum achievable oxidation numbers increase from left to right within the first half of a given transition metal row (up to  $\text{Mn}^{\text{VII}}$ ,  $\text{Ru}^{\text{VIII}}$ , and  $\text{Os}^{\text{VIII}}$ , respectively) but drop back in the second half. While the discovery of  $\text{Cu}^{\text{IV}}$  in  $\text{Cs}_2\text{CuF}_6$ <sup>[3a]</sup> and of  $\text{Au}^{\text{V}}$  in  $\text{CsAuF}_6$ <sup>[3b]</sup> have stimulated interest in group 12 elements exhibiting oxidation states beyond II, there is only one report of a short-lived, electrochemically generated  $\text{Hg}^{\text{III}}$  species in solution.<sup>[4]</sup>

The first four ionization potentials of Zn, Cd, and Hg (cf. Table 1) clearly show that mercury is the most likely candidate for the occurrence of oxidation states higher than II (which invariably involve d orbitals in bonding) within this group. At least in part this is due to relativistic effects which stabilize and contract the 6s orbital but destabilize and expand the 5d orbitals (spin-orbit coupling also splits the d levels).<sup>[5]</sup> Thus, ionization from d levels becomes easier and simultaneously sd hybridization is energetically more favorable with Hg than with Zn or Cd. The same effects are responsible for the great importance of the III or V oxidation states in gold chemistry compared to copper or silver<sup>[6]</sup>.

Table 1. Ionization energies [eV] of the group 12 elements.

	I	II	III	IV
Zn exp. [a]	9.391	17.96	39.7	59.4
calcd. [b]	9.2	17.7	39.3	59.2
Cd exp. [a]	8.991	16.904	37.47	
calcd. [b]	8.8	16.6	37.2	53.4
Hg exp. [a]	10.43	18.751	34.2	
calcd. [b]	10.2	18.3	34.7	48.0

[a] Cf. ref. [15]. [b] This work: Averaged coupled pair functional results (cf., e.g. ref. [12 b]) with quasirelativistic 20-valence-electron pseudopotentials [8 e, 16] and 6s5p3d2f valence basis sets. No spin-orbit coupling has been considered.

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Table 2. Reaction energies [ $\text{kJ mol}^{-1}$ ] involving  $\text{HgF}_4$  or  $\text{KrF}_2$  [a].

Reaction	ZPE [b]	QCISD [c]	QCISD(T) [c]	exp.
(a) $\text{HgF}_4 \rightarrow \text{HgF}_2 + \text{F}_2$	-7.1	-12.5	+18.7	
(b) $\text{KrF}_2 \rightarrow \text{Kr} + \text{F}_2$	-3.8	-93.3	-75.5	-60.2 [d]
(c) $\text{HgF}_2 + \text{KrF}_2 \rightarrow \text{HgF}_4 + \text{Kr}$	+3.3	-80.8	-94.2	
(d) $\text{F}_2 \rightarrow 2 \text{F}$	-7.1	+114.5	+142.9	+159.7 (+154.2) [e, f]
(e) $\text{KrF}_2 \rightarrow \text{Kr} + 2 \text{F}$	-10.9	+21.3	+67.4	+99.5 [d]
(f) $\text{HgF}_4 \rightarrow \text{Hg} + 4 \text{F}$	-23.4	+562.2	+642.7	
(g) $\text{HgF}_2 \rightarrow \text{Hg} + 2 \text{F}$	-9.2	+460.2	+481.2	
(h) $\text{HgF}_4 \rightarrow \text{HgF}_2 + 2 \text{F}$	-14.2	+102.9	+161.6	

[a] Calculations at the QCISD-optimized structures. [b] Unscaled HF zero-point vibrational energy contributions. [c] Quadratic CI results [9, 10] without vibrational energy corrections. [d] Cf. ref. [7c]. [e] Cf. ref. [17]. [f]  $D_0(D_0)$  values given.

At the ANO-QCISD(T) level of theory, the  $\text{F}_2$  and  $\text{KrF}_2$  atomization energies [Table 2, Eqs. (d) and (e)], which are quite demanding to calculate,<sup>[7d, 12]</sup> agree within about 17 and 40  $\text{kJ mol}^{-1}$  to those values obtained from experiment (i.e. the average binding energies are underestimated by ca. 17 and 20  $\text{kJ mol}^{-1}$ , respectively). The accuracy for the at-

omization energies of  $\text{HgF}_4$  and  $\text{HgF}_2$  [Eqs. (f) and (g)] is somewhat less certain as, for example, spin-orbit coupling was not included in the QCI calculations. Unfortunately no accurate experimental value for gaseous  $\text{HgF}_2$  is available. However, the remaining correlation energy errors in  $\text{HgF}_4$  will be larger than those in  $\text{HgF}_2$  (as seen by the larger contribution of triple excitations to the average binding energy, cf. Table 2). Thus we probably *underestimate* rather than overestimate the stability of  $\text{HgF}_4$  relative to  $\text{HgF}_2$ .<sup>1</sup> Due to error compensation the  $\text{F}_2$  elimination reactions will exhibit smaller errors than the atomization energies (in these reactions the number of electron pairs is kept constant). Indeed, the error in the QCISD(T) reaction energy for  $\text{F}_2$  elimination from  $\text{KrF}_2$  [Eq. (b)] is only about 19  $\text{kJ mol}^{-1}$ . We estimate the error in the energy for oxidation of  $\text{HgF}_2$  by  $\text{KrF}_2$  [Eq. (c)] also to be below about 20–30  $\text{kJ mol}^{-1}$ . A detailed account of the performance of various theoretical approaches, and of the influence of relativistic effects on the reaction energies, will be published elsewhere.<sup>11,31</sup>

The atomization energies given in Table 2 [Eqs. (e)–(g)] show that, while the average Hg–F binding energy in  $\text{HgF}_4$  (ca. 160  $\text{kJ mol}^{-1}$ ) is considerably smaller than that in  $\text{HgF}_2$  (ca. 240  $\text{kJ mol}^{-1}$ ), it is still significant and much larger than the average Kr–F binding energy in  $\text{KrF}_2$  (50  $\text{kJ mol}^{-1}$  [7c]). The two additional Hg–F bonds in  $\text{HgF}_4$  together account for a gain of about 160  $\text{kJ mol}^{-1}$  compared to  $\text{HgF}_2 + 2\text{F}$  [Eq. (h)]. Thus, in the gas phase the formation of  $\text{HgF}_4$  from  $\text{HgF}_2$  and atomic fluorine also would be significantly exothermic. In the solid state  $\text{HgF}_2$  will be favored by its lattice energy: Preliminary calculations indicate that there is no significant stabilization of  $\text{HgF}_4$  by aggregation or anionic complexation.<sup>11,31</sup> We expect  $\text{HgF}_4$  to be a rather volatile substance.

The results of the harmonic vibrational frequency analysis (at the HF level<sup>18a1</sup>) for  $\text{HgF}_4$  are listed in Table 3. Due to the high symmetry present, the IR and Raman spectra are expected to contain only four and three bands, respectively. Thus, it should be possible to identify  $\text{HgF}_4$ , if obtained, by means of vibrational spectroscopy (the wavenumbers calculated for  $\text{HgF}_2$ <sup>14,41</sup> are significantly different). In view of the good agreement between Hartree–Fock and experimental frequencies of  $\text{HgF}_2$ <sup>14,41</sup> and  $\text{AuF}_4$ ,<sup>16c1</sup> we expect a similar accuracy (ca. 10–20  $\text{cm}^{-1}$ ) in the calculated wavenumbers for  $\text{HgF}_4$ .

Table 3. Calculated harmonic vibrational wavenumbers for  $\text{HgF}_4$  [a].

Symmetry	$\omega$ [ $\text{cm}^{-1}$ ]	Character	IR [b]	Raman [b]
$b_{2u}$	179	out of plane	yes	no
$A_{2u}$	233	out of plane	yes	no
$b_{2g}$	252	in plane	no	yes
$E_u$	261	in plane	yes	no
$b_{1g}$	650	stretch	no	yes
$A_{1g}$	652	stretch	no	yes
$E_u$	721	stretch	yes	no

[a] Cf. ref. [8a]. [b] Infrared or Raman activity.

In conclusion, our calculations indicate that it should be possible to prepare and characterize (e.g. by matrix isolation spectroscopy) mercury(IV) fluoride. Even if decomposition into  $\text{HgF}_2 + \text{F}_2$  [Eq. (a)] were slightly exothermic, the significant nuclear reorganization involved (two Hg–F bonds are broken and one F–F bond is formed), and the small reaction energy suggest a significant activation barrier for this reaction. Unfortunately, our attempts to obtain an accurate esti-

mate for the barrier height have failed up to now. The wavefunction near the transition state has strong multireference character (i.e. large nondynamical electron correlation effects have to be considered), and the internal nuclear coordinates are strongly coupled (spin–orbit coupling may also complicate the situation).

The gas-phase reaction  $\text{HgF}_2 + \text{KrF}_2 \rightarrow \text{HgF}_4 + \text{Kr}$  [Eq. (c)] is considerably exothermic. Perhaps, a solvent-based low-temperature variant of this reaction is a route into  $\text{Hg}^{\text{IV}}$  chemistry. The calculated vibrational frequencies should aid in the experimental characterization of  $\text{HgF}_4$ .

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