# HgH₄ and HgH₆: further candidates for high-valent mercury compounds

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**Mercury tetrahydride ($D_{4h}$) is calculated to have similar bond lengths and vibrational frequencies as the already known HgH₂ and to lie energetically 200 kJ mol⁻¹ above HgH₂ + H₂, in a local well, about 40 kJ mol⁻¹ below a transition state.**

Each new oxidation state of an element is now a chemical achievement and a larger achievement at that, if a new atomic shell is formally oxidized or reduced for that particular element. Granted the existence of Au(III), which in fact is the most stable oxidation state of gold, the possible existence of Hg(IV), partially oxidizing the 5d shell, has been expected for some time. Jørgensen mentioned both Hg(III) and Hg(IV) as future possibilities.[1] Kaupp *et al.*[2,3] indeed calculated the formation reaction $HgF_2 + F_2 \rightarrow HgF_4$ ($D_{4h}$) to be exothermic. Although the prediction was confirmed by later calculation,[4] no successful experiments have been reported.

How about hydrogen? The inner bonding of H₂ is much stronger than that of F₂; the $D_0$ are 432.07 and 154.57 kJ mol⁻¹, respectively.[5] While this would disfavour the mercury tetrahydride over the mercury tetrafluoride, the small size of the hydrogen might actually lead to a better hybridization with the mercury 5d shell. The relativistic destabilisation of the Hg 5d shell is expected to make Hg the best candidate in Group 12. Furthermore hydrogen as reagent has experimental advantages over fluorine. We have in mind either matrix spectroscopic or high-pressure experiments.

The known mercury hydride species comprise the diatomic HgH and HgH⁺[5] as well as HgH₂ that has been studied both theoretically[6,7] and using matrix spectroscopy.[8] The latter authors also present evidence for HHgHgH. No earlier studies on HgH₄ were found. It should be noted that it is valence isoelectronic with the known square planar PtH₄²⁻ anion, present *e.g.* in K₂PtD₄[9] (Pt–D 163 pm).

We here report *ab initio* pseudo-potential calculations on HgH₄ and related systems. For technical calibration we add HgH⁺ and HgH₂. Also, noting that the 18-valence electron rule would favour HgH₆, we have included it.

We used the hybrid density functional B3LYP,[10,11] MP2, and CCSD(T) methods implemented in Gaussian 98 sotware package[12] together with the Stuttgart small-core relativistic pseudopotential and corresponding basis set for mercury,[13] augmented by 2f functions with $\alpha = 1.7$ and $\alpha = 0.6$,[7] and by one g function with $\alpha = 1.0$. The TZVP basis set for hydrogen[14] was used.

The calculated Hg–H distances are listed in Table 1 and vibrational frequenceis in Table 2. Somewhat surprisingly, the Hg–H bond lengths actually decrease from HgH₂ to HgH₄ and HgH₆. The symmetric stretch frequencies are nearly constant along the same series and so are the antisymmetric vibrations ($\Sigma_u$, $E_u$ and $T_{1u}$, respectively). The energies of formation (compared with Hg(g) + $n$H₂(g)) are included in Table 1. They increase from the (CCSD(T)) 116 kJ mol⁻¹ for the observed HgH₂ to 340 and 575.3 kJ mol⁻¹ for HgH₄ and HgH₆, respectively. Noting that $3D_0(H_2)$ is 1296 kJ mol⁻¹ even the hexahydride is far below the atoms. Note that H atoms in rare-gas matrices are easy to create.

The planar $C_{2v}$ transition state for dissociation of HgH₄

(B3LYP) is shown in Fig. 1. It lies 39 kJ mol⁻¹ above the $D_{4h}$ minimum at B3LYP level (including the zero-point energy correction), or 34 kJ mol⁻¹ at the MP2 level. The dissociation leads to the in-plane loss of one H₂ molecule. HgH₆ also has a $C_{2v}$ transition state, leading to H₂ + HgH₄. It lies 30 kJ mol⁻¹ above the hexahydride at both B3LYP and MP2 levels.

The bonding of HgH₄ is delightfully simple. The B3LYP molecular orbitals are shown in Fig. 2. Letting the Hg–H bonds

**Table 1** The Hg–H distances and zero-point energy corrected energies of formation for systems considered

| System | Method | Hg–H/pm | $\Delta E$/kJ mol⁻¹ |
|---|---|---|---|
| HgH₆ | B3LYP | 163.6 | 607.1 |
| | MP2 | 161.9 | 598.2 |
| | CCSD(T) | 163.5 | 575.3 |
| HgH₄ | B3LYP | 164.1 | 312.1 |
| | MP2 | 161.8 | 348.7 |
| | CCSD(T) | 163.5 | 339.7 |
| HgH₂ | B3LYP | 165.3 | 104.4 |
| | MP2 | 162.5 | 129.0 |
| | CCSD(T) | 164.5 | 115.7 |
| | CCSD(T)[a] | 163.9 | 100.6 |
| HgH⁺ | B3LYP | 161.0 | |
| | MP2 | 157.9 | |
| | CCSD(T) | 160.7 | |
| | CCSD(T)[a] | 159.6 | |
| | Exptl.[b] | 159.4 | |

[a] Ref. 7. [b] Ref. 15.

**Table 2** Harmonic vibrational frequencies with intensities in parentheses; frequencies in cm⁻¹, intensities in km mol⁻¹

| Species | Symmetry | B3LYP | MP2 | Exptl. |
|---|---|---|---|---|
| HgH₆ | $E_g$ | 2090 | 2165 | |
| | $A_{1g}$ | 2063 | 2129 | |
| | $T_{1u}$ | 1984 (266) | 2080 (187) | |
| | $T_{1u}$ | 810 (56) | 789 (69) | |
| | $T_{2g}$ | 755 | 759 | |
| | $T_{2u}$ | 695 | 688 | |
| HgH₄ | $B_{1g}$ | 2085 | 2194 | |
| | $A_{1g}$ | 2060 | 2154 | |
| | $E_u$ | 1959 (356) | 2058 (310) | |
| | $B_{2u}$ | 884 | 909 | |
| | $A_{2u}$ | 839 (10) | 842 (7) | |
| | $B_{2g}$ | 759 | 772 | |
| | $E_u$ | 764 (40) | 757 (58) | |
| HgD₄ | $B_{1g}$ | 1475 | | |
| | $A_{1g}$ | 1457 | | |
| | $E_u$ | 1393 (178) | | |
| | $B_{2u}$ | 625 | | |
| | $A_{2u}$ | 599 (5) | | |
| | $B_{2g}$ | 537 | | |
| | $E_u$ | 543 (21) | | |
| HgH₂ | $\Sigma_g$ | 2033 | 2164 | |
| | $\Sigma_u$ | 1922 (442) | 2023 (425) | 1896[a] |
| | $\Pi_u$ | 799 (32) | 821 (31) | 773[a] |
| HgH⁺ | $\Sigma_g$ | 1987 (137) | 2092 (158) | 2028[b] |

[a] Ref. 15. [b] Ref. 5.

lie in the $x$ and $y$ directions, the lowest bonding MO is the $b_{1g}$, $5d_{x^2-y^2} + 1s$. The next one, HOMO-4 is the $a_{1g}$ $5d_{3z^2-r^2} + 1s$. Its
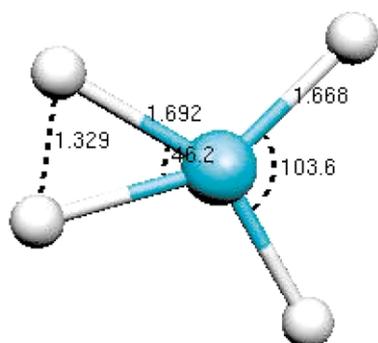


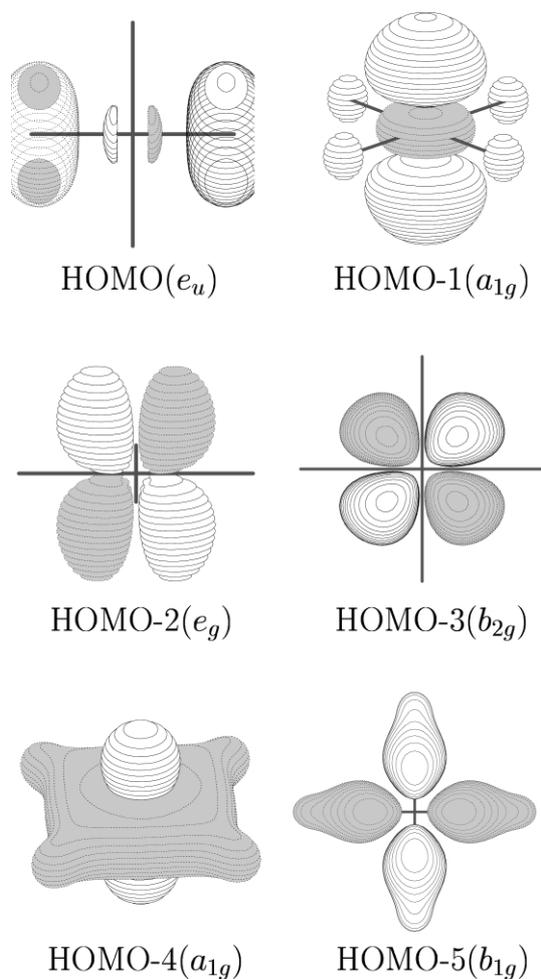**Fig. 1** The geometry of the transition state for HgH$_4$ disociation.



HOMO($e_u$)  HOMO-1($a_{1g}$)

HOMO-2($e_g$)  HOMO-3($b_{2g}$)

HOMO-4($a_{1g}$)  HOMO-5($b_{1g}$)

**Fig. 2** The molecular orbitals of HgH$_4$.

**Table 3** The natural orbital occupancies and charges

| System | H (1s) | Hg (5d) | Hg (6s) | Hg (6p) | $Q$(H) | $Q$(Hg) |
|---|---|---|---|---|---|---|
| HgH$_6$ | 1.20 | 9.59 | 1.00 | 0.17 | −0.21 | 1.24 |
| HgH$_4$ | 1.28 | 9.72 | 1.03 | 0.10 | −0.29 | 1.14 |
| HgH$_2$ | 1.39 | 9.89 | 1.26 | 0.04 | −0.40 | 0.81 |
| HgH$^+$ | 0.94 | 9.93 | 1.12 | 0.01 | 0.05 | 0.95 |

weakly antibonding counterpart is the HOMO-1. Note that the two lowest, strongly bonding orbitals lie below the pure-5d core orbitals. Finally, the bonding $e_u$ 6p + 1s HOMO and non-bonding, purely d orbitals HOMO-(2,3), complete the picture. The four bonding molecular orbitals 2 × $e_u$, $a_{1g}$ and $b_{1g}$ essentially result in four single Hg–H bonds for HgH$_4$. The Natural Bond Orbital analysis is shown in Table 3 and gives an idea of the 5d hole and 6p occupation.

We conclude, that the Hg(IV) compound HgH$_4$ and even the Hg(VI) compound HgH$_6$ are possible synthetic objects for matrix spectroscopic experiments. Deuteration may be necessary to slow down decay by tunneling.

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