

Mercury Is a Transition Metal: The First Experimental Evidence for HgF_4^{**}

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Group 12 of the periodic table, consisting of zinc, cadmium, and mercury, is usually considered a post-transition-metal group, because the outermost shell of d orbitals is filled and does not participate significantly in chemical bonding. Therefore, the highest experimentally established oxidation state for elements in this group is +II.^[1,2]

For any higher oxidation state, the d orbitals would have to be involved in bonding. A report of a short-lived, electrochemically generated mercury(III) species in 1976^[3] has never been confirmed. Nevertheless, speculations about higher oxidation states of mercury have been around since the 1970s and 1980s.^[4,5] In 1993, Kaupp et al. reported quantum-chemical calculations that indicated HgF_4 , with mercury in the oxidation state +IV, to be a stable molecule in the gas phase.^[6,7] The most relevant gas-phase reaction $\text{HgF}_4 \rightarrow \text{HgF}_2 + \text{F}_2$ for decomposition of HgF_4 was computed to be endothermic, with a current best estimate of about 30–40 kJ mol⁻¹.^[8] That is, HgF_4 should be a thermochemically stable species in the gas phase (disregarding thermal contributions^[9]). This square-planar low-spin d⁸ complex would indeed make the Group 12 element mercury a transition metal. In the condensed phase, the larger aggregation energy of HgF_2 will shift the equilibrium significantly to the right and thereby destabilize HgF_4 .^[7] These results have been confirmed over the years at higher and higher computational levels, and calculations were also extended to other mercury(IV) species.^[8,10–12] Importantly, the stability of HgF_4 was found to derive from relativistic effects, owing to the high positive charge of the heavy mercury nucleus and the ensuing

high average speed of the electrons passing near the nucleus.^[7] Therefore, the homologous, lighter, and “less relativistic” ZnF_4 and CdF_4 molecules were computed to eliminate F_2 in a strongly exothermic fashion and to be much less likely to exist.^[7] In contrast, the “more relativistic” eka-mercury analogue of HgF_4 , (112) F_4 , has been predicted to be even more stable than HgF_4 with respect to F_2 elimination.^[13]

In spite of the large amount of computational evidence for HgF_4 , and of an appreciable number of (largely unpublished) attempts to synthesize it,^[14] experimental confirmation for its existence has been lacking to date. Because of the unfavorable effect of aggregation of HgF_2 , and because calculations suggest the reaction $\text{HgF}_2 + 2\text{F} \rightarrow \text{HgF}_4$ to be exothermic by more than 150 kJ mol⁻¹, preparation by matrix isolation appears to be the most attractive route to HgF_4 . This assessment holds in particular in view of the mobility of F atoms in solid argon^[15] and even more so in solid neon. We report herein the detection of HgF_4 from the photochemical reaction of Hg and F_2 in solid neon and argon at 4 K. Similar methodology has been used for four decades to produce and add fluorine atoms to small molecules in solid matrixes.^[16–18]

Twenty experiments were performed to maximize mercury fluoride product absorptions from the ultraviolet photochemical reaction of mercury atoms and fluorine. Figure 1 illustrates infrared spectra from our most productive investigation using 1 % F_2 in neon and less than 0.1 % mercury atoms, which gave a spectrum free of significant absorption on sample deposition (Figure 1 a). Irradiation with 240–380-nm light from the mercury arc (Figure 1 b) produced the strong sharp absorption at 657.5 cm⁻¹, which can be assigned to HgF_2 on the basis of previous observation of this molecule at 642 cm⁻¹ in solid krypton at 20 K^[19] and at 645 cm⁻¹ in solid argon.^[20] Additional weak bands were observed at 703, 637, and 613 cm⁻¹, and a higher-frequency band was detected at 1508 cm⁻¹, where OOF should absorb in solid neon, considering its strong band at 1490 cm⁻¹ in solid argon.^[21] Further irradiation with the full light of the mercury arc increased the intensity of these bands (Figure 1 c). Annealing the sample to 8 K to allow further reagent aggregation increased the intensity of the 703 cm⁻¹ band at the expense of the 657.5 cm⁻¹ band (Figure 1 d). Subsequent annealing to 10 and 12 K slightly reduced the intensity of the two bands (Figure 1 e,f). A similar experiment using 0.5 % F_2 in neon and irradiation with the full light of the mercury arc produced the strong sharp absorption at 657.5 cm⁻¹ and weak bands at 703 and 637 cm⁻¹ (Figure 2 a,b). Annealing the sample to 8 K to allow further reagent aggregation slightly broadened all absorptions, but further irradiation increased their intensity slightly (Figure 2 c,d). A final annealing to 10 K reduced the intensity of the above bands and produced a new, weaker band at

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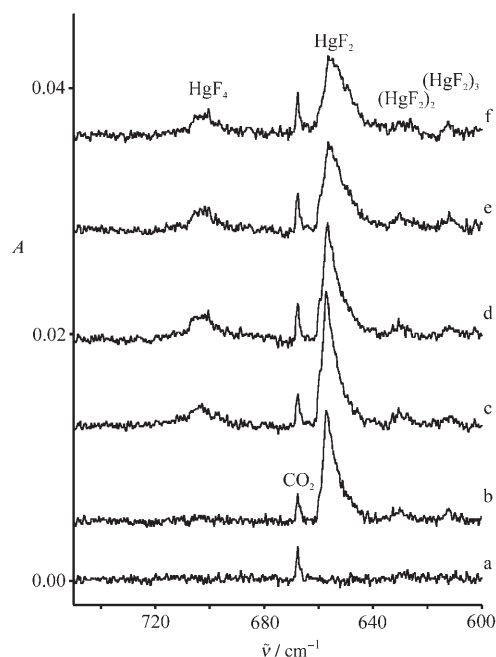


Figure 1. Infrared spectra in the 750–600 cm^{-1} region for reaction products of mercury and fluorine. a) Hg and 1% F_2 in solid neon at 4 K. b) After 240–380 nm irradiation for 15 min through a glass filter. c) After irradiation above 220 nm for 15 min using full arc. d) After annealing to 8 K. e) After annealing to 10 K. f) After annealing to 12 K.

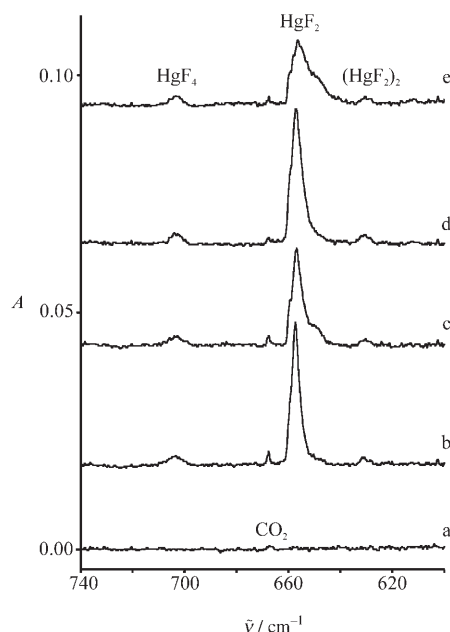


Figure 2. Infrared spectra in the 740–610 cm^{-1} region for reaction products of mercury and fluorine. a) Hg and 0.5% F_2 in solid neon at 4 K. b) After irradiation above 220 nm for 15 min through a glass filter. c) After annealing to 8 K. d) After second irradiation above 220 nm using full arc. e) After annealing to 10 K.

613 cm^{-1} (Figure 2e). An additional band at 587 cm^{-1} was observed in another experiment.

An analogous investigation in excess argon produced the spectra shown in Figure 3. The strong band for HgF_2 is at

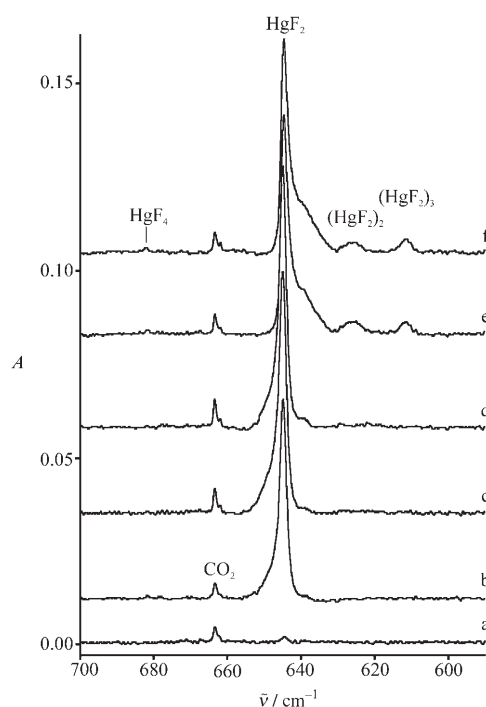


Figure 3. Infrared spectra in the 700–600 cm^{-1} region for reaction products of mercury and fluorine. a) Hg and 2% F_2 in solid argon at 4 K. b) After 240–380 nm irradiation for 15 min through a glass filter. c) After irradiation above 220 nm using full arc. d) After annealing to 20 K. e) After annealing to 30 K. f) After annealing to 35 K.

644.9 cm^{-1} , and the weak band at 682 cm^{-1} , along with OOF at 1489.6 cm^{-1} , is produced upon 240–380 nm irradiation. The intensity of the 682 cm^{-1} and OOF bands increases slightly on annealing to 20, 30, and 35 K, and lower-frequency bands for HgF_2 clusters appear at 626 and 612 cm^{-1} . While mercury isotopes from ^{197}Hg through ^{204}Hg are expected to contribute to the spectra with appreciable natural abundances, the overall range of isotopic shifts is computed to be only about 0.5 cm^{-1} , which is too small to be resolved under the experimental conditions.

Similar experiments were performed with laser-ablated $\text{Zn}^{[22]}$ and F_2 in excess neon, and a very strong, resolved natural zinc isotopic triplet absorption with 5:3:2 relative intensities was measured at 781.0, 776.7, and 772.6 cm^{-1} (see the Supporting Information, Figure S1). This triplet corresponds to the ZnF_2 isotopic spectrum observed in solid krypton^[19] and in solid argon and neon,^[23] which demonstrates the participation of a single metal atom in this product and vibrational mode.^[22] In contrast to HgF_4 compared to HgF_2 (see below), the degenerate E_u stretching frequency of ZnF_4 is predicted by computations to be at lower frequency (by 94 cm^{-1} at the CCSD(T)/aug-cc-pVQZ level) than that of ZnF_2 . Ultraviolet irradiation increased the intensity of the ZnF_2 triplet, but no band in the predicted lower-frequency range was detected. Furthermore, laser-ablation experiments with boron and aluminum and the same fluorine sample did not produce any absorption at 703 cm^{-1} . Several studies with mercury and chlorine in solid neon (see the Supporting Information, Figure S2) gave new absorptions at 417.4 and

413.7 cm^{-1} after ultraviolet irradiation, which are appropriate for HgCl_2 with chlorine isotopes in natural abundance and are consistent with previous work in argon.^[20] No absorptions appropriate for HgCl_4 could be detected.

These investigations produced a large spectroscopic yield of HgF_2 , as attested by the strong antisymmetric stretching fundamental of the linear molecule. The bands at lower frequencies on annealing are attributed to oligomer clusters $(\text{HgF}_2)_n$ ($n = 2, 3, 4$), which is consistent with earlier work.^[19,20] Our calculations at the B3LYP/aug-cc-pVTZ level give highest IR-active frequencies for dimer, trimer, and tetramer about 25 cm^{-1} and about 60–70 cm^{-1} below the monomer HgF_2 band, which is consistent with the observed bands (see the Supporting Information, Table S1).

The new higher-frequency bands at 703 cm^{-1} in solid neon and at 682 cm^{-1} in solid argon are in the region predicted for the degenerate E_u Hg–F stretching mode of the square-planar HgF_4 molecule.^[7] These bands appear upon UV irradiation of the HgF_2 molecule, and their intensity increases slightly on annealing under conditions where F atoms diffuse through the solid lattice,^[15–17,21] when OOF radical is also produced from the combination of F atoms and O_2 impurity in fluorine. Hence, the weak bands appear under reaction conditions for which HgF_4 has been predicted to form,^[6–8] namely the exothermic reaction of HgF_2 with F_2 , and in particular reaction with two fluorine atoms (see above). Our calculations at the CCSD(T)/aug-cc-pVQZ (B3LYP/aug-cc-pVTZ) level with relativistic pseudopotentials for Hg indicate the highest IR-active frequencies to be 686 cm^{-1} (660 cm^{-1}) for HgF_4 and 663 cm^{-1} (636 cm^{-1}) for HgF_2 (see the Supporting Information, Table S2). The highest-frequency fundamental for the tetrafluoride is thus computed to be approximately 23–24 cm^{-1} higher than that of the difluoride. Experimentally, our new weak absorption is 45 cm^{-1} higher in solid neon and 37 cm^{-1} higher in solid argon.

These discrepancies between the experimental and computed shifts may in principle arise from several sources. Evaluation of different fluorine basis sets (see the Supporting Information, Table S2) suggests that still larger basis sets may increase the absolute frequencies, but not the relative shift, by up to 10 cm^{-1} . Corrections for anharmonicities (B3LYP/aug-cc-pVTZ level, see the Supporting Information, Table S3) reduce the frequencies for both HgF_4 and HgF_2 by approximately 9.5 cm^{-1} and thus also leave the relative shift unaltered. Our best frequency estimates for IR frequencies are thus close to the CCSD(T)/aug-cc-pVQZ values given above. The computed frequency for gas-phase HgF_4 is close to the weak band measured in the argon matrix, whereas the computed frequency for gas-phase HgF_2 is closer to its neon-matrix value. The most likely reason for the measured difference between product molecule bands to be larger than the computed difference is thus related to different interactions with the matrix environment for HgF_4 and HgF_2 (the precise magnitude of such an interaction is difficult to estimate).

Solid neon and argon have different interactions with solute guest molecules. Neon is less polarizable and can be repulsive (sometimes with a blue matrix shift), whereas argon supports a more attractive interaction.^[24] Two relevant cases

are OOF, with bands at 1508 cm^{-1} in a neon matrix (this work), 1489.6 cm^{-1} in an argon matrix (this work and reference [21]), and 1486.9 cm^{-1} in the gas phase,^[25] and MgF_2 with absorptions at 862 cm^{-1} in a neon matrix and 840 cm^{-1} in an argon matrix^[26] and with an estimated gas-phase frequency of $825 \pm 20 \text{ cm}^{-1}$.^[27] Clearly HgF_2 sets an example, with bands at 658 cm^{-1} in a neon matrix and 645 cm^{-1} in an argon matrix, and our new bands for HgF_4 at 703 and 682 cm^{-1} , respectively, follow suit. Assuming a best gas-phase value of about 690 cm^{-1} (see above), a larger blue shift of the HgF_4 absorption than of the HgF_2 absorption in the neon matrix provides straightforward rationalization for our observations. Moreover, we have found solid neon to be superior to solid argon for the photoproduction of HgF_4 .

Most importantly, however, all other conceivable Hg–F species are expected to exhibit their high-frequency fundamentals below that of HgF_2 . This assessment holds for HgF_3 and HgF (its fundamental is at 483 cm^{-1} [28]), for Hg_2F_2 (see the Supporting Information, Table S2), and for HgF_2 clusters (see above and the Supporting Information, Table S1). Note that any complexes of HgF_2 with F_2 or other small molecules in the matrix are also expected to give rise to lower frequencies than free HgF_2 .^[20] Additional supporting chemical evidence comes from the experiments with zinc, in which the reaction of laser-ablated and excited zinc atoms produced only ZnF_2 , with no evidence of a ZnF_4 species. This result agrees with the above discussion of exothermic F_2 elimination from ZnF_4 and with the extra stabilization of HgF_4 brought about by the effects of special relativity.^[6,7]

In conclusion, experiments in both neon and argon matrixes clearly show IR absorptions at the position (absolute and relative to HgF_2) predicted for HgF_4 by accurate quantum-chemical calculations. From the measured intensities and the computed vibrational transition probabilities, we estimate the ratio of HgF_4 formed relative to HgF_2 to be about 1:10. This yield is reasonable for such a photolysis product in the neon matrix.

HgF_4 is a square-planar low-spin d^8 transition-metal complex (Figure 4), in which the 5d orbitals of mercury are

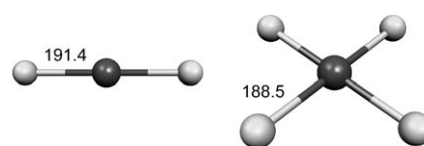


Figure 4. Structures of HgF_2 and HgF_4 (with bond lengths in pm) computed at the CCSD(T)/aug-cc-pVQZ level of theory.

strongly involved in bonding.^[7,8] Mercury should therefore be viewed as a genuine transition-metal element rather than as a post-transition metal, and thus the observation of HgF_4 changes the way we should view the periodic table. This interpretation is confirmed by a comparison of the electron localization function (ELF) plots in Figure 5 for HgF_2 (left) and HgF_4 (right). The relatively round and smooth boundaries of the Hg valence-shell basin (brown area) and the wide low-ELF nodal region between Hg and F basins (blue area) in the difluoride indicate rather ionic, s-orbital dominated

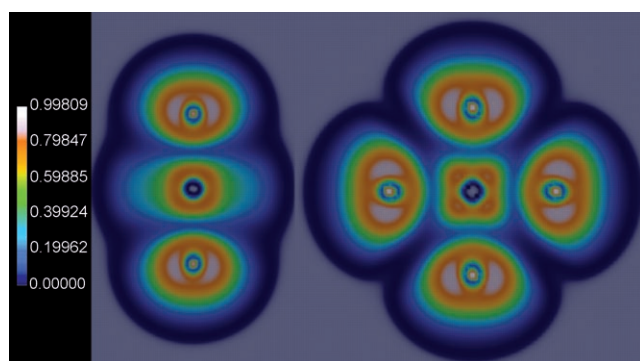


Figure 5. Color-scale plot of the electron localization function (ELF) for HgF_2 (left) and HgF_4 (right). High ELF values indicate areas with low local kinetic energy densities owing to relatively low Pauli repulsion.

bonding with a filled, only somewhat polarized d^{10} shell.^[29] The more pronounced deformation of the Hg valence shell in HgF_4 (with splitting into four sub-domains) by Pauli repulsion with the fluorine ligands, together with the stronger deformation of the fluorine valence basins, is consistent with much more covalent, d-orbital-dominated bonding^[7] in the genuine low-spin d^8 complex. The picture resembles ELF plots of typical d^8 complexes of Groups 9–11 (see, for example, reference [30]).

These results are also relevant in the context of a recent theoretical prediction of a linear decrease of the maximum attainable oxidation states in the 6th period from Os^{VIII} to Tl^{III} .^[31] With our detection of Hg^{IV} and a recent disproof of the existence of Au^{VII} ,^[32,33] the predicted^[31] state Ir^{VII} has become the last missing piece in the experimental verification of this linear trend. We hope this work will inspire further bulk synthetic efforts for Hg^{IV} species with larger quantities of material.

Experimental Section

Mercury atoms were evaporated from a stainless steel reservoir at 55 °C through a stainless steel valve (Nupro SS4BK), as described previously,^[34,35] into neon (or argon) and fluorine condensing onto a cesium iodide window at 4 K.^[36] IR spectra were recorded on a Nicolet 750 instrument at 0.5 cm^{-1} resolution. Samples were irradiated by a mercury arc street lamp (Sylvania H39 KB-175) with the outer globe removed. The intensity of the full arc irradiation is critical for the new product formation, as HgF_4 is photosensitive. Commercial fluorine (Matheson) was handled in a dedicated, well-passivated stainless steel manifold and spray-on line. Our 1-L fluorine reservoir was cooled to 77 K while preparing the matrix sample to retain most of the common impurity molecules in commercial fluorine. We have found solid neon to be superior to solid argon for the photo-production of HgF_4 .

Molecular structures were optimized at the density functional theory (DFT) level (with B3LYP functional^[37–40]) and coupled-cluster CCSD(T) level using the programs Gaussian03^[37] for the DFT and Molpro 2006.1^[41] for the CCSD(T) calculations. Because of their size, the odd-electron species HgF_3 and the larger oligomers $(\text{HgF}_2)_3$ and $(\text{HgF}_2)_4$ were studied only at the DFT (B3LYP) level. Quasirelativistic, energy-adjusted, small-core pseudopotentials (effective-core potentials, ECP) of the Stuttgart group were used for the mercury atom.^[42] The associated (8s7p6d)/[6s5p3d] valence basis set was augmented by two f-type polarization functions and one g-type

function ($\alpha_f = 1.58, 0.545, \alpha_g = 1.384$).^[43] Several Dunning correlation-consistent fluorine basis sets [double- ζ (aug-cc-pVDZ), triple- ζ (aug-cc-pVTZ), and quadruple- ζ (aug-cc-pVQZ)] were used to evaluate basis-set effects on the harmonic vibrational frequencies.^[44] Anharmonic corrections of the vibrational spectra have been calculated at the DFT (B3LYP/aug-cc-pVTZ) level using the program package GAMESS 2006.^[45]

Given the extended basis sets, contributions of basis-set superposition errors (BSSE) to the energetics were not estimated. See reference [8] for a more detailed quantum-chemical description including BSSE corrections. Spin-orbit corrections were also not considered, as they have been found to be small for the elimination reaction $\text{HgF}_4 \rightarrow \text{HgF}_2 + \text{F}_2$.^[10] They are expected to be even less important for the vibrational frequencies.

For graphical bonding analyses, the electron localization function (ELF)^[46] has been displayed for cuts containing the molecular plane using the conventional color scale of ELF.^[47] The plots were made using the Molekel program.^[48]

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