# Electronic Supplementary Information

## Infrared Spectroscopic and Theoretical Studies of the $OTiF_2$, $OZrF_2$ and $OHfF_2$ Molecules with Terminal Oxo Ligands

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Table S1. Vibrational Frequencies (cm$^{-1}$) Observed in Solid Argon and Calculated Modes (Infrared Intensities, km/mol) for the OTiF Radical in the $^2$A’ Ground State Using the same DFT Methods as for Table 1. [a]

| | | $^{16}$OTiF | | $^{18}$OTiF | |
|---|---|---|---|---|---|
| | mode | obs. | calc. | obs. | calc. |
| OTiF | Ti-O str.[b] | 962.7 | 1021.7(289) | 922.3 | 978.6 (273) |
| | Ti-F str | 609.4 | 626.8 (157) | 608.6 | 626.0 (154) |
| | O-Ti-F bend | not obs. | 123.9 (31) | not obs. | 120.9 (30) |

[a] Computed structural parameters: Ti-O=1.626 Å, Ti-F= 1.851 Å, O-Ti-F=125.3° .

Table S2. CCSD(T) Calculated and Experimental Bond Distances, M-O Frequencies, Bond Dissociation Energies and Singlet-Triplet Splittings for Diatomic MO for M = Ti, Zr, and Hf.

| Property | TiO calc | TiO expt | ZrO calc | ZrO expt | HfO calc | HfO expt |
|---|---|---|---|---|---|---|
| State | $^3\Delta$ | $^3\Delta_r$ | $^1\Sigma^+$ | $^1\Sigma^+$ | $^1\Sigma^+$ | $^1\Sigma^+$ |
| R (Å) | 1.6391 | 1.6202[a] | 1.7194 | 1.7116[a] | 1.7198 | 1.72307[a] |
| $\omega_e$ (cm$^{-1}$) | 1003.3 | 1009.0[a] | 975.86 | 969.7[a] | 969.83 | 974.09[a] |
| $\omega_e x_e$ (cm$^{-1}$) | 4.59 | 4.498[a] | 3.29 | 4.9 [a] | 3.09 | 3.228[a] |
| $D_0^0$ (eV) | 6.76 | 6.87[a] | 7.84 | 7.85[a] | 8.36 | 8.19[a] |
|  |  | 6.96 ± 0.1[b] |  | 7.94 ± 0.1[b] |  | 8.30 ± 0.13[b] |
|  |  | 6.93[b] |  |  |  |  |
| ΔE(S-T) kcal/mol | -14.4 | -16.2[a,c] | 2.8 | 4.9 ± 0.7[a] | 30.1 |  |

[a] Reference 58.

[b] Reference 59.

[c] $^3\Delta_r$ - $^1\Sigma^+$. Calculated from the value for the $^1\Delta$ state (3440 ± 10 cm$^{-1}$) plus the $^1\Delta$ - $^1\Sigma^+$ energy difference of 2215.6 cm$^{-1}$.

Table S3. CCSD(T) Calculated Properties of $MF_2$ for M = Ti, Zr, Hf

| Property | Ti | Zr | Hf |
|---|---|---|---|
| Electronic State | $^3\Delta_g$ | $^3B_1$ | $^1A_1$ |
| R(M-F) Å | 1.832 | 1.920 | 1.864 |
| <(FMF) ° | 180.0 | 138.9 | 124.9 |
| M-F sym stretch $cm^{-1}$ | 594.6 | 627.7 | 662.5 |
| M-F asym stretch $cm^{-1}$ | 754.5 | 641.9 | 683.3 |
| F-M-F bend | 213(π)[a] | 99.7 | 107.6 |

[a] Due to symmetry breaking issues in the bends in the numerical second derivative calculations, only the symmetric and asymmetric stretches were taken from the CCSD(T) calculations. The bending frequency is taken from the MRCI calculations in Ref. 61.

Table S4. Electronic Energy Contribution to the Total Atomization Energies in kcal/mol for the Ground States of MO, $MF_2$, and $MOF_2$ (M=Ti, Zr, Hf).[a]

| molecule | $\Delta E_{(n=D)}$ | $\Delta E_{(n=T)}$ | $\Delta E_{(n=Q)}$ | $\Delta E_{CBS}$[e] | $\Delta E_{(AWCTZ\text{-}DK)}$[c,f] | $\Delta E_{(AWCTZ\text{-}PP)}$[c,g] | $\Delta E_{(SR)}$[c,h] | $\Delta E_{(PP,corr)}$[i] | $\Delta E_{(CV)}$ | $\Delta E_{(ZPE)}$ | $\Delta E_{SO}$ | $\Sigma D_0$[j] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $TiOF_2$[b] | 426.56 | 435.91 | 441.30 | 444.61 | 437.81 | 439.75 | -2.65 | 0.71 | 3.06 | -4.31 | -1.64 | 439.78 |
| $ZrOF_2$[c] | 461.04 | 474.86 | 480.80 | 484.33 | 475.14 | 475.09 | -2.12 | 2.17 | 0.54 | -3.83 | -3.06 | 478.03 |
| $HfOF_2$[d] | 468.19 | 481.94 | 488.01 | 491.64 | 474.54 | 482.16 | -2.11 | -5.50 | 0.55 | -3.82 | -8.84 | 471.92 |
| TiO[b] $^3\Delta_g$ | 145.64 | 151.28 | 153.91 | 155.50 | 154.53 | 154.57 | -0.58 | 0.54 | 2.58 | -1.41 | -0.86 | 155.77 |
| ZrO[c] $^1\Sigma^+$ | 173.75 | 180.56 | 182.75 | 184.00 | 181.04 | 180.78 | -0.43 | 0.68 | 0.21 | -1.40 | -2.28 | 180.79 |
| HfO[d] $^1\Sigma^+$ | 194.42 | 200.98 | 203.32 | 204.67 | 198.52 | 201.20 | -0.43 | -2.25 | 0.22 | -1.39 | -8.06 | 192.76 |
| $TiF_2$[b] $^3\Delta_g$ | 274.43 | 278.53 | 281.45 | 283.28 | 279.94 | 281.14 | -1.85 | 0.65 | 2.44 | -2.54 | -1.42 | 280.56 |
| $ZrF_2$[c] $^3B_1$ | 294.10 | 300.41 | 303.56 | 305.48 | 300.56 | 300.42 | -1.62 | 1.77 | 0.30 | -1.96 | -2.84 | 301.13 |
| $HfF_2$[d] $^1A_1$ | 317.15 | 323.37 | 325.90 | 327.40 | 318.97 | 323.39 | -1.54 | -2.88 | 0.30 | -2.08 | -8.62 | 312.58 |

[a] Each term calculated from the energy difference between the ground states of the atoms ( $^3F_2$ for Ti, Zr, and Hf )and the compound.

[b] Geometries from CCSD(T) level with aV*n*Z-PP for Ti and aV*n*Z for O and F (n=D,T). Energies for n=Q obtained from CCSD(T)/ aVTZ-PP geometry.

[c,d] Geometries from CCSD(T) level with awCV*n*Z-PP for Ti and aV*n*Z for O and F (n=D,T). Energies for n=Q obtained from CCSD(T)/ awCVTZ-PP geometry.

[e] Extrapolated CCSD(T) energies with n = D, T, and Q using the composite approach described in the text.

[f] Electronic energies calculated at CCSD(T)-DK/ awCVTZ-DK. For $HfOF_2$, the $5s^2$,$5p^6$,$4f^{14}$ of Hf and $1s^2$ of O and F were also correlated.

*g* Electronic energies calculated at CCSD(T)/ awCVTZ-PP. The $(n\text{-}1)s^2$,$(n\text{-}1)p^6$, of Ti (n=4), Zr(n=5), and Hf(n=4) and $1s^2$ of O and F were also correlated.

*h* MVD expectation values of the CISD/aVTZ-PP wave function.

*i* $\Delta E_{(PP,corr)} = \Delta E_{(AWCTZ\text{-}DK)} - (\Delta E_{(AWCTZ\text{-}PP)} - \Delta E_{(SR)})$

*j* $\Sigma D_0 = \Delta E_{elec}(CBS) + \Delta E_{SR} + \Delta E_{PP,corr} + \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SO}$

Table S5. Vibrational frequencies of all the group 4 $OMF_2$ molecules calculated at CCSD(T) level

| | | | |
|---|---|---|---|
| $OTiF_2$[a] $C_{2v}$ | $a_1$ | 1046.6 | Ti=O stretch |
| | $a_1$ | 662.6 | Ti-F sym stretch |
| | $a_1$ | 191.2 | bend |
| | $b_1$ | 70.9 | out of plane inversion |
| | $b_2$ | 781.7 | Ti-F asym stretch |
| | $b_2$ | 262.9 | bend |
| $OZrF_2$[b] $C_s$ | a' | 938.4 | Zr=O stretch |
| | a' | 643.0 | Zr-F sym stretch |
| | a' | 168.7 | bend |
| | a' | 81.0 | out of plane inversion |
| | a'' | 613.6 | Zr-F asym stretch |
| | a'' | 233.1 | bend |
| $OHfF_2$[c] $C_s$ | a' | 940.7 | Hf=O stretch |
| | a' | 617.2 | Hf-F sym stretch |
| | a' | 183.3 | bend |
| | a' | 112.4 | out of plane inversion |
| | a'' | 614.8 | Hf-F asym stretch |
| | a'' | 244.1 | bend |

[a] CCSD(T)/aug-cc-pwCVTZ/aug-cc-pwCVTZ-PP includes 1s, 2s, 2p electrons on F and O and 3s, 3p, 4s, and 3d electrons on Ti.

[b] CCSD(T)/aug-cc-pwCVTZ/aug-cc-pwCVTZ-PP includes 1s, 2s, 2p electrons on F and O and 3s, 3p, 4s, and 3d electrons on Zr.

[c] CCSD(T)/ aug-cc-pwCVTZ-DK includes 2s and 2p electrons on F and O and 4d, 4f, 5s, 5p, 6s, and 5d electrons on Hf.

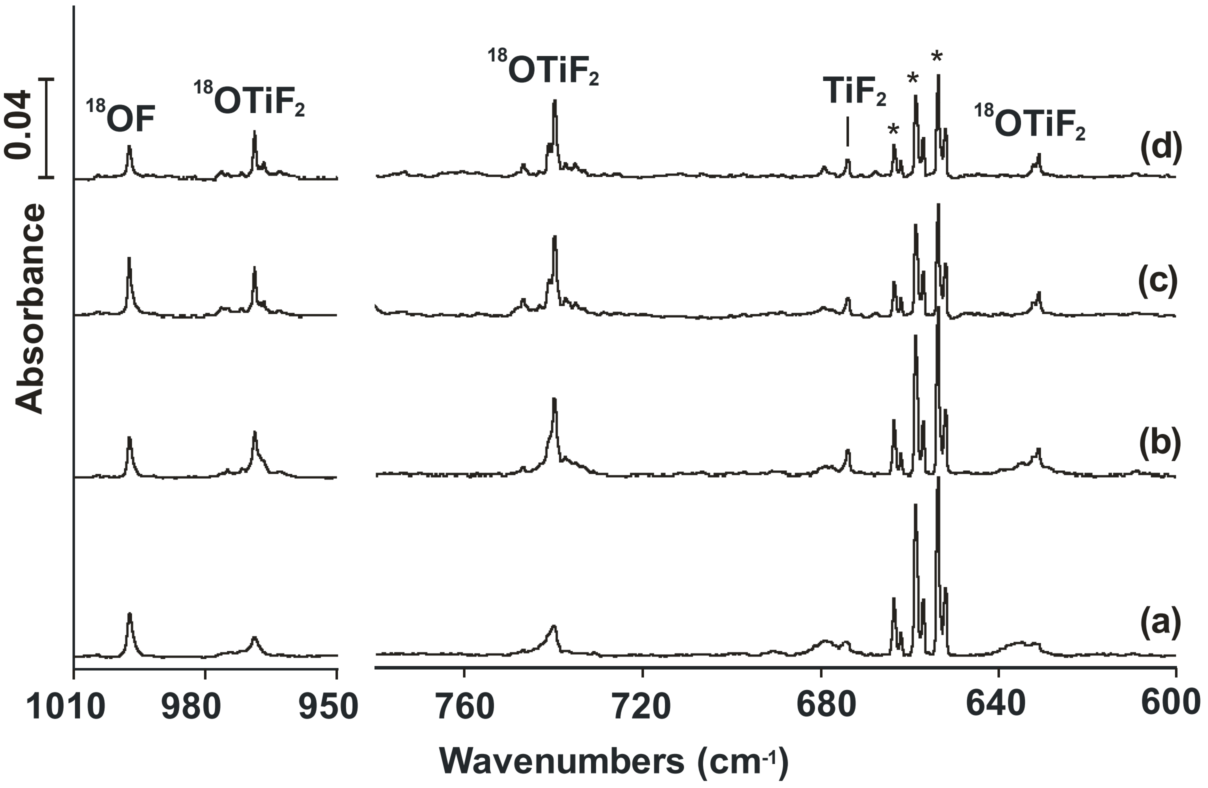

Figure S1. Infrared spectra of the laser-ablated titanium atom and $^{18}OF_2$ (91% enriched) reaction products in solid argon:

(a) Ti + 1.0% $^{18}OF_2$ deposition for 60 min; (b) after annealing to 20 K; (c) after λ > 220 nm irradiation;

(d) after annealing to 30 K. The asterisks denote the 16-16, 16-18, and 18,18 oxygen isotopic absorptions

of $CO_2$ impurity in the matrix sample.

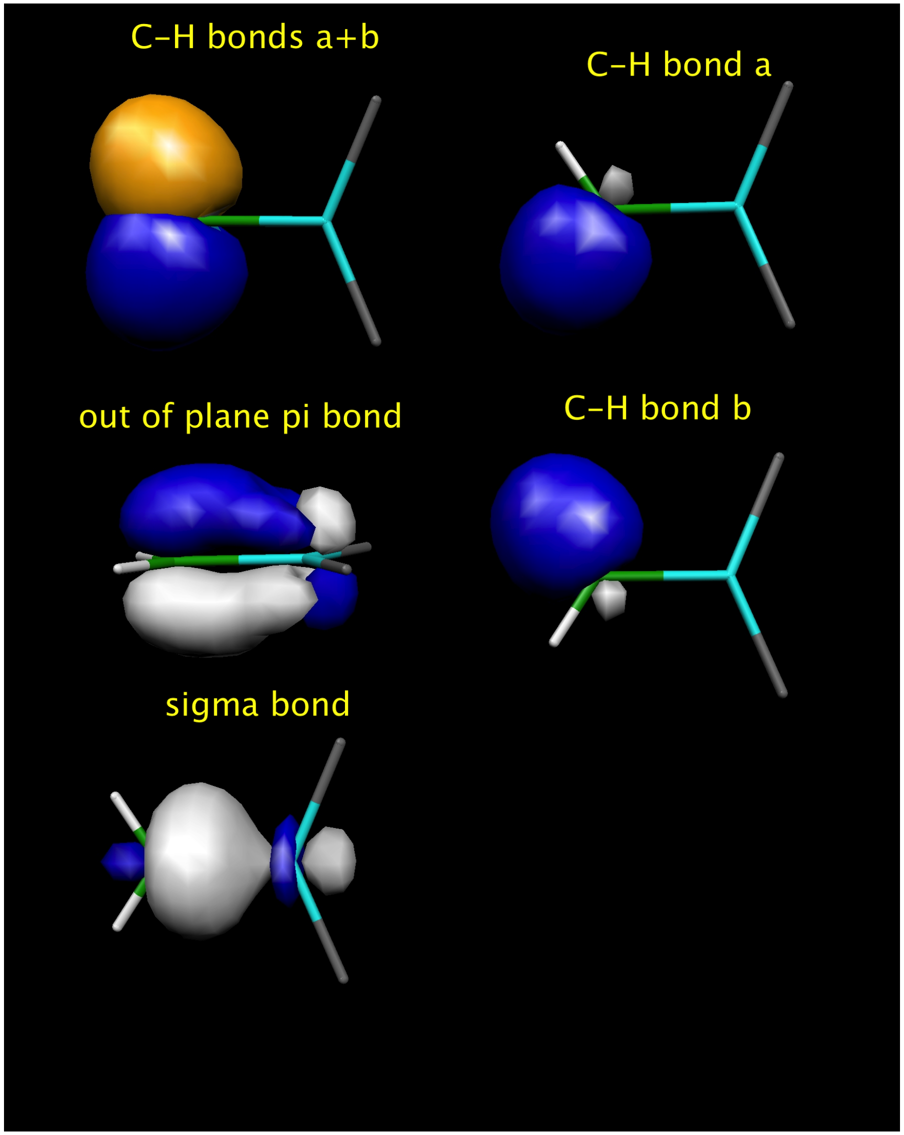

Figure S2. Selected bonding orbitals for $CH_2TiF_2$ from NBO analysis.

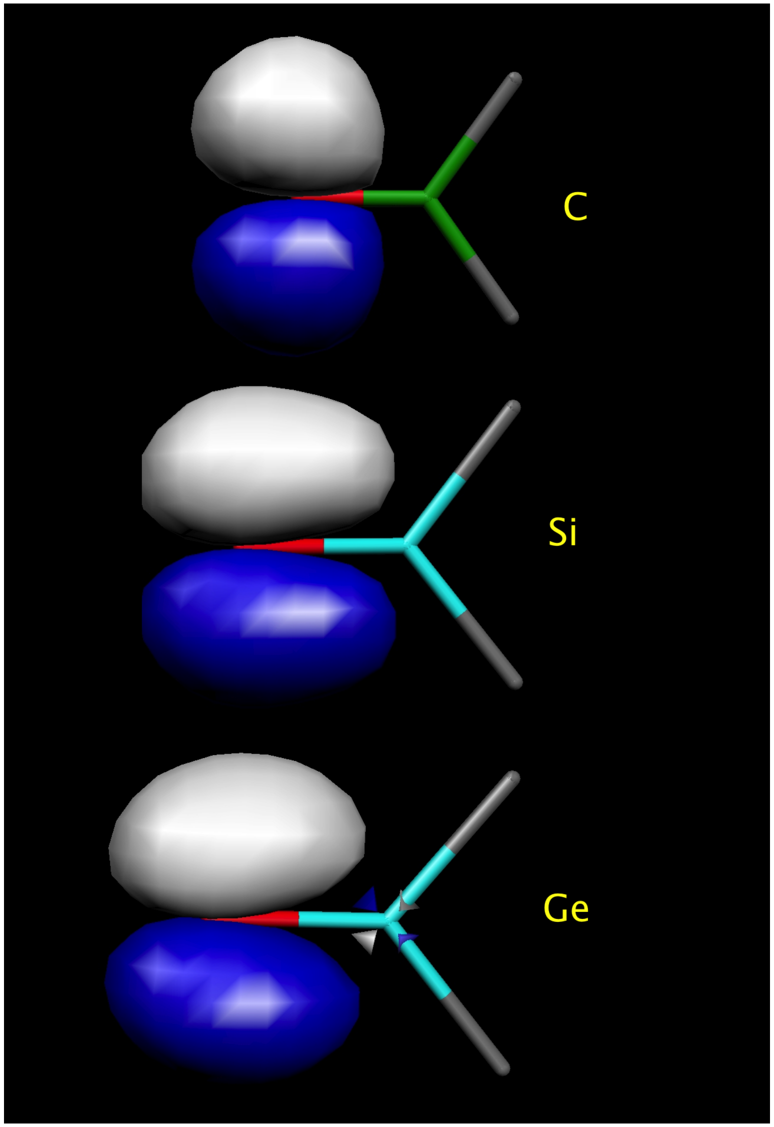

Figure S3. The oxygen in plane orbitals for $OCF_2$, $OSiF_2$ and $OGeF_2$.from NBO analysis of B3LYP orbitals.