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Supporting Information

Molecular Oxofluorides OMF_n of Nickel, Palladium and Platinum:

Oxyl Radicals with Moderate Ligand Field Inversion

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Part 1. Experimental and Computational Details, Comments on the Reaction of Group 10 Metals with OF_2, and Details to the Computational Results

Experimental Details: Matrix Isolation

The experimental set-up used for the IR-laser ablation of group 10 metals (Ni, Pd, Pt) and their reaction with OF_2 diluted in excess of the rare gases neon and argon, as well as their deposition at 5 K (Ne) and 10-15 K (Ar), respectively, using a closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK-205D) inside a self-made vacuum chamber (10^{-7} mbar) has been described in more detail in our previous works.[1,2] A pulsed Nd:YAG laser (Continuum, Minilite II, $\lambda = 1064$ nm, 10 Hz repetition rate, 7 ns pulse width and a pulse energy of up to 60 mJ/cm²) was focused onto the rotating metal target (∅ 10 mm) using a plano-convex lens (∅ 25.4 mm, focal length of 125.0 mm), which gave an energetic plasma beam reacting with OF_2 and spreading towards the cold gold-plated matrix-support.

$^{16/18}OF_2$ was synthesized by a known procedure using elemental fluorine and $^{16/18}OH_2$ dispersed in solid NaF.[3] FTIR spectra were recorded on a Bruker Vertex 80v spectrometer using an MCTB detector (range 4000-450 cm^{-1}) with a resolution of 0.5 cm^{-1}. The deposits were annealed up to temperatures of 10 K (Ne) and 25 K (Ar), respectively, prior to and after irradiation using different light sources such as a medium pressure mercury arc street lamp with the globe removed ($\lambda > 220$ nm), selective irradiations with high-power LED's ($\lambda = 455$-405, 365 nm), and a solid-state Nd:YAG laser with quadrupled frequency (266 nm), respectively.

Computational Methods and Software Packages

Basis sets. Dunning's correlation consistent polarized valence basis sets of double-, triple- and quadruple-zeta quality (cc-pV*n*Z, abbreviated as V*n*Z (*n* = D, T, Q)) were used in both DFT and *ab initio* calculations for F, O and the 3*d* elements. In many cases, diffuse augmentation functions (aug-cc-pV*n*Z) were included for either all elements of a given molecule (denoted as AV*n*Z) or only the fluoro- and oxo ligands (denoted as (A)V*n*Z). Scalar- relativistic effects were considered by using relativistic energy-adjusted small core pseudopotentials for the 4*d* and 5*d* transition metals[4,5] as well as the corresponding AV*n*Z-PP basis sets (this basis set combination is denoted as AV*n*Z(-PP)). For molecules including only O, F and 3*d* elements, additional scalar-relativistic calculations were performed at different *ab-initio* levels of theory using the second order Douglas-Kroll-Hess (DKH) Hamiltonian[6–9] and the corresponding (A)V*n*Z-DK basis sets; in our notation, the -DK suffix for the basis sets also implies the use of the DKH Hamiltonian.

DFT calculations. All DFT calculations were performed using the Gaussian16 program package.[10] The exchange correlation energy was evaluated at DFT level using the pure GGA functional BP86[11,12] as well as the hybrid functional B3LYP as implemented in Gaussian16.[13–15]

Ab-initio calculations. Calculations at different *ab-initio* levels of theory were carried out using the Molpro19 suite of programs[16] in order to obtain more accurate results for energies and vibrational frequencies. Both single-reference (CISD, CCSD(T)) and where necessary also multi-reference (CASSCF,[17,18] MRCI,[19,20] CASPT2[21,22]) methods were used. A restricted open-shell HF (ROHF) wavefunction served as the reference function in the single-reference calculations, and the frozen core approximation was applied when calculating the correlation energies for the evaluation of which only the valence electrons of the respective elements (2*s*2*p* (O,F), (*n* + 1)*snd* for the *nd* elements) were considered.

Multireference calculations at the CASPT2 and MRCI levels of theory were performed for the ground states of ONiF ($^4\Sigma^-$) and OCuF ($^3\Sigma^-$) as well as for different electronic states of $ONiF_2$ and $OCuF_2$ which cannot be sufficiently well described by a single determinant wave function (see CI coefficients in the Supporting Information). The choice of the active space (AS) is the most critical decision in any

CASSCF calculation. General rules for the selection of a suitable AS for a transition metal complex were published elsewhere[23,24] and these were followed here: all five 3*d* nickel orbitals were included in the AS together with the 2*p* orbitals of oxygen, the fluorine ligands are considered as redox-inactive. This resulted in CAS(n,8)SCF reference function with n = 12 ($ONiF_2$), n = 13 (ONiF, $OCuF_2$), and n = 14 (OCuF) electrons distributed in 8 orbitals. For the high-spin states of C_{2v}-symmetric $ONiF_2$ ($^5A_1$, $^5A_2$) and $OCuF_2$ ($^4A_2$), as well as for OCuF ($^3\Sigma^-$), the inclusion of one additional totally symmetric orbital (corresponding to the 4*s*(M = Ni, Cu) atomic orbital) in the AS was necessary, leading to CAS(n,9) wavefunctions.

Symmetry. In preliminary calculations, all molecules were fully optimized (by relaxing all parameters) without symmetry restrictions in order to determine the most stable structure for each spin state. Subsequent optimizations, especially at the *ab-initio* levels of theory were done within the restrictions of the respective point groups, and the results were checked against those obtained without the use of symmetry (C_1 point group).

Frequency calculations. Relevant stationary points on the potential energy surfaces were characterized by harmonic frequency calculations for all possible isotopologues using analytical second derivatives where possible and numerical differentiation in all other cases as implemented in the respective software packages. All frequency analyses were performed using full molecular symmetry except for multi-reference levels of theory or when explicitly noted otherwise.

Wavefunction analysis. Natural orbitals and spin populations from Mulliken population analysis were calculated using Molpro program[16] based on a CASSCF wavefunction at the optimised structures at the highest available level of theory for a given molecule with an active space consisting of the 4*s*3*d*(M) and 2*p*(O) orbitals. The same wavefunction was used for subsequent calculation of AIM (atoms in molecules) charges using the program Multiwfn,[25] as well as of natural atomic charges which were obtained from natural population analysis (NPA) using the NBO program.[26] Kohn-Sham molecular orbitals were analyzed and plotted using the program Chemcraft.[27]

Comments on the Reaction of Group 10 Metals with OF_2

Excited metal atoms generated by IR-laser ablation are assumed to insert initially into the O−F bond of OF_2 to yield the hypofluorites FMOF (M = Ni, Pd, Pt), Equation (1). However, the hypofluorite intermediate was detected only in the experiments using palladium. The main products formed in these experiments are the oxodifluorides, OMF_2, most likely formed by an exothermic rearrangement of the initially formed hypofluorites (Equation 2). In addition to this rearrangement cleavage of the weak F−O bond in the hypofluorites yields the linear three-atomic OMF molecules (Equation 3). In case of nickel also the bent NiOF molecule was observed. Several routes may lead to NiOF. This could be formed by cleavage of the Ni−F bond in the hypofluorite intermediate (Equation 4). Other possible routes are the reaction of nickel atoms and OF radicals or by rearrangement of FNiO. The OF radical and fluorine atoms are major by-products of the laser ablation process in the presence of OF_2. IR-Laser ablation of metals not only produces excited metal atoms but also a broad-band radiation from the plasma plume. Thus, OF and atomic fluorine radicals were formed by photo-decomposition of the OF_2 precursor and the initially formed hypofluorites and oxofluorides. The free fluorine radicals thus produced exhibit a limited mobility within the solid matrices and can initiate secondary reactions with metal species trapped nearby. In the experiments carried out with platinum, an additional oxofluoride of platinum was detected, which does not fit into the reaction scheme shown in equations 1 to 4 and which was ultimately assigned to $OPtF_3$. The platinum(V) oxofluoride was likely formed within the solid rare-gas matrices from $OPtF_2$ by the reaction with fluorine atoms (Equation 5). The broad-band radiation from the plasma plume can also lead to the photo-decomposition of light-sensitive products, which may escape detection. For example, the photo-sensitive hypofluorites FMOF of M = Ni and Pt were not detected in these experiments, but as mentioned above, in the experiments using palladium metal ablation. In these latter experiments two different planar FOPdF isomers were obtained (see also Figure 3 in the main text and in Table S4.1). In the initially obtained solid argon deposit the lowest-energy FOPdF ($^3A''$) isomer was detected (Figure S2.7), which likely was formed by Equation 1. In contrast, the higher-energy *anti*-FOPdF ($^3A'$) isomer was observed through UV-light photolysis of $OPdF_2$ (Equation 6, Figures S2.5 - S2.7). Both FOPdF isomers rearrange to $OPdF_2$ under red light radiation (λ = 730±10 nm, Figures S2.5, S2.7).

$M^* + OF_2 \rightarrow FMOF\ (^3A'')$ (M = Ni, Pd, Pt) (1)
$FMOF \rightarrow OMF_2$ (M = Ni, Pd, Pt) (2)
$FMOF \rightarrow FMO + F$ (M = Ni, Pd, Pt) (3)
$FMOF \rightarrow MOF + F$ (M = Ni) (4)
$OMF_2 + F \rightarrow OMF_3$ (M = Pt) (5)
$OMF_2 + h\nu$ (UV-light) $\rightarrow$ *anti*-FOPdF ($^3A'$) (6)

As shown in Table S3.6 the computed reaction energies for the formation of the group 10 oxofluorides OMF_2, from OF_2 and IR laser-ablated metals of group 10, M = Ni, Pd and Pt, as well as for the formation of $OPtF_3$ according to Equation (5), are strongly exothermic.

IR spectra were recorded from the novel species isolated in solid noble gas matrices (Ne, Ar). In addition to the group 10 oxofluorides the symmetric and antisymmetric stretching frequencies of the $^{16/18}OF_2$ precursor give rise to strong bands in the mid-IR range at 926.2 (892.0) cm^{-1} (a_1) and 825.5 (798.5) cm^{-1} (b_1) for the $\nu_s(OF_2)$ and $\nu_{as}(OF_2)$ of $^{16}OF_2$ and $^{18}OF_2$ (in parentheses) in solid Ne and at 919.7 (892.7) cm^{-1} (a_1) and 825.5 (798.5) cm^{-1} (b_1) in solid Ar matrices, respectively.[28] Other by-products of the IR-laser ablation of the group 10 metals in the presence of OF_2 are the OF radical and the molecular binary metal fluorides MF_n (n = 1, 2). The vibrational band of the OF radical, located at 1031.3 (1028.6) cm^{-1} ^{16}OF in solid Ne (Ar in parenthesis))[1] and at 1000.2 (997.7) cm^{-1} (^{18}OF in Ne (Ar))[1], is always present in the IR spectra of the deposits. The bands of the mono and difluorides MF_n (n = 1, 2; M = Ni,[29–34] Pd,[35] and Pt[36–39]) were safely assigned in oxygen-free experiments, in which OF_2 was replaced by elemental fluorine. In these experiments none of the bands assigned to an oxygen-containing species appeared. Our band positions for these binary fluorides are listed in Table S3.2. Their vibrational frequencies agree well with previously reported experimental ones and with computed values that are also listed in Table S3.2 for comparison. In the experiments with laser-ablated nickel atoms, a weak band appeared at 646.2 cm^{-1} in solid neon that reveals a well-resolved $^{58}Ni/^{60}Ni/^{62}Ni$ isotope splitting (marked by an asterisk in Figures S2.1, S2.2). We were tempted to assign this weak feature to a hitherto unpublished rare gas Ne-NiF compound, but its frequency is significantly higher than a recent estimate for the gas-phase IR band of ^{58}NiF ($X^2\Pi_{3/2}$) at 634.7 cm^{-1},[29] which nicely agrees with our computed value of 639.1 cm^{-1} at our highest CCSD(T)/AVTQZ-DK level (Table S3.2), we have to leave this band unassigned for now. On the contrary, in the corresponding experiment using a solid argon matrix a broadened band appeared at 625.4 cm^{-1} (Figures S2.2, S2.3), which we assign to NiF in solid argon (Table S3.2). We note that a similar behaviour was recently reported for CuF ($X^1\Sigma^+$), which also gives rise to a fairly strong and broadened band in solid argon, but only a very tiny feature in solid neon.[1]

Supporting Details to the Computational Results

Nickel(I) Hypofluorite NiOF

Electronic structure calculations of the hypofluorite NiOF were performed for the lowest-energy doublet $^2A'$ and the quartet $^4A''$ spin states at the RHF, CISD and CCSD(T) levels of theory using different basis sets (Table S3.1). We note that DFT B3LYP and particularly BP86 calculations failed to predict reliable O−F stretching frequencies for this hypofluorite (Table S4.2). The reference RHF wave-function, used subsequently in CISD and CCSD(T), was obtained without the use of symmetry as to allow the molecular structure to relax into the ground state. Structure optimization and normal mode analysis were carried out in the reduced point group symmetry C_1 and subsequently checked against the corresponding calculations in point group C_s. RHF, CISD and CCSD(T) energies (in E_h), structural parameters (bond lengths in Å and angles in degree), T_1 parameters (CCSD(T) calculations) and harmonic vibrational frequencies (ω in cm^{-1}) together with their intensities (I in km/mol) and their relative intensities (I_r) are listed for both spin states of NiOF in Tables S5.1-S5.14.

Molecular orbitals for the ^{2}A′ and the ^{4}A″ spin states of NiOF obtained at their respective CCSD(T)/AVTZ-DK equilibrium structures are listed in Tables S5.1 (^{2}A′) and S5.8 (^{4}A″). The unpaired electron in the ground-state configuration resides in a nonbonding metal-based orbital of a′ symmetry (MO 17.1, Table S5.1). The quartet ^{4}A″ state arises by promotion of an electron from a non-bonding metal-based a″-MO into a metal-dominated a′-MO of mainly Ni(4*s*)-character (see Table S5.8, MOs 17.1, 18.1 and 6.2). The presence of a doublet ground-state and a close-lying excited quartet term was also observed for the related NiF molecule.[40,41] These two low-lying molecular terms arise from different electron configurations of the Ni$^+$ ion: ^{2}D($3d^9$) and ^{4}F($3d^8 4s^1$).[42] The electronic configuration of the ^{2}A′ term of NiOF corresponds to the $^2\Sigma^+$ configuration of NiF ($3d^9$) and the high-spin ^{4}A″ state of NiOF to the configuration of the $^4\Sigma^-$ term of NiF ($3d^8 4s^1$).

The harmonic vibrational frequencies obtained for both states of NiOF (Tables S5.4-S5.7 (^{2}A′) and S5.11-S5.14 (^{4}A″) are considerably basis-set dependent. At the CCSD(T)/AVXZ-DK level the Ni−O stretching frequency of the ^{2}A′ term increases strongly from 487 cm^{-1} to 573 cm^{-1} as the basis set increases from the double zeta (X = D) to the triple-zeta basis and increases further only slightly to 580 cm^{-1} using the quadruple-zeta basis. The OF-stretching frequency is about twice as strong and much less basis-set dependent (Table S5.4). For comparison of experimental frequencies with the computed values the results obtained with the triple and quadruple zeta basis are expected to give the most reliable estimates. The Ni−O stretching frequency of the ^{2}A′ term is higher, and the O−F stretch slightly lower than those of the ^{4}A″ state.

Ni(III) Oxofluoride ONiF

The $^4\Sigma^-$ electronic state of ONiF was investigated by the multireference methods CASSCF[17,18], MRCI[19,20] and CASPT2[21,22]. The CASSCF wave-functions which served as reference for the MRCI and CASPT2 calculations included 13 electrons and 8 orbitals in the active space (13,8). All five Ni 3*d*-orbitals were included in the CAS together with the three oxygen 2*p*-orbitals. The fluorine ligand is considered as redox-inactive and the inclusion of the fluorine 2*p* orbitals into the AS will not affect our results concerning a possible oxyl radical character and the electronic structure of this nickel oxo species. This was shown for ONiF and $ONiF_2$ in a previous work[43] and is further validated in the present work by the reasonable agreement between the computational and experimental vibrational frequencies (see main text, Table 1, and Table S3.3).

Structure optimization and normal mode analysis for the $^4\Sigma^-$ electronic state of ONiF were carried out in the reduced point group symmetry C_1. To confirm the electronic state the results were checked against the calculation carried out in the C_{2v} point group symmetry. Natural orbitals (CASSCF-level) were obtained at the structure optimised at the CASTP2/VTZ-DK level for the electronic ground state and listed in Tables S6.8.

The analysis of the multiconfigurational wave function of the $^4\Sigma^-$ electronic ground state of ONiF in terms of the weights of the contributing configuration state functions (CSFs, Table S6.8) reveal that the wave function is dominated by only 72% by the configuration $\delta^4\ \sigma^2\ \pi^4\ \pi^{*2}\ \sigma^{*1}$. The δ orbitals [$3d(x^2-y^2)$, $3d(xy)$] are nonbonding, whereas the π and σ orbitals reveal considerably mixing of the 3*d*(xz), 3*d*(yz) and the $3d(z^2)$ with the oxygen-based 2*p*(x), 2*p*(y) and the 2*p*(z) orbitals, respectively. The next dominant CSFs comprise simultaneous single excitations, one exclusively within the π-space (11%) and two further within the σ and σ*-MOs and one set of the π-π* MO's (3%, Table S6.8).

Nickel Oxodifluoride, $ONiF_2$

In Table S4.1 we have listed results from preliminary DFT (B3LYP and BP86) and CCSD(T)/AV*n*Z-DK (*n* = D, T) calculation for the two lowest-energy spin-states of $ONiF_2$. Increasing the basis in the CCSD(T) calculations from double to triple zeta results in a minor decrease of the Ni−O and Ni−F bond lengths. While the T_1 diagnostics for the $^3A_2$ states is well within the recommended range for a reliable single reference calculation on a 3rd row ***TM*** ($T_1 < 0.05$)[44,45] a T_1 value of 0.055 for the $^5A_1$ term indicates significant multireference character for this spin-state.

Four triplet states of $ONiF_2$ were optimized at the CASSCF level with an active space of 12 electrons in 8 orbitals (12,8) with subsequent CASPT2 correlation treatment using a CASSCF/VTZ-DK reference wave function and a state-averaging formalism, where each irreducible representation was included with equal weights of 0.25 for the four states $^3A_1$, $^3B_1$, $^3B_2$, $^3A_2$. In the AS for these triplet states, the five 3*d* orbitals of nickel and the three 2*p* orbitals of oxygen were included. Again, the fluorine valence orbitals were considered to be essentially doubly occupied. Subsequently, the $^3A_2$ ground state was re-optimized in C_1 point group symmetry using a state-specific (SS)CASSCF(12,8) wave function for the CASPT2 treatment (Table S7.6). The calculation of the quintet states required the inclusion of one more a_1 MO into the active space (corresponding to the 4*s*(Ni) atomic orbital), resulting in an active space of (12,9). For the quintet states, a state-averaged wavefunction with equal weights of 0.5 for $^5A_1$ and $^5A_2$ was used. CI vectors and the natural orbitals obtained at the CASSCF(12,8)/CASPT2/VTZ-DK (triplet states) and the CASSCF(12,9)/CASPT2/VTZ-DK (quintet states) levels, respectively, are listed for all six spin states of $ONiF_2$ in Tables S7.2-S7.9.

Table S7.1 lists optimized structural parameters for each considered state and relative CASPT2 state energies ($\Delta E_{\mathrm{CASPT2}}$) relative to the lowest state within the triplet and quintet state manifolds. In addition, the relative energies for the two quintet states related to the triplet $^3A_2$ ground state are given as ΔE_{MRCI}. These were obtained from MRCI single point calculations using state-averaged reference wave functions by mixing the three spin states $^3A_2$, $^5A_1$ and $^5A_2$ with equal weights and an AS of (12,9) at the minimum structures from the respective CASPT2 structure optimizations. The MRCI single point energies suggest a very small triplet-quintet gap of only 5 kJ mol^{-1} in favour of the triplet $^3A_2$ state.

While the $^3A_2$ term has the shortest Ni−O bond lengths of 1.613 Å of all considered spin states, the quintet states show significantly longer Ni−O bond lengths, but also longer r(Ni−F) and larger FNiF angles (Table S7.1). Like the CASPT2 results presented in Table S7.1 also the CCSD(T)/AVTZ-DK calculations predict a lengthening of the Ni−O and Ni−F bonds by about 7 and 14%, respectively, for the quintet state (Table S4.1).

Vibrational data of $ONiF_2$ ($^3A_2$) were obtained in the C_1 point group symmetry at the CASSCF(12,8)/CASPT2/VTZ-DK level (Table S7.6). This procedure failed for the lowest quintet $^5A_2$ term, probably because numerical displacements without symmetry restrictions lead to jumps between potential energy surfaces (PES) of different quintet electronic states.

Additional results for the different spin-states of $ONiF_2$ such as Ni−O bond orders, spin populations and atomic charges are collected in Tables S7.5-S7.7. Interestingly, the small negative NPA charge of the oxo ligand decreased on the transition from the low spin state ($^3A_2$: −0.226) to the high spin state ($^5A_1$: −0.127), and the spin density at the oxo group increases considerably ($^3A_2$: 1.03, $^5A_1$: 1.75) (Tables S7.6 and S7.7). To shed light on these counterintuitive features the wave functions for these two spin states were analysed. The wave function for the $^3A_2$ spin state (CASSCF(12,8)/CASPT2/VTZ-DK, Table S7.3) is well dominated by a single CSF (78%) with two unpaired electrons in two mainly Ni−O antibonding π*-orbitals. Other significant contributions to this wave function come from CSFs which involve two simultaneous single excitations within the π-π* MOs (4%), and a double excitation from σ to σ* MOs (3%). The leading configuration can be described as $d(x^2)^2\ d(xy)^2\ \pi(y)^2\ \pi(x)^2\ \sigma(z)^2\ \pi^*(y)^1\ \pi^*(x)^1\ \sigma^*(z)^0$, with two doubly occupied and mainly nonbonding metal 3*d*-orbitals [$d(x^2)$, $d(xy)$], and two singly occupied Ni−O antibonding π* MOs (π(x) perpendicular to the molecular plane Table S7.3).

The leading configurations for the close-lying $^5A_1$ and $^5A_2$ terms differ from the dominant $^3A_2$ configuration by a single electron excitation from a nonbonding *d*(xy) ($^5A_1$) and *d*(x^2) ($^5A_2$) MO into the σ(z)* MO, respectively (Tables S7.7, S7.8). These CSF comprise 80% ($^5A_1$) and 86% ($^5A_2$) of the wave function at the CASSCF(12,9)/CASPT2/VTZ-DK level (for other significant CSFs see Tables S7.7, S7.8). A closer look at the natural orbitals for the leading CSF of the $^5A_1$ state discloses an antibonding mixing in this singly occupied nickel-dominated 3*d*(xy) MO with the fluorine 2*p*(x) orbitals (Table S7.7). The higher occupation of the antibonding σ(z)* MO in these quintet terms is consistent with the computed longer Ni−O and Ni−F bond lengths compared to that of the $^3A_2$ term (see main text. Table S7.1).

Copper Oxofluorides, $OCuF_n$ ($n = 1, 2$)

The copper compounds OCuF ($^3\Sigma^-$) and $OCuF_2$ ($^2B_2$, $^4A_2$)[1,43] were re-investigated at CCSD(T) and CASSCF levels of theory (Table S3.1) Structure optimization and normal mode analysis were carried out in the C_{2v} point group symmetry at the CCSD(T) level (Table S4.5). Using the optimized structures, natural orbitals were obtained at the CASSCF level with an active space of *m* electrons in *n* orbitals (*m*,*n*) (for OCuF (14,9); for $OCuF_2$ (13,8)), and listed in Tables S9.1-S9.9 respectively. The calculated bond lengths for the linear OCuF molecule in the $^3\Sigma^-$ ground state, Cu–F (1.712 Å) and Cu–O (1.668 Å), are in good agreement with our previous study where scalar relativistic effects were taken into account by means of a relativistic small core ECP for copper.[1] Because of a high T_1-diagnostics value in the CCSD(T) calculation of 0.081, which indicates significant multi-reference character of the wavefunction (Table S4.5), we have carried out calculation at the CASSCF(14,9)/CASPT2 level of theory (Table S9.1), which lead to shorter bond lengths of $d_{Cu–O}$ = 1.634 Å and $d_{Cu–O}$ = 1.687 Å.

For $OCuF_2$, one $^2B_2$ and two different energetically low-lying $^4A_2$ states were calculated which all have planar C_{2v} symmetric structures. At the CCSD(T)/VTZ-DK level of theory, we found the doublet state to lie about 20 and 45 kJ mol^{-1} lower in energy (Tables S4.5 and S9.2) than the two $^4A_2$ states, thus confirming our previous CCSD(T) result.[1] The two $^4A_2$ states show very different Cu−O bond lengths and F−Cu−F angles (Table S4.5) The energetically preferred $^4A_2$ state (labelled $^4A_2$-2) corresponds to a loosely bound adduct between linear CuF_2 and an oxygen atom, leading to a T-structure with a large Cu–O distance of 2.045 Å and a F−Cu−F angle of 168.8°. The second $^4A_2$ state ($^4A_2$-1) adopt a short Cu–O bond length of 1.700 Å and a significant stronger bent F−Cu−F unit with an angle of 131.6°. However, the T_1-diagnostics values of 0.050 ($^2B_2$), 0.053 ($^4A_2$-1), and 0.027 ($^4A_2$-2) indicate already a considerably multi-reference character of the wave functions for the $^2B_2$ and the $^4A_2$-1 states.[44,45] Therefore, we have also performed CASSCF(13,8)/CASPT2/VTZ-DK and CASSCF(13,9)/VTZ-DK calculations for all three states (Tables S9.4-S9.9), as well as comparable NEVPT2/VTZ-DK calculations for the two $^4A_2$ states (Table S9.3). These calculations confirm the multi-reference character for the $^2B_2$ and the $^4A_2$-1 states, since the contribution of the most dominant configuration to its wave function at the CASPT2 level comprises only 74.9% and 85.2%, respectively. Interestingly, the energetic order of these states is changed drastically at this level, and in contrast to our CCSD(T) calculations, but in agreement with the previous work,[43] the two bound states are now predicted very close in energy with the $^2B_2$ state lying slightly higher in energy (6.6 kJ mol^{-1}) than the $^4A_2$-1 state, whereas the unbound $^4A_2$-2 state was found to lie about 32 kJ mol^{-1} above the $^4A_2$-1 state (Table S9.2).

An analysis of the electronic structures of the two spin states showed that the single unpaired electron of the $^2B_2$ state occupies the antibonding Cu–O π*[*p*y(O)-*d*(yz)] orbital which is mainly localized at the oxygen atom (Figure S2.17). The $^2B_2$ and $^4A_2$ states only differ for the occupation of the in-plane π* MO [*p*x(O)-*d*(xz)] (doubly occupied in $^2B_2$ and singly occupied in both $^4A_2$ states) and the antibonding σ-MO [*p*z(O)-*d*(z^2-y^2)] (unoccupied in $^2B_2$, see Figure S2.15). The two singly occupied π*-MOs in $^4A_2$-1 are involved in three-electron π-bonding interactions to the copper atom, while they represent two nonbonding oxygen 2*p*-orbitals in $^4A_2$-2.

The $^4A_2$-1 structure was reported to be very sensitive to the computational level in terms of the Cu−O bond length and the F−Cu−F bond angle.[43] At the CCSD(T) level the Cu−O fundamental is predicted for the two bound states $^2B_2$ and $^4A_2$-1 at lower wavenumbers than the Cu−F$_2$ stretches between 580 cm^{-1} and 600 cm^{-1} (Table S4.5). This prediction is also lower than the computed Ni−O frequency for the high-spin ONiF$_2$ ($^5A_1$) state (630 cm^{-1} - 660 cm^{-1}, Table S4.2), for which the leading configuration differs from that for OCuF$_2$ ($^4A_2$-1) only in the occupation of a nonbonding 3*d*(xy)-MO (Table S7.6). This result agrees well with the result of a previous study, in which only the bound $^4A_2$-1 state of OCuF$_2$ was considered and in which consistent Cu−O frequencies for this state were predicted at the CCSD(T) (568.9 cm^{-1}) and CASPT2 (588.8 cm^{-1}) levels of theory.[43] Our CASPT2 calculation strongly overestimates the π-bond interaction and therefore the Cu−O frequency for the $^4A_2$-1 state (around 1070 cm^{-1}). This prompted us to carrying out analogous NEVPT2 calculations which indeed yield a lower Cu−O frequency of 890 cm^{-1} (Table S9.3), but which is still significantly higher than the one previously reported, which is currently the best estimate for the Cu−O frequency of the $^4A_2$-1 state.

Only the strongest band of OCuF$_2$, the antisymmetric ν_{as}(^{63}Cu−F$_2$) stretching band was previously reported at 772.0 cm^{-1}.[1] Since this band did not show any Δν($^{16/18}$O) isotope shift, these experiments did not allow a clear determination of the electronic ground state of OCuF$_2$. More future experiments are therefore needed for an unambiguous experimental assignment of the lowest electronic state of OCuF$_2$.

Palladium and Platinum Oxofluorides, OMF$_n$ (M = Pd, Pt, *n* = 1-3)

The linear molecules OPdF and OPtF, like ONiF, have $^4\Sigma^-$ ground states, where the three unpaired electrons are accommodated in two degenerate π*[$p_{x,y}$(O)-*d*(xz, yz)] and a σ*[*d*(z^2)-p_z(O)] MOs (see main text, Figure 9). A spin density analysis (Figure S2.16) revealed that the unpaired electrons that reside in the π*-MOs are well shared between the metal and the oxo ligand (see below for further discussion), which results in a considerable oxyl type radical character of the oxo ligand.

CCSD(T)/AVTZ(-PP) calculations were performed on OPtF$_2$ and OPdF$_2$ using DFT BP86/AVTZ(-PP) optimized C_{2v} structure as starting structures. The lowest-energy triplet $^3A_2$ and quintet $^5A_1$ states were both investigated. The triplet states are found to be lower in energy than the quintet states by 142 and 113 kJ mol^{-1} (PB86/AVTZ(-PP)) for OPtF$_2$ and OPdF$_2$, respectively (Table S4.1). These two states show different M−O bond lengths. The M−O bond lengths of the high-spin states (1.868 Å (OPdF$_2$) and 1.908 Å (OPtF$_2$), BP86/AVTZ(-PP)) are longer than those in the corresponding ground states (1.741 Å (OPdF$_2$), 1.743 Å (OPtF$_2$)). A reasonable explanation for this observation is that the excited state configuration arises formally by an electron excitation out of a doubly occupied nonbonding metal centered MO (n*d*(xy)) in the ground state into an M−O antibonding MO (σ*: p_z(O)-*d*(x^2-y^2)). Although OPdF$_2$ and OPtF$_2$ have very similar M−O bond lengths the harmonic M−O stretching vibrational frequency of OPtF$_2$ is predicted at a higher frequency ($^3A_2$: 871 cm^{-1}) than that of OPdF$_2$ ($^3A_2$: 828 cm^{-1}) at the CCSD(T) level, which indicates a higher covalence of the Pt−O bond. Ground-state spin densities of both compounds are displayed in Figure S2.17 and further structural parameters and computed vibrational frequencies at different levels of theory for the two considered states are listed in the Tables S4.1, S4.3-S4.4.

The planar triplet FOPdF chain molecules have a Pd(d^8) configuration with two unpaired electrons accommodated in predominantly Pd(4*d*)-MOs. For the lowest-energy FOPdF ($^3A''$) the SOMOs consist of the in-plane 4*d*(xz) and the 4d(z^2)-MOs with some admixtures of the corresponding oxygen 2*p*(x) and 2*p*(z) atomic orbitals, respectively, while the unpaired electrons of the *anti*-FOPdF ($^3A'$) isomer reside in the 4*d*(z^2)-MO and the 4*d*(x^2–y^2)-MO, which would be a non-bonding δ-type-MO in a linear O–Pd–F chain. The leading configuration for OPtF$_3$, ($^4A_1$) (92 %) is well described by σ(PtO)^2 π(x)^2 π(y)^2 5*d*(x^2)^2 π*(x)^1 π*((y)^1 5*d*(xy)^1 σ*^{0} (Table S8.3), where three unpaired electrons are accommodated in one weakly Pt−F antibonding (*d*(xy)) and two antibonding π*($p_{x,y}$(O)-*d*(xz,yz))-MOs.

Comments to the Estimation of the Degree of Covalence and Inversion (DCI)

The metal-ligand σ-interaction in the T-shaped oxodifluorides and the planar $OPtF_3$ are arranged along the metal $d(z^2{-}y^2)$-orbital density, moving this orbital to a high energy. For the high-spin states of $ONiF_2$ and $OCuF_2$ this MO is singly occupied and adopt a high 3*d*-orbital contribution ($ONiF_2$ ($^5A_1$): 77 % Ni; $OCuF_2$: 72 % Cu ($^4A_2$-1), 94 % Cu ($^4A_2$-2) with some 4*s*, 4*p* admixtures. In contrast, this MO is not occupied in the low-spin states of the oxo difluorides and for $OPtF_3$ and here it adopts a larger metal-oxygen σ-antibonding character. The high metal contribution of this singly occupied σ-MO is shown by the considerably lower oxygen DCI values for the σ-spaces of the high-spin states $ONiF_2$ ($^5A_1$) and $OCuF_2$ ($^4A_2$-1) compared to those for the corresponding low-spin states (Table 3 in the main text), since for reasons of consistency this highest-energy metal n*d*-MO was chosen for the estimation of these DCI values and not the likely more antibonding metal (n+1)*s*-MO.

The MO analysis and the DCI values for the π-bonded $^4A_2$-1 state of $OCuF_2$ reveal a surprising similarity to those of the related high-spin $ONiF_2$ ($^5A_1$) state (Table 3 in the main text). However, as already noted in the computational section, our CASSCF(13,9)/VTZ-DK calculations overestimates the π-interaction in the $^4A_2$-1 state of $OCuF_2$ and yield an unreasonable short Cu−O bond length of 1.596 Å (Table S9.7), which is significantly shorter than that of the $^2B_2$ state of $OCuF_2$ (1.748 Å, Table S9.5) and also of the Ni−O bond in the $^5A_1$ state of $ONiF_2$ (1.725 Å, Table S7.7). With this in mind it can therefore safely conclude that the inversion of the π-space will significantly increase going from $ONiF_2$ to $OCuF_2$, and the π-bond order will decrease accordingly. Consistent with the long Cu−O bond in the loosely bound $^4A_2$-2 state of $OCuF_2$ (*d*(CuO) = 1.945 Å, Table S9.9) its π*-MOs are heavily inverted (about 98 % oxygen contribution, Table 3 in the main text). The analysis of the natural orbitals (Table S9.9) revealed two singly occupied oxygen 2*p*(π)-orbitals that do not interact with the appropriate copper 3*d*-orbitals, and both contribute about one unpaired electron to the total spin population of 2.0 at the oxo group (Table 3, main text).

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Part 2. Figures

Matrix-IR Spectra

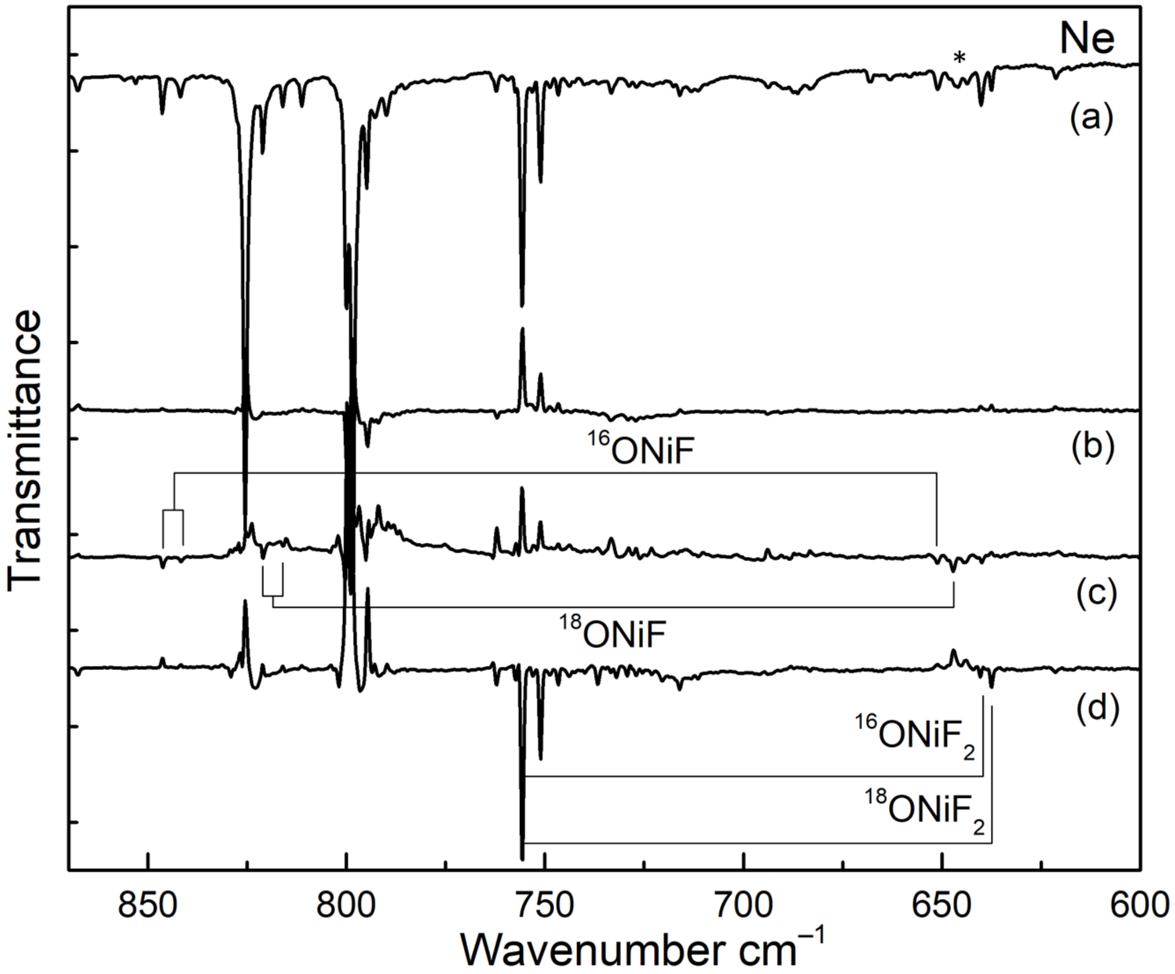


Figure S2.1. IR Spectra of the reaction products of laser-ablated Ni atoms with $^{16/18}OF_2$ (0.1%) seeded in excess Ne: **(a)** co-deposited for 120 min at 5 K, **(b)** difference spectra obtained after $\lambda = 470$ nm (LED) irradiation for 40 min, followed by **(c)** $\lambda = 193$ nm (excimer laser) irradiation for 10 min, and **(d)** subsequent annealing to 11 K. An unassigned feature is marked by an asterisk.

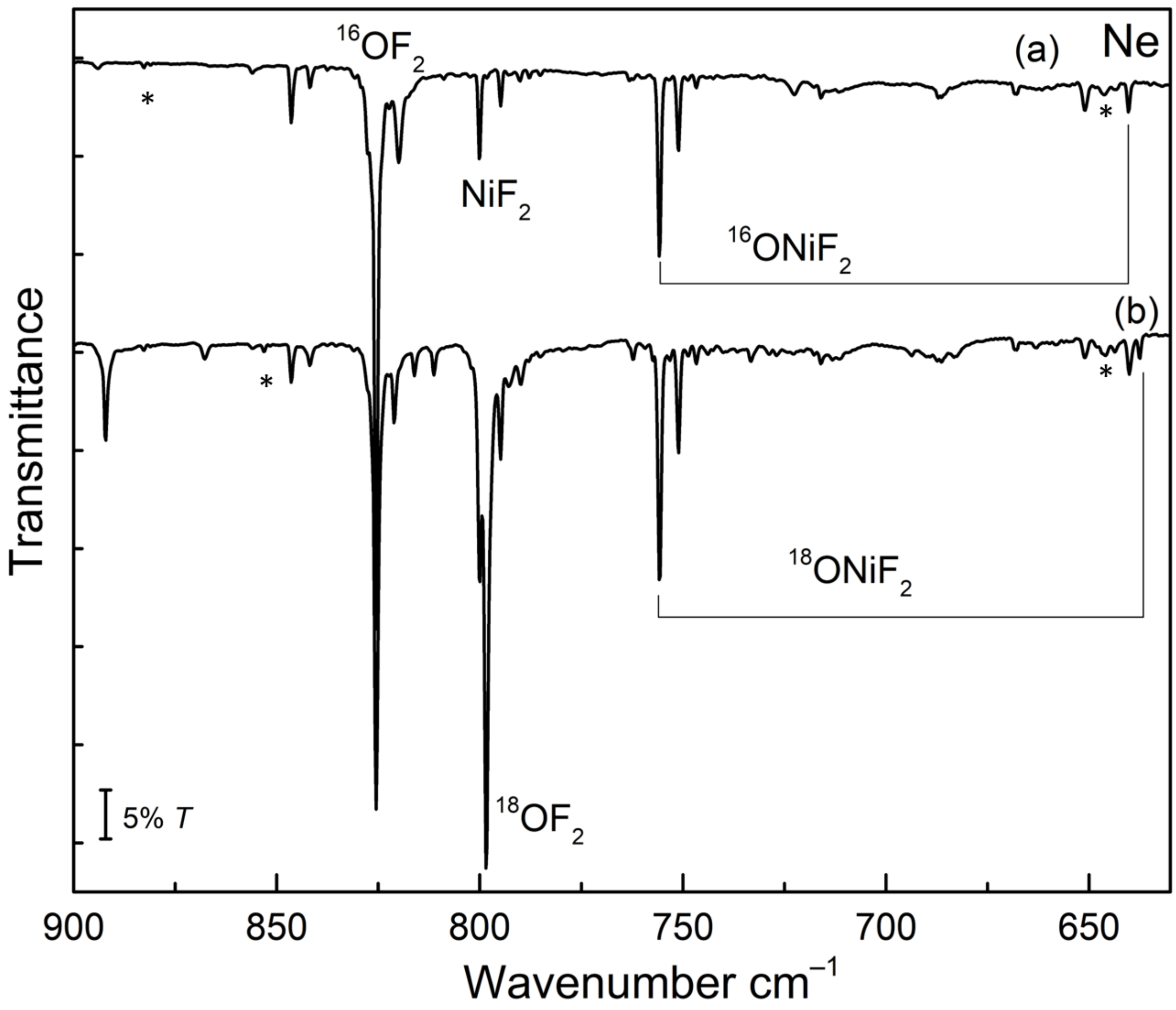


Figure S2.2. IR spectra of the reaction products of laser-ablated Ni with **(a)** $^{16}OF_2$ (0.05%) and **(b)** $^{16/18}OF_2$ (0.1%) seeded in excess Ne and co-deposited for 120 min at 5 K. Unassigned features are indicated by an asterisk.

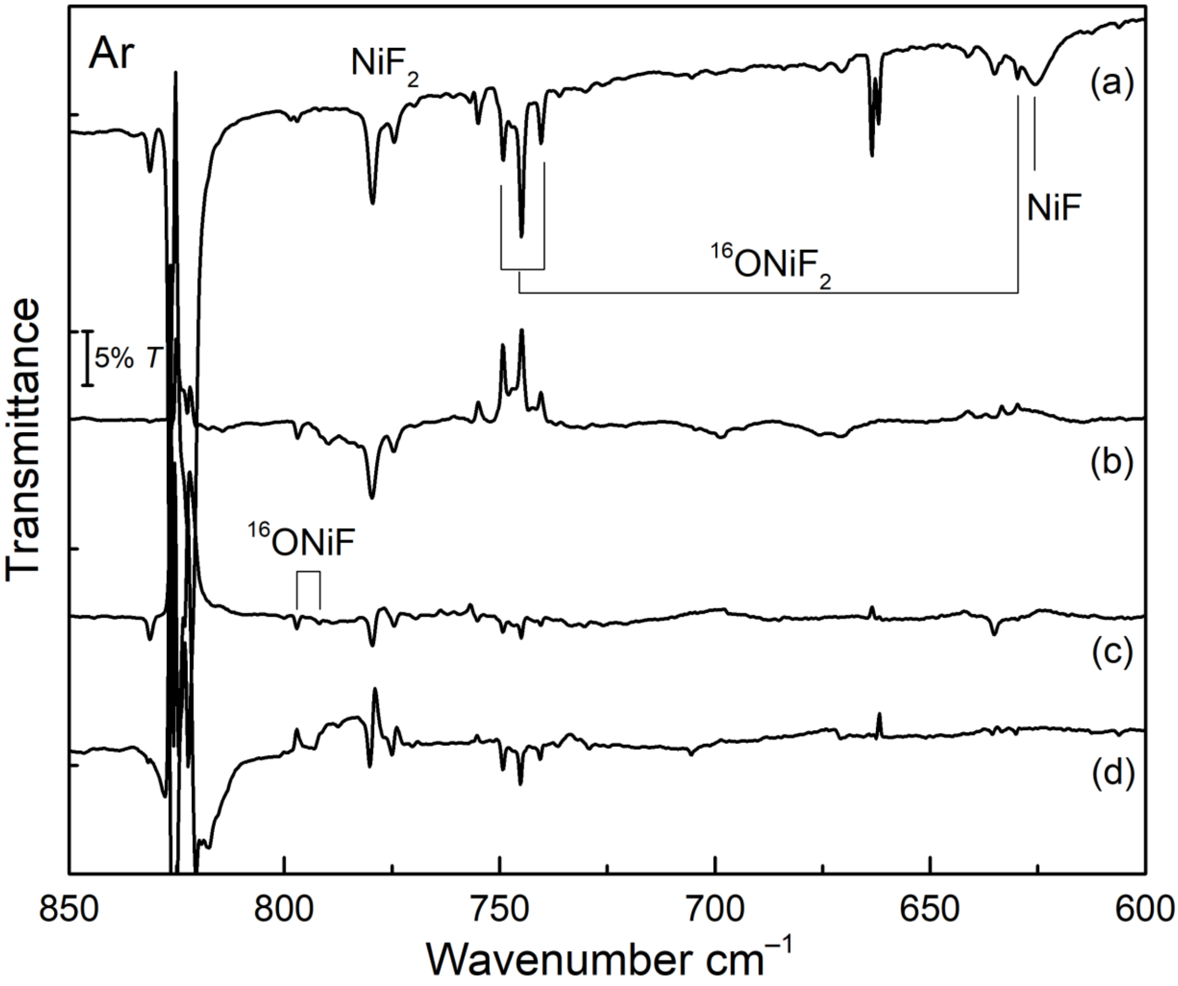


Figure S2.3. IR Spectra of the reaction products of laser-ablated Ni with $^{16}OF_2$ (0.5%) seeded in excess Ar: **(a)** co-deposited for 105 min at 12 K, **(b)** difference spectra obtained after λ = 470 nm (LED) irradiation for 40 min, followed by **(c)** λ = 193 nm (excimer laser) irradiation for 8 min, and **(d)** subsequent annealing to 20 K.

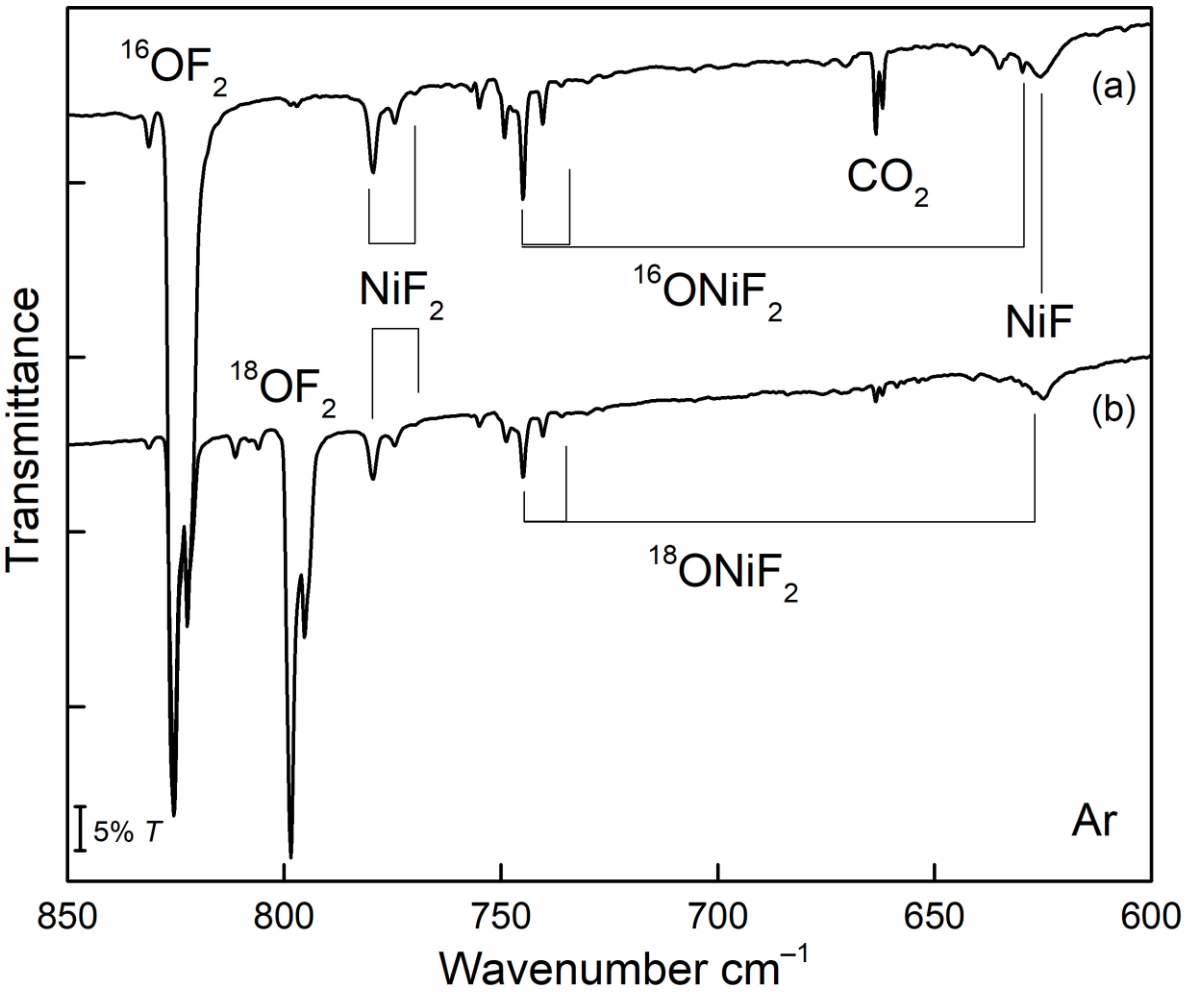


Figure S2.4. IR Spectra of the reaction products of laser-ablated Ni with 0.5% **(a)** $^{16}OF_2$ and **(b)** $^{18}OF_2$ seeded in excess Ar and co-deposited at 12 K.

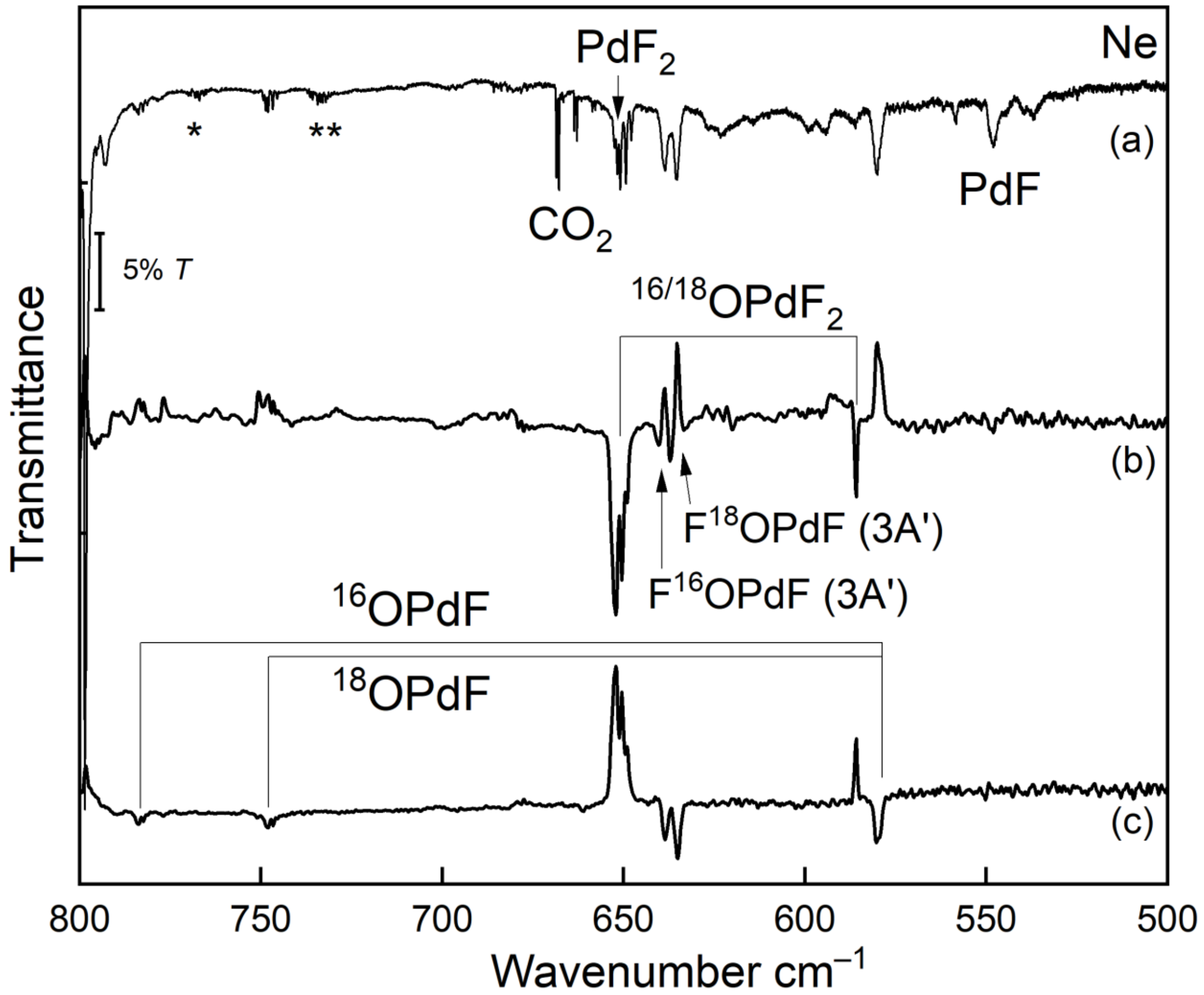


Figure S2.5. IR spectra of the reaction products of laser-ablated Pd atoms with $^{16/18}OF_2$ (0.1%) seeded in excess Ne: **(a)** co-deposition for 180 min at 5 K, **(b)** difference spectra obtained after λ = 730 nm (LED) irradiation for 15 min, and **(c)** subsequent λ = 266 nm (LED) irradiation for 50 min. An unassigned O=Pd band is indicated by * (^{16}O isotopologue) and ** (^{18}O), respectively (see Table S3.4).

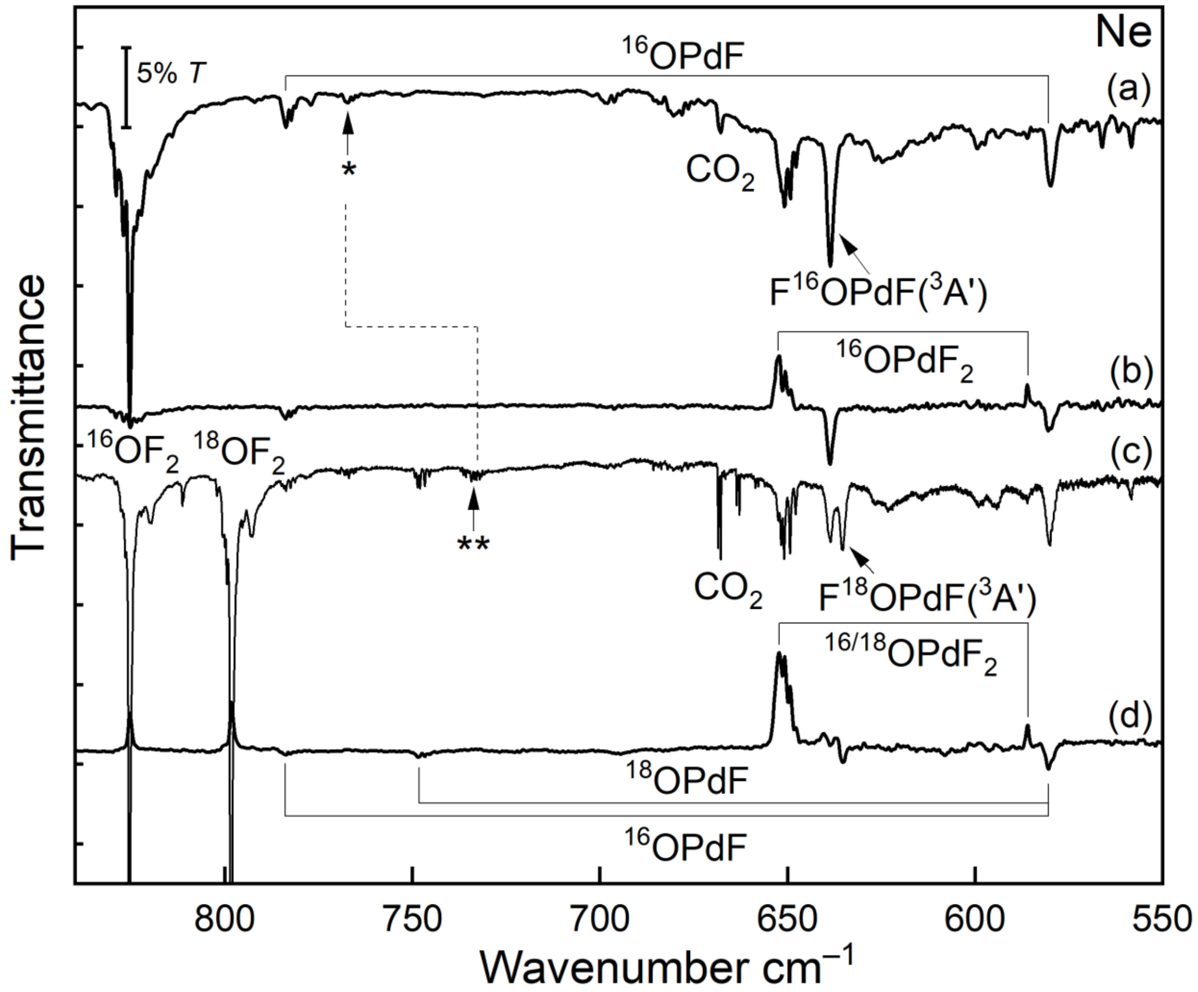


Figure S2.6. IR spectra of the reaction products of laser-ablated Pd with **(a)** $^{16}OF_2$ and **(c)** $^{16/18}OF_2$ seeded in excess Ne and co-deposited for 180 min at 5 K, and difference spectra obtained after $\lambda = 273$ (LED) irradiations for **(b)** 10 and **(d)** 20 min, respectively. An unassigned O=Pd band is indicated by * (^{16}O isotopologue) and ** (^{18}O), respectively (see Table S3.4).

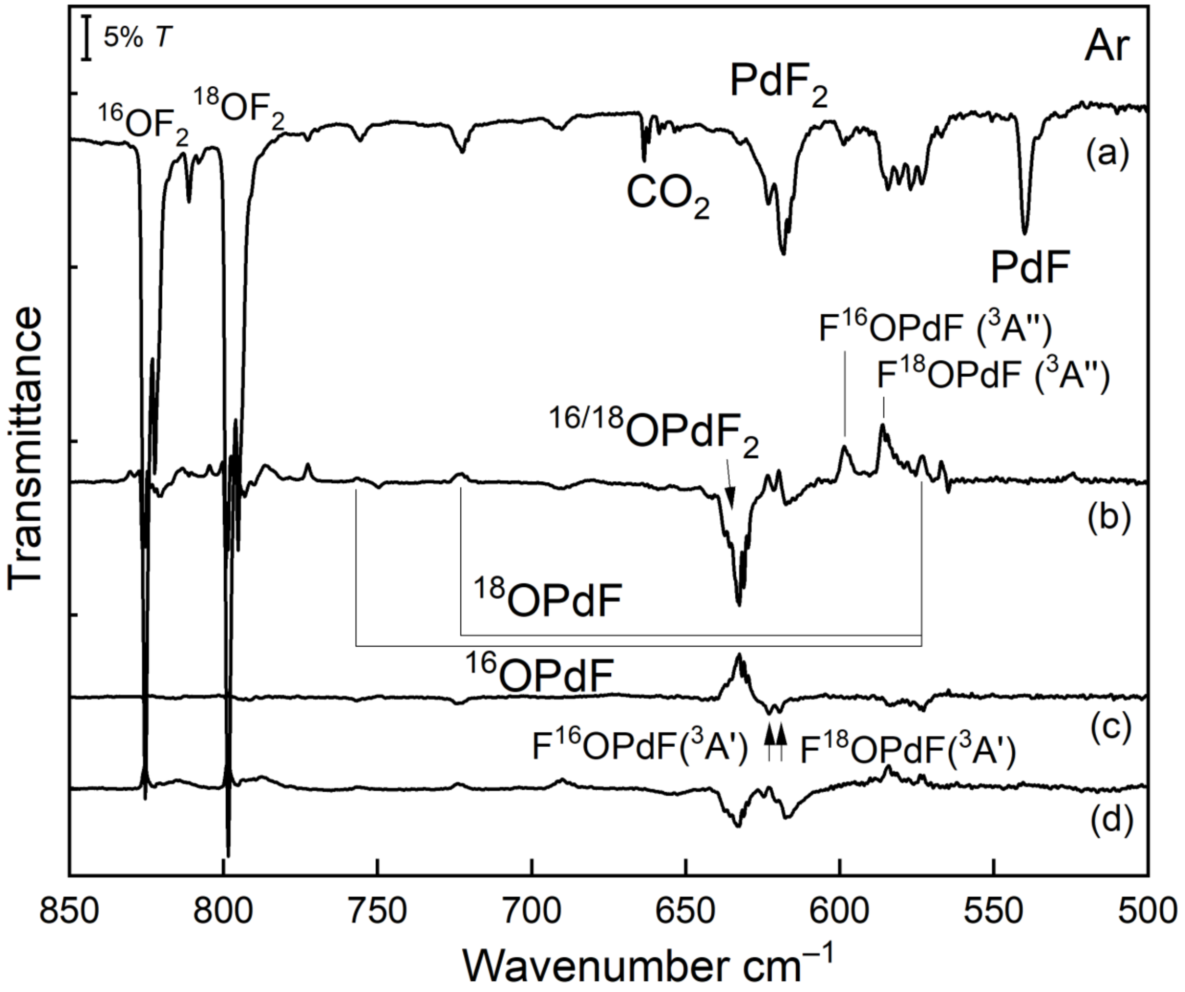


Figure S2.7. IR spectra of the reaction products of laser-ablated Pd with $^{16/18}OF_2$ (0.5%) seeded in excess Ar: **(a)** after co-deposition for 90 min at 15 K, **(b)** difference spectrum obtained after $\lambda = 730$ nm (LED) irradiation for 25 min, followed by **(c)** $\lambda = 590$ nm (LED) and **(d)** $\lambda = 455$ nm (LED) irradiation for 10 min.

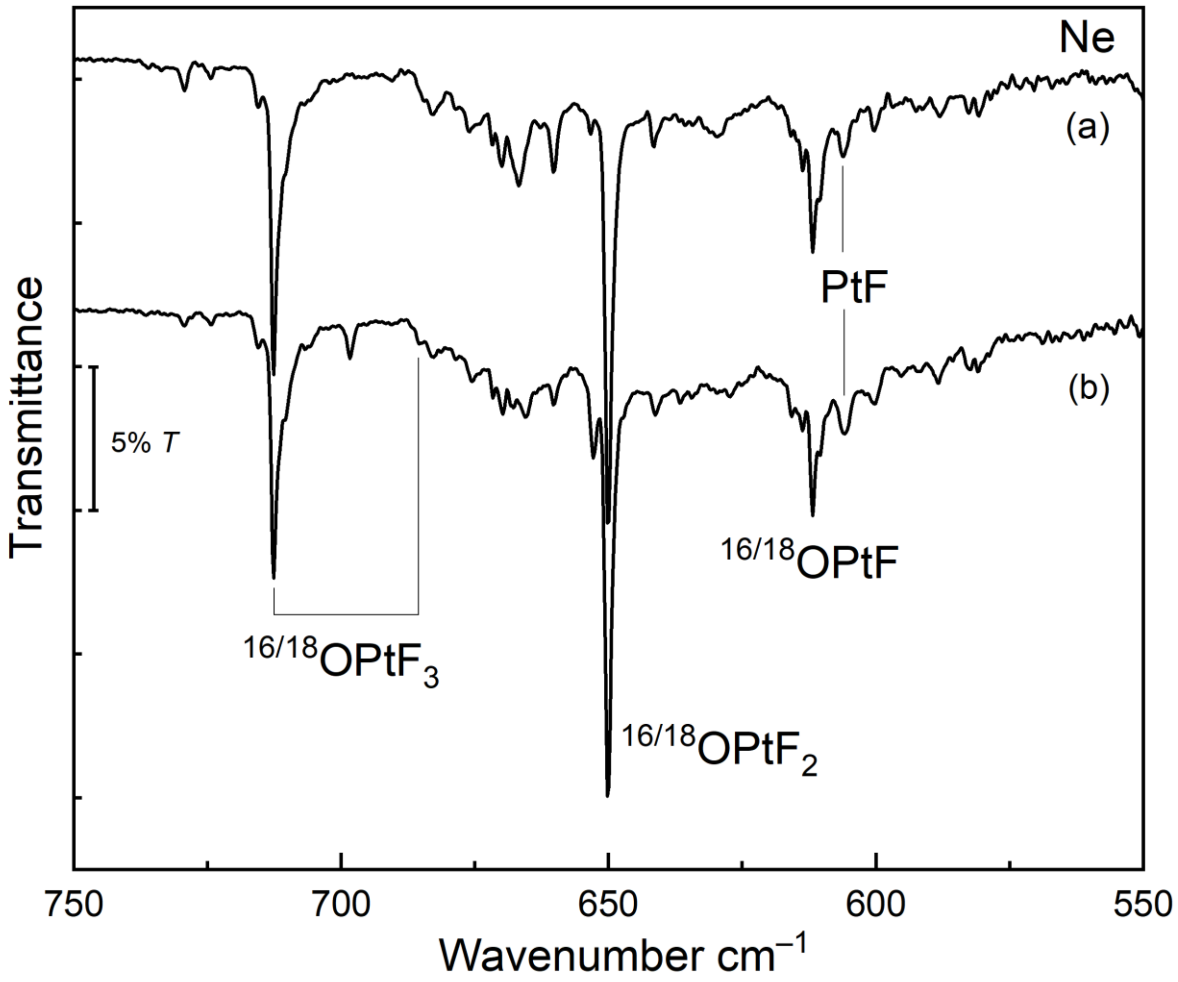


Figure S2.8. IR spectra of the reaction products of laser-ablated Pt with **(a)** $^{16}OF_2$ (0.05%) and **(b)** $^{18}OF_2$ (0.05%) co-deposited in excess Ne.

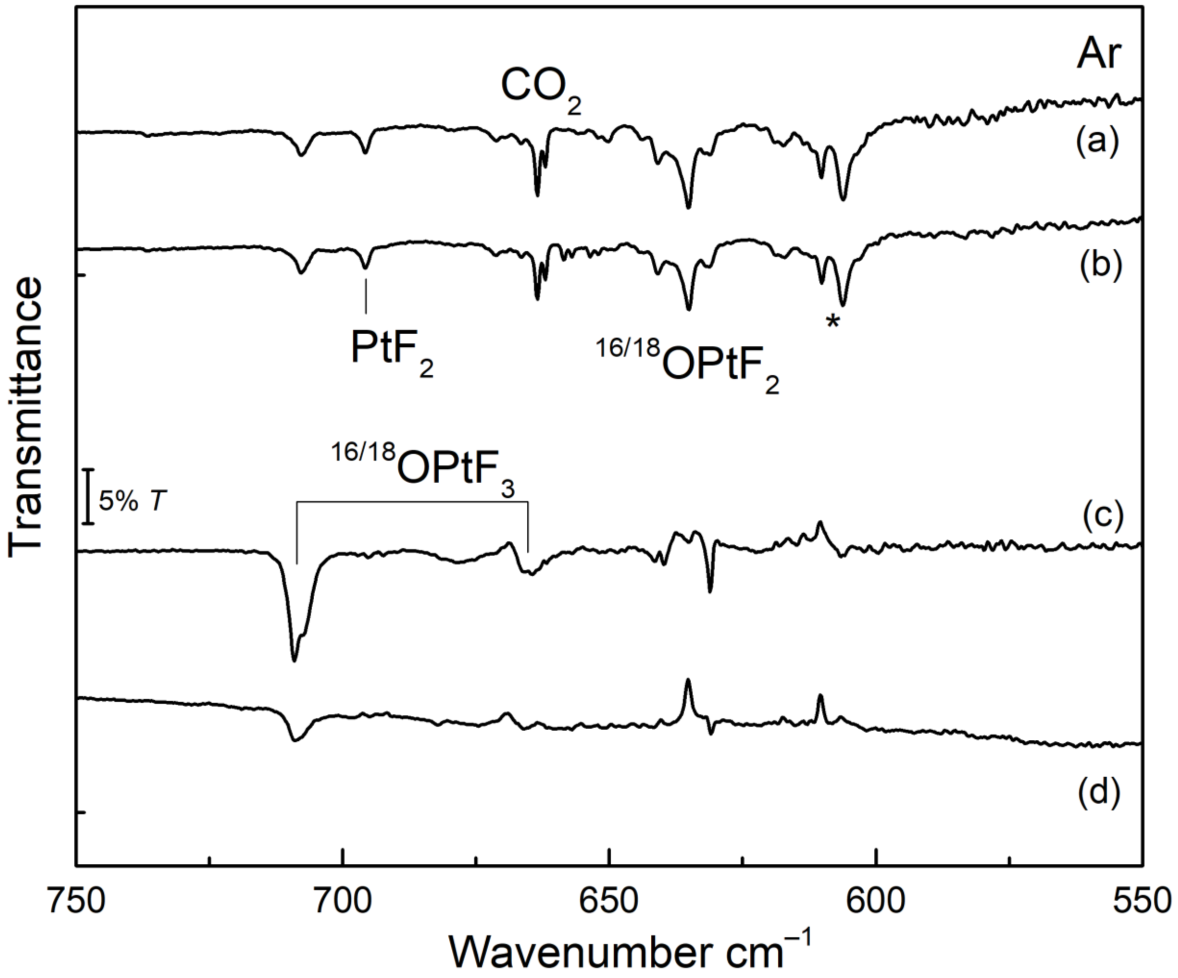
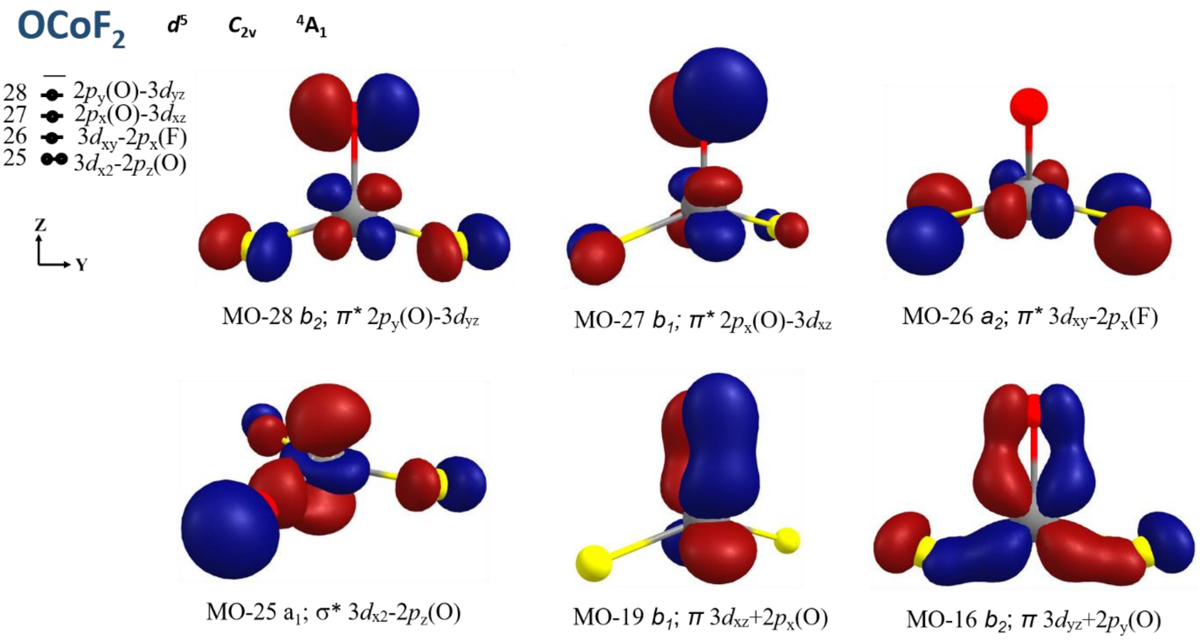


Figure S2.9. IR spectra of the reaction products of laser-ablated Pt with **(a)** $^{16}OF_2$ (0.5%) and **(b)** $^{18}OF_2$ (0.5%) co-deposited in solid Ar, **(c)** difference spectra obtained after λ = 730 nm (LED) irradiation for 30 min, followed by **(d)** λ = 455 nm (LED) irradiation for 60 min. An unassigned feature is indicated by an asterisk.

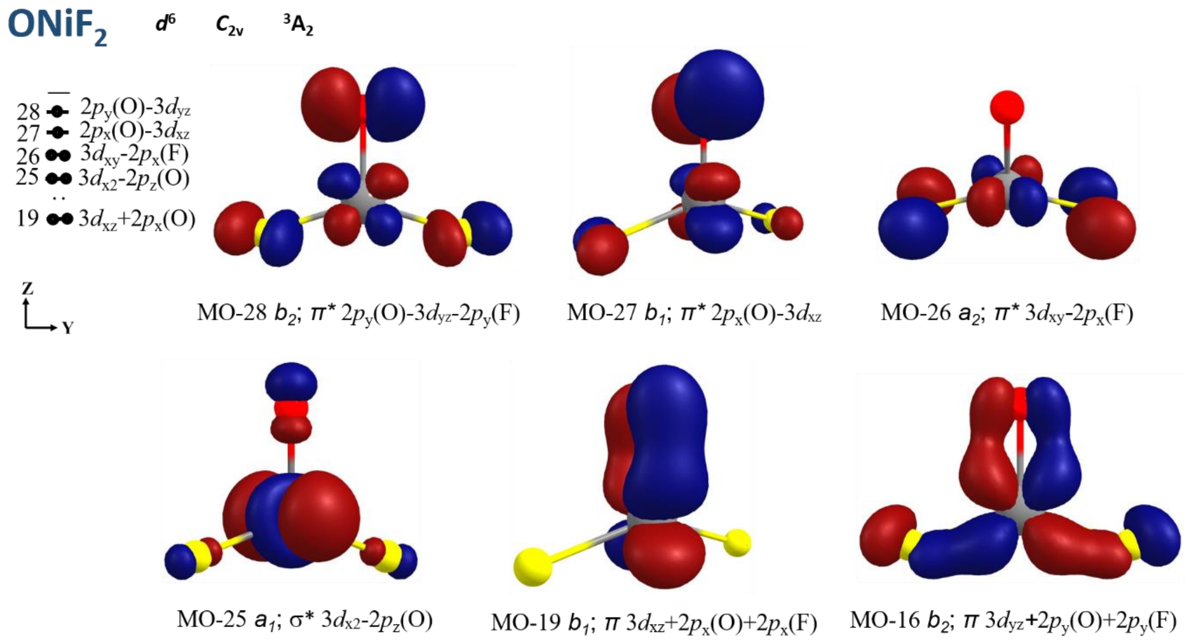
Molecular Orbitals of Selected Oxodifluorides OMF_2 and Spin Densities of OMF (M = group 9, 10, 11) and OMF_2 (M = group 10, 11) Compounds



MO-28 b_2; π^* $2p_y(O)-3d_{yz}$ MO-27 b_1; π^* $2p_x(O)-3d_{xz}$ MO-26 a_2; π^* $3d_{xy}-2p_x(F)$

MO-25 a_1; σ^* $3d_{x2}-2p_z(O)$ MO-19 b_1; π $3d_{xz}+2p_x(O)$ MO-16 b_2; π $3d_{yz}+2p_y(O)$

Figure S2.10. Selected molecular orbitals of $OCoF_2$ ($^4A_1$, C_{2v}). (B3LYP/AVTZ, Kohn-Sham orbitals with α spin; iso-surface = 0.08 electron a.u.$^{-3}$)



MO-28 b_2; π^* $2p_y(O)-3d_{yz}-2p_y(F)$ MO-27 b_1; π^* $2p_x(O)-3d_{xz}$ MO-26 a_2; π^* $3d_{xy}-2p_x(F)$

MO-25 a_1; σ^* $3d_{x2}-2p_z(O)$ MO-19 b_1; π $3d_{xz}+2p_x(O)+2p_x(F)$ MO-16 b_2; π $3d_{yz}+2p_y(O)+2p_y(F)$

Figure S2.11. Selected molecular orbitals of $ONiF_2$ ($^3A_2$, C_{2v}). (B3LYP/AVTZ, Kohn-Sham orbitals with α spin; iso-surface = 0.08 electron a.u.$^{-3}$)

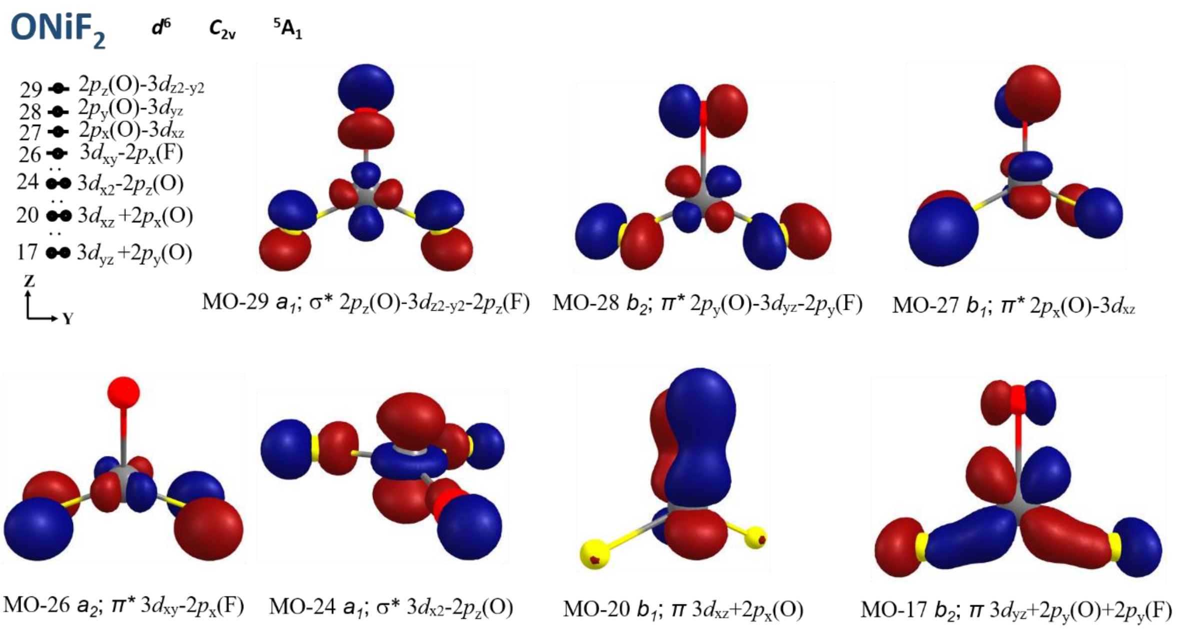


Figure S2.12. Selected molecular orbitals of ONiF$_2$ ($^5A_1$, C_{2v}). (B3LYP/AVTZ, Kohn-Sham orbitals with α spin; iso-surface = 0.08 electron a.u.$^{-3}$)

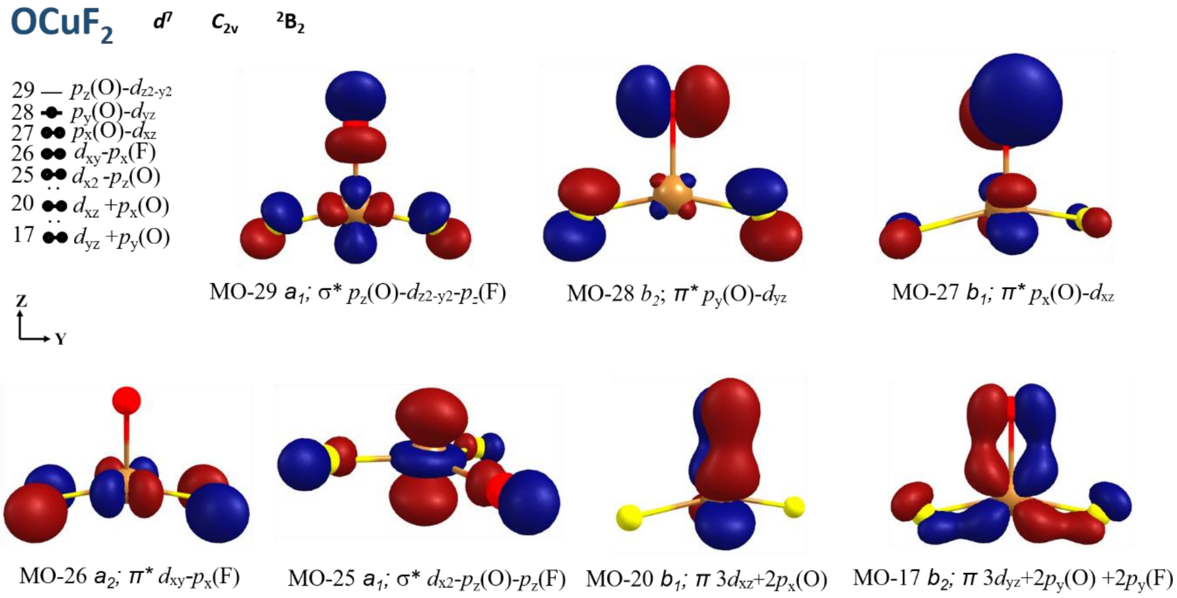


Figure S2.13. Selected molecular orbitals of OCuF$_2$ ($^2B_2$, C_{2v}). (BP86/AVTZ(-PP), Kohn-Sham orbitals with α spin; iso-surface = 0.08 electron a.u.$^{-3}$)

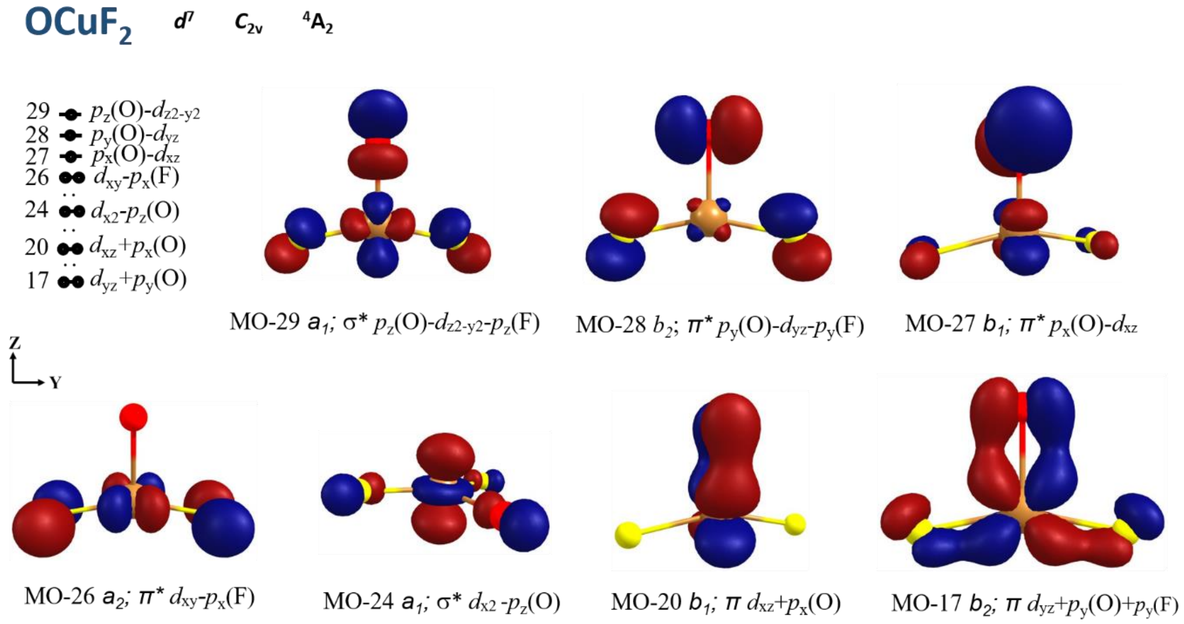


Figure S2.14. Selected molecular orbitals of $OCuF_2$ ($^4A_2$-1, C_{2v}). (BP86/AVTZ(-PP), Kohn-Sham orbitals with α spin; iso-surface = 0.08 electron a.u.$^{-3}$)

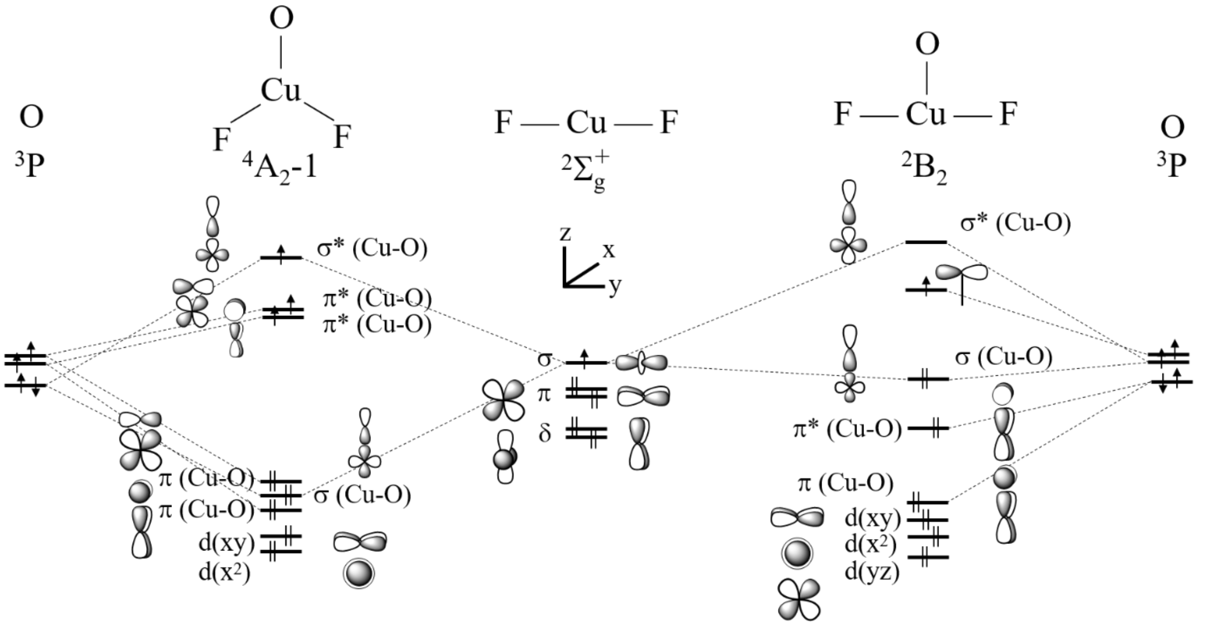


Figure S2.15. Qualitative molecular orbital scheme showing the interaction between CuF_2 and an oxygen atom that leads to $OCuF_2$ in the two different spin states $^2B_2$ (Right) and $^4A_2$-1 (Left). The frontier MOs for the two $OCuF_2$ spin states were derived from CASSCF(13,9)/VTZ-DK calculations (Tables S9.5 and S9.7). Contributions by fluorine 2*p* orbitals are not shown.

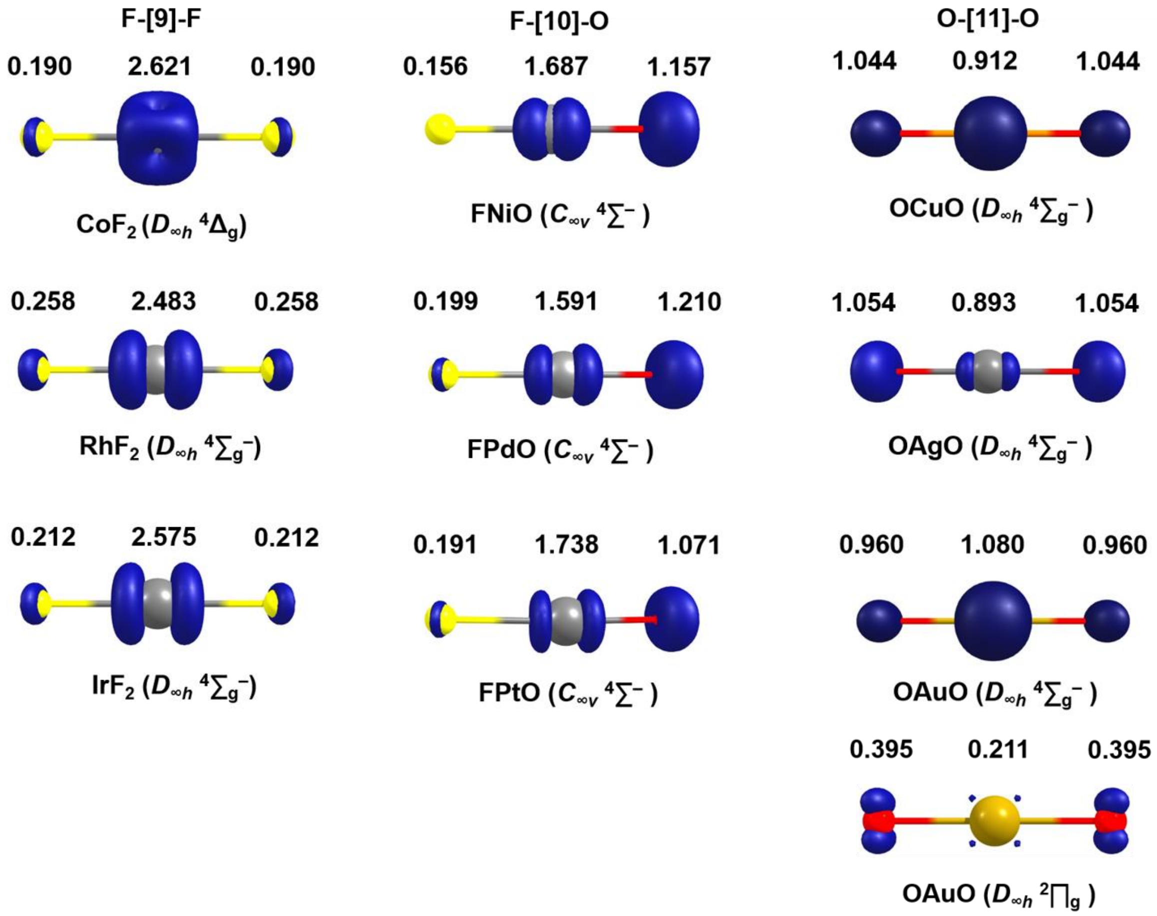


Figure S2.16. Spin densities of isoelectronic (d^7) group [9, 10 and 11] transition metal compounds (BP86/AVTZ(-PP), iso-surface = 0.08 electron a.u.$^{-3}$).

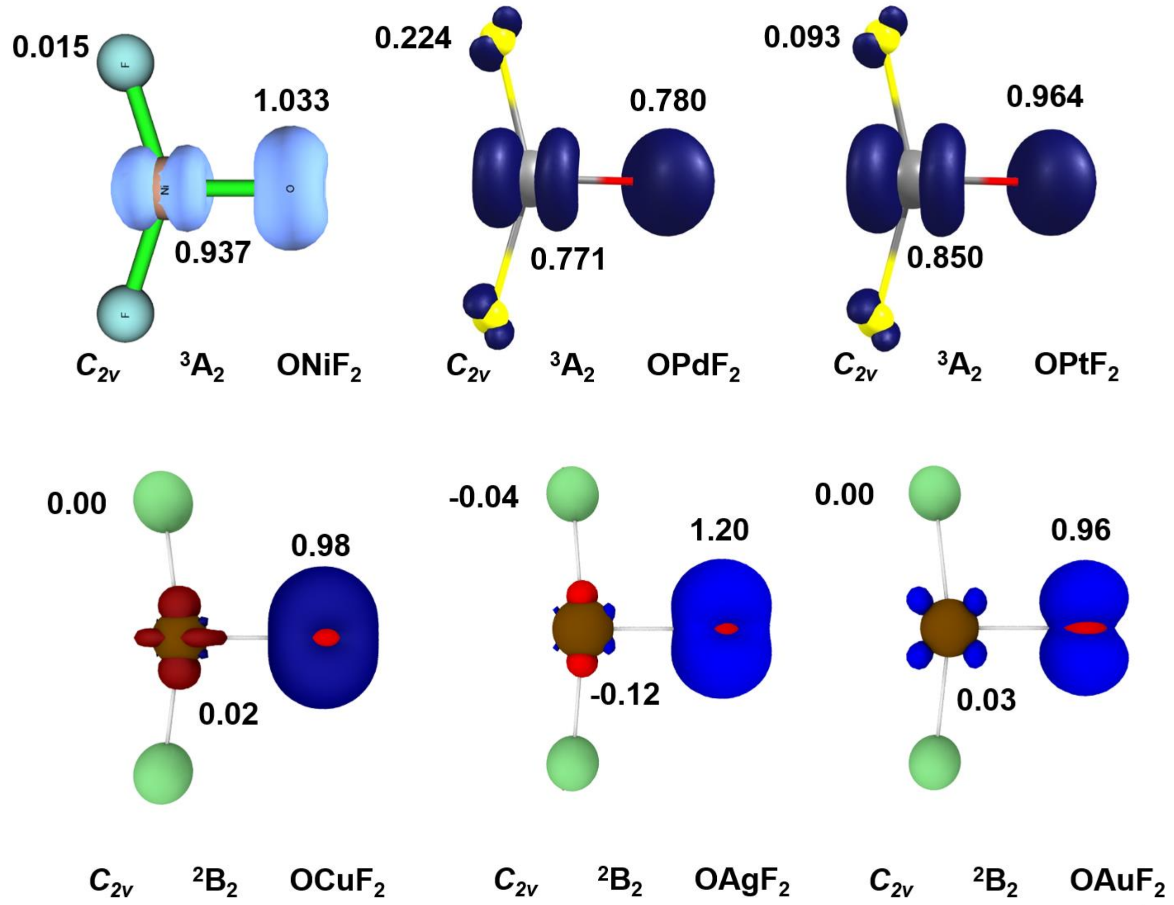


Figure S2.17. The spin density of OMF_2 group [10 and 11] transition metal compounds obtained at the BP86/AVTZ(-PP) level for M = Pd and Pt (iso-surface = 0.03 electron a.u.$^{-3}$), CASPT2/VTZ-DK level for M = Ni and at the B3LYP/AVTZ(-PP) level for M = Cu, Ag and Au (iso-surface = 0.03 electron Å^{-3}).[1]

Part 3. Tables to the main text:

Table S3.1. Overview about the quantum-chemical calculations performed in this work.

	Structure optimisation and frequency calculation	
Molecule(s)	Method(s)	Basis set(s)
NiOF	B3LYP, BP86	AVTZ
	RHF, CISD, CCSD(T)	AVnZ, AVnZ-DK (n = D, T, Q)
ONiF	B3LYP, BP86	AVTZ
	CCSD(T)	AVnZ, AVnZ-DK (n = T, Q)
	CASSCF, MRCI, CASPT2	AVnZ, AVnZ-DK (n = D, T, Q)
	MRCI [a)]	VTZ-DK [a)]
$ONiF_2$	B3LYP, BP86	AVTZ
	CCSD(T)	AVnZ, AVnZ-DK (n = D, T)
	CASSCF, CASPT2 [a)]	VTZ-DK [a)]
$OCuF_n$ ($n = 1, 2$)	B3LYP	AVTZ(-PP)
	CCSD(T)	AVTZ(-PP)
	CCSD(T)	VTZ-DK [a)], (A)VTZ-DK
	CASSCF, CASPT2 [a)]	VTZ-DK [a)]
OMF_n (M = Pd, Pt; $n = 1, 2$)	B3LYP, BP86	AVTZ(-PP)
	CCSD(T) [a)]	AVTZ(-PP) [a)]
FOMF (M = Ni, Pd, Pt)	B3LYP, (BP86)	AVTZ(-PP)
	CCSD(T)	AVTZ(-PP)
OMF_3 (M = Pd, Pt)	B3LYP, BP86	AVTZ(-PP)
	CCSD(T)	AVTZ(-PP)
$OPtF_3$	CASSCF, CASPT2 [a)]	AVTZ(-PP) [a)]
OMF_4 (M = Pd, Pt)	B3LYP, BP86	AVTZ(-PP)

[a)]: Optimized structure was used for single point calculations at the CASSCF level using the same basis set(s) to obtain spin densities, natural orbitals, NPA and AIM charges.

Table S3.2. Comparison of observed and computed vibrational frequencies (in cm^{-1}) for binary metalfluorides, MF_n (M = Ni, Pd, Pt; n = 1, 2)

	Sym.	Ground State	Exp.			Calc. (Int.)				Modes
			Ne	Ar	*Ar [Ref]*	CCSD(T)-DK[a]	CCSD(T)[b]	B3LYP[c]	BP86[d]	
NiF	$C_{\infty v}$	$^2\Pi$				639.13	612.98	614.44(78)	618.04(69)	$\nu(^{58}\text{Ni-F}), \Sigma^+$
			646.2	625.4	*634.7*[e] [29,31]	636.50	610.46	611.91(78)	615.50(69)	$\nu(^{60}\text{Ni-F}), \Sigma^+$
						-	-	611.91(78)	613.10(68)	$\nu(^{62}\text{Ni-F}), \Sigma^+$
NiF_2	$D_{\infty h}$	$^3\Sigma_g^-$	800.1	779.5	*779.4* [33]	819.17	806.42	804.01(180)	794.56(123)	$\nu(^{58}\text{Ni–F}_2), \Sigma_u^+$
			794.9	774.4	*774.3* [33]	813.75	801.09	798.69(177)	789.30(121)	$\nu(^{60}\text{Ni–F}_2), \Sigma_u^+$
			790.0	769.4	*769.3* [33]	-	-	793.68(175)	784.35(120)	$\nu(^{62}\text{Ni–F}_2), \Sigma_u^+$
PdF	$C_{\infty v}$	$^2\Pi$	-	-	-	542.5[f]				$\nu(^{102}\text{Pd-F}), \Sigma^+$
			-	-	-	541.7[f]				$\nu(^{104}\text{Pd-F}), \Sigma^+$
			-	-	-	541.3[f]				$\nu(^{105}\text{Pd-F}), \Sigma^+$
			547.5	540.3	*540.9* [35]	540.9[f]				$\nu(^{106}\text{Pd-F}), \Sigma^+$
			544.5		*540.1* [35]	540.1[f]				$\nu(^{108}\text{Pd-F}), \Sigma^+$
					539.4 [35]	539.4[f]				$\nu(^{110}\text{Pd-F}), \Sigma^+$
PdF_2	$D_{\infty h}$	$^3\Sigma_g^-$	-	-	-	621.2[f]				$\nu(^{102}\text{Pd-F}_2), \Sigma_u^+$
			-	-	*619.5* [35]	619.6[f]				$\nu(^{104}\text{Pd-F}_2), \Sigma_u^+$
			-	-	*618.8* [35]	618.8[f]				$\nu(^{105}\text{Pd-F}_2), \Sigma_u^+$
			650.8	618.1	*618.1* [35]	618.0[f]				$\nu(^{106}\text{Pd-F}_2), \Sigma_u^+$
			649.2	616.6	*616.5* [35]	616.5[f]				$\nu(^{108}\text{Pd-F}_2), \Sigma_u^+$
			647.8	615.1	*615.1* [35]	615.0[f]				$\nu(^{110}\text{Pd-F}_2), \Sigma_u^+$
PtF	$C_{\infty v}$	$^2\Pi$	605.6	590.0	-	-	-	-	575.15(47)	$\nu(^{195}\text{Pt-F}), \Sigma^+$
PtF_2	$D_{\infty h}$	$^3\Sigma_g^-$	710.1	695.6	-	-	731.36	-	708.17(118)	$\nu(^{195}\text{Pt-F}_2), \Sigma_u^+$

Values are calculated at the CCSD(T)/AVT(Q)Z level with DK [a] and without DK [b] and the DFT [c] B3LYP/AVTZ(-PP) and [d] BP86/AVTZ(-PP) levels. [e] $\omega_{eX1.5}$= 634.7 cm^{-1} in gas phase. [f] SVFF: simple valence force field.

Table S3.3. Comparison of observed and computed vibrational frequencies (cm^{-1}) for ONiF$_n$ (n = 1, 2)

	Sym.	Ground State	Exp.		Calc. (Int.)		Modes
			Ne	Ar	BP86^a	B3LYP^b	
^{16}ONiF	$C_{\infty v}$	$^4\Sigma^-$	846.5	797.1	863.59(15)	868.52(62)	ν(^{58}Ni-^{16}O), Σ^+
			841.9	792.0	860.36(14)	863.93(60)	ν(^{60}Ni-^{16}O), Σ^+
			837.6	-	857.35(14)	859.64(58)	ν(^{62}Ni-^{16}O), Σ^+
			651.1	-	647.68(49)	654.67(71)	ν(^{58}Ni-F), Σ^+
^{18}ONiF			821.2	-	825.69(15)	839.48(72)	ν(^{58}Ni-^{18}O), Σ^+
			816.1	-	822.26(14)	834.51(70)	ν(^{60}Ni-^{18}O), Σ^+
			-	-	819.06(14)	829.85(68)	ν(^{62}Ni-^{18}O), Σ^+
			647.1	-	639.93(42)	645.34(61)	ν(^{58}Ni-F), Σ^+
^{16}ONiF$_2$	C_{2v}	$^3A_2$	755.8	744.9	716.49(122)	746.90(159)	ν$_{as}$(^{58}NiF$_2$), B$_2$
			751.1	740.3	712.02(121)	742.16(157)	ν$_{as}$(^{60}NiF$_2$), B$_2$
			746.8	736.0	707.82(119)	737.70(155)	ν$_{as}$(^{62}NiF$_2$), B$_2$
			640.3	629.7	611.85(12)	628.11(18)	ν(^{58}NiF$_2$), A$_1$
^{18}ONiF$_2$			755.8	744.9	712.02(121)	746.90(159)	ν$_{as}$(^{58}NiF$_2$), B$_2$
			751.0	740.3	712.02(121)	742.16(157)	ν$_{as}$(^{60}NiF$_2$), B$_2$
			746.7	736.0	707.81(119)	737.69(155)	ν$_{as}$(^{62}NiF$_2$), B$_2$
			637.6	627.2	610.61(11)	627.23(18)	ν(^{58}NiF$_2$), A$_1$
Ni^{16}OF	C_s	$^2A'$	557.4	-	665.94(74)	559.19(23)	ν(^{58}Ni-^{16}O), A′
			554.7	-	664.10(74)	557.16(23)	ν(^{60}Ni-^{16}O), A′
Ni^{18}OF			536.1	-	642.52(78)	534.51(21)	ν(^{58}Ni-^{18}O), A′
			533.6	-	640.70(79)	532.38(21)	ν(^{60}Ni-^{18}O), A′

Values are calculated at the DFT BP86 ^{a} & B3LYP/AVTZ levels ^{b} using the Gaussian 16 package.

Table S3.4. Comparison of observed and computed vibrational frequencies (cm^{-1}) for OPdF$_n$ (n = 1, 2)

Species	Sym.	State	Exp.		Calc. (Int.)		Modes
			Ne	Ar	BP86[a]	B3LYP[b]	
^{16}OPdF$_2$	C_{2v}	^{3}A$_2$	653.6	634.3	621.69(132)	643.38(166)	ν_{as}(^{104}PdF$_2$), B$_2$
			652.9	633.6	620.94(132)	642.60(165)	ν_{as}(^{105}PdF$_2$), B$_2$
			652.1	632.7	620.21(131)	641.83(165)	ν_{as}(^{106}PdF$_2$), B$_2$
			650.7	631.3	618.79(131)	640.32(164)	ν_{as}(^{108}PdF$_2$), B$_2$
			649.3	629.9	617.35(130)	638.80(163)	ν_{as}(^{110}PdF$_2$), B$_2$
			586.1	-	560.60(14)	575.26(21)	ν_s(^{106}PdF$_2$), A$_1$
^{18}OPdF$_2$			653.5	634.0	621.68(132)	643.38(166)	ν_{as}(^{104}PdF$_2$), B$_2$
			652.7	633.3	620.94(132)	642.60(165)	ν_{as}(^{105}PdF$_2$), B$_2$
			652.1	632.5	620.21(131)	641.83(165)	ν_{as}(^{106}PdF$_2$), B$_2$
			650.6	631.1	618.78(131)	640.32(163)	ν_{as}(^{108}PdF$_2$), B$_2$
			649.2	629.7	617.34(130)	638.80(163)	ν_{as}(^{110}PdF$_2$), B$_2$
			585.9	-	560.60(14)	575.08(21)	ν_s(^{106}PdF$_2$), A$_1$
F^{16}OPdF	C_s	^{3}A″	-	598.4	-	637.48(149)	ν(^{105}Pd-F)
			-	597.3	-	636.73(148)	ν(^{106}Pd-F)
			-	596.2	-	635.27(148)	ν(^{108}Pd-F)
F^{18}OPdF			-	586.0	-	630.16(153)	ν(^{105}Pd-F)
			-	584.6	-	629.44(153)	ν(^{106}Pd-F)
			-	583.4	-	628.02(152)	ν(^{108}Pd-F)
F^{16}OPdF	C_s	^{3}A′	638.7	623.4	-	-	ν(Pd-F)
F^{18}OPdF			635.4	619.8	-	-	ν(Pd-F)
^{16}OPdF	$C_{\infty v}$	$^4\Sigma^-$	784.9	757.4	791.40(43)	778.82(33)	ν(O-^{104}Pd)
			784.2	756.8	790.75(43)	777.54(32)	ν(O-^{105}Pd)
			783.7	755.5	790.12(42)	778.17(32)	ν(O-^{106}Pd)
			782.5	754.3	788.88(41)	776.30(31)	ν(O-^{108}Pd)
			781.8	753.3	787.64(41)	775.06(31)	ν(O-^{110}Pd)
			580.2	573.7	594.55(65)	602.04(96)	ν(^{106}Pd-F), Σ^+
^{18}OPdF			749.3	723.3	755.56(47)	743.92(40)	ν(O-^{104}Pd)
			748.6	722.7	754.84(46)	739.72(37)	ν(O-^{105}Pd)
			747.9	722.0	754.13(46)	742.48(39)	ν(O-^{106}Pd)
			746.7	720.7	752.76(45)	741.11(38)	ν(O-^{108}Pd)
			745.5	719.4	751.39(44)	739.72(37)	ν(O-^{110}Pd)
			580.2	573.7	591.38(59)	598.32(88)	ν(^{106}Pd-F), Σ^+
unknown band * (^{16}O)			768.1	-			ν(O-^{104}Pd)
			766.9	-			ν(O-^{105}Pd)
			765.6	-			ν(O-^{106}Pd)
unknown band ** (^{18}O)			735.7	-			ν(O-^{104}Pd)
			734.3	-			ν(O-^{105}Pd)
			732.9	-			ν(O-^{106}Pd)

Values calculated at the DFT BP86 [a] and B3LYP/AVTZ(-PP) [b] levels using the Gaussian 16 package.

Table S3.5. Comparison of observed and computed vibrational frequencies (cm^{-1}) for $OPtF_n$ (n = 1-3)

Species	Sym.	State	Exp.		Calc. (Int.)		Modes
			Ne	Ar	BP86^a	B3LYP^b	
$^{16}OPtF_3$	C_{2v}	$^4A_1$	712.6	709.1	663.18(87)	691.05(118)	$\nu_{as}(^{195}Pt\text{-}F_2)$, B_2
			-	666.6	632.04(44)	661.60(60)	$\nu(^{195}Pt\text{-}F')$, A_1
$^{18}OPtF_3$			712.6	709.1	663.17(87)	691.04(118)	$\nu_{as}(^{195}Pt\text{-}F_2)$, B_2
			-	665.9	631.81(43)	661.25(58)	$\nu(^{195}Pt\text{-}F')$, A_1
$^{16}OPtF$	$C_{\infty v}$	$^4\Sigma^-$	611.8	-	619.87(90)	629.64(115)	$\nu(^{195}Pt\text{-}F)$, Σ^+
$^{18}OPtF$			611.8	-	619.61(89)	629.43(114)	$\nu(^{195}Pt\text{-}F)$, Σ^+
$^{16}OPtF_2$	C_{2v}	$^3A_2$	650.2	635.2	611.85(138)	628.94(160)	$\nu_{as}(^{195}Pt\text{-}F_2)$, B_2
$^{18}OPtF_2$			650.2	635.2	611.79(139)	628.92(160)	$\nu_{as}(^{195}Pt\text{-}F_2)$, B_2

Values calculated at the BP86 ^{a} & B3LYP/AVTZ(-PP) ^{b} level using the Gaussian 16 package.

Table S3.6. Thermochemistry of metal oxo fluorides in kJ mol^{-1} [a]

	B3LYP/AVTZ(-PP)		CCSD(T)/AVTZ(-PP)	
$Ni + OF \rightarrow ONiF$	-561.12	*-559.22*	-593.27	*-591.37*
$Ni + OF \rightarrow NiOF$	-261.73	*-261.86*	-286.30	*-286.43*
$Ni + OF_2 \rightarrow ONiF_2$	-596.20	*-595.41*	-609.57	*-608.79*
$Pd + OF \rightarrow OPdF$	-401.29	*-401.49*	-365.36	*-365.56*
$Pd + OF \rightarrow PdOF$	-200.84	*-213.12*	-185.80	*-191.88*
$Pd + OF_2 \rightarrow OPdF_2$	-446.12	*-446.70*	-393.05	*-393.63*
$Pd + OF_2 \rightarrow FOPdF$ ($^3A''$)	-372.15	*-372.19*	-317.15	*-317.19*
$Pt + OF \rightarrow OPtF$	-540.00	*-539.07*	-540.79	*-518.74*
$Pt + OF \rightarrow PtOF$	-198.75	*-210.34*	-245.60	*-257.19*
$Pt + OF_2 \rightarrow OPtF_2$	-637.44	*-630.36*	-630.42	*-630.36*
$OPtF_2 + F \rightarrow OPtF_3$	-257.56	*-213.96*	-230.19	*-226.35*

[a] Values in *italic* style are corrected for ZPE (B3LYP/AVTZ(-PP)) obtained from a harmonic frequency analysis.

Table S3.7. Charge analysis (Effective electron count: EC(2*p*))[a] and spin population (spin density: SD(2*p*))[b] of the oxygen 2*p*-orbitals in OMF_n (M = Ni, Cu, *n* = 1, 2; M = Pd, *n* = 2; M = Pt, *n* = 2, 3).

	Spin State	EC(2*p*) on oxygen p(x)	EC(2*p*) on oxygen p(y)	EC(2*p*) on oxygen s(z)	EC(2*p*) on oxygen nb	SD(2*p*) on oxygen p(x)	SD(2*p*) on oxygen p(y)	SD(2*p*) on oxygen s(z)
ONiF [c]	$^4\Sigma^-$	1.42	1.42	1.39	0.38	0.43	0.43	0.15
OCuF [c]	$^3\Sigma^-$	1.30	1.30	1.21	0.72	0.53	0.53	0.02
$\mathrm{ONiF_2}$ [c]	$^3A_2$	1.47	1.30	0.93	0.42	0.45	0.57	0.01
$\mathrm{ONiF_2}$ [c]	$^5A_1$	1.11	1.23	1.19	0.56	0.79	0.65	0.30
$\mathrm{OPdF_2}$ [d]	$^3A_2$	1.28	1.33	1.09	0.28	0.63	0.57	0.04
$\mathrm{OPtF_2}$ [d]	$^3A_2$	1.33	1.43	1.07	0.27	0.58	0.48	0.01
$\mathrm{OCuF_2}$ [e]	$^2B_2$	1.93	0.99	0.74	0.38	0.00	0.91	0.24
$\mathrm{OCuF_2}$ [e]	$^4A_2$-1	1.11	1.25	1.15	0.59	0.77	0.60	0.34
$\mathrm{OCuF_2}$ [e]	$^4A_2$-2	1.00	1.00	1.55	0.38	0.98	0.98	0.03
$\mathrm{OPtF_3}$ [d]	$^4A_1$	1.20	1.17	1.19	0.49	0.67	0.69	0.02

[a]: EC(2*p*) values according to the Equation: EC(2*p(i)*) = $\sum_n (\mathrm{ON}(n)\ \mathrm{x}\ C(2p(i),n)$. Here, ON(*n*) represent the occupation number and *C*(2*p(i)*, *n*) the percent oxygen 2*p(i)* composition of the *n*th natural orbital obtained at the CASSCF level (see parts 6-9 in the SI). For the π- and the σ-subspaces the sum was formed over the corresponding bonding (n″) and antibonding (n′) orbitals only, whereas nb denotes the sum of oxygen 2*p* electrons contributing to non-bonding MOs. [b]: Mulliken spin population analysis. [c]: CASSCF(*m*,*n*)/CASTP2/VTZ-DK level: ONiF (*m* = 13, *n* = 8), OCuF (14,9), $\mathrm{ONiF_2}$ ($^3A_2$: (12,8), $^5A_1$: (12,9)). [d]: CASSCF(12,8)/AVTZ(-PP) level: $\mathrm{OPdF_2}$, $\mathrm{OPtF_2}$ (*n* = 12); $\mathrm{OPtF_3}$ (*n* = 11). [e]: CASSCF(13,9)/VTZ-DK level.

The effective electron count of the oxygen 2*p*-orbitals (EC(2*p*)) in the π- and σ-orbital subspaces are affected by three factors: i) electron correlation effects where more than one configuration contributes to the ground-state. These effects were taken into account by considering multireference CASSCF wavefunctions. ii) polarization of bonding electrons, which is accounted for by the CID ratios (Table 3 main text) and, iii) delocalization of oxygen 2*p* electrons into more than the two selected MOs (n″ and n′). The latter contributions can be analyzed explicitly by examining the respective oxygen contributions to these additional MOs, which in most cases are non-bonding (nb) MOs, or by comparison of the EC(2*p*) values from the π- and σ-subspaces to the total Mulliken population for the respective oxygen 2*p* orbitals (see Table S3.7, 6th column). We note that the Mulliken spin population in open-shell electronic structures can be affected by a minority spin density from orthogonal orbital subspaces due to spin polarization.[1]

References to Part 3

1 S. K. Singh, J. Eng, M. Atanasov and F. Neese, Covalency and chemical bonding in transition metal complexes: An *ab initio* based ligand field perspective, *Coord. Chem. Rev.*, **2017**, 344, 2–25.

Part 4. DFT and CCSD(T) calculations

Table S4.1. Structural parameters (bond lengths r in Å, angles in deg) for OMF_n (M = Ni, n = 1, 2; M = Pd and Pt, n = 1-4) compounds.

$ONiF_n$, n = 1, 2

NiOF, C_s

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)
$^2A''$	B3LYP/AVTZ	-1683.40851	1.772, 1.462, 108.7
$^2A''$	BP86/AVTZ	-1683.628938	1.685, 1.542, 111.7
$^2A'$	B3LYP/AVTZ	-1683.407623	1.801, 1.475, 101.4
$^2A'$	BP86/AVTZ	-1683.621418	1.710, 1.547, 103.9

ONiF, $C_{\infty v}$

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)	T_1 parameter
$^4\Sigma^-$	B3LYP/AVTZ	-1683.520949	1.618, 1.733, 180.0	
$^4\Sigma^-$	BP86/AVTZ	-1683.742678	1.621, 1.734, 180.0	
$^4\Sigma^-$	CCSD(T)/AVTZ	-1682.120430	1.660, 1.736, 180.0	0.05439496
$^4\Sigma^-$	CCSD(T)/AVQZ	-1682.205289	1.649, 1.736, 180.0	0.09263727

$ONiF_2$, C_{2v}

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)	T_1 parameters
$^3A_2$	B3LYP/AVTZ	-1783.359261	1.595, 1.720, 107.0	
$^3A_2$	BP86/AVTZ	-1783.603238	1.609, 1.730, 108.7	
$^3A_2$	CCSD(T)/AVDZ	-1781.546784	1.590, 1.719, 108.7	0.049
$^3A_2$	CCSD(T)/AVTZ	-1781.826432	1.583, 1.711, 108.2	0.047
$^3A_2$	CCSD(T)/AVDZ-DK	-1793.975167	1.583, 1.712, 109.0	0.049
$^3A_2$	CCSD(T)/AVTZ-DK	-1794.256127	1.576, 1.703, 108.6	0.047
$^5A_1$	B3LYP/AVTZ	-1783.366192	1.720, 1.738, 114.2	
$^5A_1$	BP86/AVTZ	-1783.592835	1.696, 1.755, 115.3	
$^5A_1$	CCSD(T)/AVDZ	-1781.550693	1.708, 1.744, 112.2	0.052
$^5A_1$	CCSD(T)/AVDZ-DK	-1793.978162	1.692, 1.736, 113.0	0.051
$^5A_1$	CCSD(T)/AVTZ-DK	-1794.253686	1.683, 1.727, 113.1	0.055

FONiF, C_s

Electronic State	Method	Total energy	r(MO), r(MF), r(OF'), ang(MOF'), ang(OMF)
$^3A''$	B3LYP/AVTZ	-1783.347492	1.759, 1.736, 1.450, 99.7, 182.3
$^3A''$	CCSD(T)/AVTZ	-1781.812767	1.786, 1.733, 1.504, 81.8, 178.7
$^3A'$	B3LYP/AVTZ	-1783.317855	1.847, 1.743, 1.496, 76.9, 160.0
$^3A'$	CCSD(T)/AVTZ	-1781.434315	1.787, 1.742, 1.502, 90.9, 179.6

$PdOF_n$, $n = 1$-4

PdOF, C_s

Electronic State	Method	Total energy	r(MO), r(OF), ang(MOF)
$^2A'$	B3LYP/AVTZ(-PP)	-302.5147411	1.947, 1.451, 104.6
$^2A'$	BP86/AVTZ(-PP)	-302.5921325	1.901, 1.486, 107.0
$^2A'$	CCSD(T)/AVTZ(-PP)	-301.7272352	1.945, 1.473, 100.2
$^2A''$	B3LYP/AVTZ(-PP)	-302.5025193	1.948, 1.437, 115.0
$^2A''$	BP86/AVTZ(-PP)	Converged to $^2A'$	
$^2A''$	CCSD(T)/AVTZ(-PP)	No convergence	

OPdF, $C_{\infty v}$

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)
$^4\Sigma^-$	B3LYP/AVTZ(-PP)	-302.5911357	1.759, 1.892, 180.0
$^4\Sigma^-$	BP86/AVTZ(-PP)	-302.6755204	1.762, 1.892, 180.0
$^4\Sigma^-$	CCSD(T)/AVTZ(-PP)	-301.7951842	1.755, 1.889, 180.0

$OPdF_2$, C_{2v}

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)
$^3A_2$	B3LYP/AVTZ(-PP)	-402.433177	1.733, 1.883, 103.4
$^3A_2$	BP86/AVTZ(-PP)	-402.531798	1.741, 1.893, 104.6
$^3A_2$	CCSD(T)/AVTZ(-PP)	-401.4941764	1.722, 1.877, 101.6
$^5A_1$	B3LYP/AVTZ(-PP)	-402.3965208	1.888, 1.909, 107.4
$^5A_1$	BP86/AVTZ(-PP)	-402.4889068	1.868, 1.929, 110.1
$^5A_1$	CCSD(T)/AVTZ(-PP)	imaginary frequency	

$OPdF_3$, C_{2v}

Electronic State	Method	Total energy	r(MO), r(MF*2), r(MF'), ang(OMF*2)
$^4A_1$	B3LYP/AVTZ(-PP)	-502.2646592	1.809, 1.856*2, 1.864, 91.2
$^4A_1$	BP86/AVTZ(-PP)	-502.3754365	1.794, 1.877*2, 1.880, 91.6
$^4A_1$	CCSD(T)/AVTZ(-PP)	-501.1688789	1.810, 1.836*2, 1.854, 90.9

$OPdF_4$, C_{4v}

Electronic State	Method	Total energy	r(MO), r(MF*4), ang(OMF)
$^3A_2$	B3LYP/AVTZ(-PP)	-602.0751199	1.725, 1.870, 99.0
$^3A_2$	BP86/AVTZ(-PP)	-602.2030694	1.748, 1.882, 99.8

FOPdF, C_s

Electronic State	Method	Total energy	r(MO), r(MF), r(OF'), ang(MOF'), ang(OMF)
$^3A''$	B3LYP/AVTZ-PP	-402.4048332	1.868, 1.888, 1.430, 111.7, 183.3
$^3A''$	CCSD(T)/AVTZ(-PP)	-401.4650966	1.860, 1.887, 1.444, 108.8, 178.1
$^3A'$	CCSD(T)/AVTZ(-PP)	-401.4460713	1.992,1.877, 1.488, 79.6, 154.7

PtOF$_n$, n = 1-4

PtOF, C_s

Electronic State	Method	Total energy	r(MO), r(OF), ang(MOF)
$^2A'$	B3LYP/AVTZ(-PP)	-294.4429487	1.938, 1.45, 107.6
$^2A'$	BP86/AVTZ(-PP)	-294.4565851	1.883, 1.466, 107.3
$^2A''$	B3LYP/AVTZ(-PP)	-294.4605045	1.813, 1.478, 114.2
$^2A''$	BP86/AVTZ(-PP)	-294.5839812	1.762, 1.585, 115.3

OPtF, $C_{\infty v}$

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)
$^4\Sigma^-$	B3LYP/AVTZ(-PP)	-294.5725826	1.754, 1.902, 180.0
$^4\Sigma^-$	BP86/AVTZ(-PP)	-294.6838978	1.761, 1.906, 180.0
$^4\Sigma^-$	CCSD(T)/AVTZ(-PP)	-293.7204063	1.740, 1.897, 180.0

OPtF$_2$, C_{2v}

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)
$^3A_2$	B3LYP/AVTZ(-PP)	-394.4351107	1.731, 1.901, 102.8
$^3A_2$	BP86/AVTZ(-PP)	-394.5575036	1.743, 1.908, 103.3
$^3A_2$	CCSD(T)/AVTZ(-PP)	-393.4432615	1.723, 1.892, 101.9
$^5A_1$	B3LYP/AVTZ(-PP)	-394.3839116	1.911, 1.892, 100.3
$^5A_1$	BP86/AVTZ(-PP)	-394.5032830	1.908, 1.900, 100.2
$^5A_1$	CCSD(T)/AVTZ(-PP)	-393.385495	1.910, 1.879, 100.1

FOPtF, C_s

Electronic State	Method	Total energy	r(MO), r(MF), r(OF'), ang(MOF'), ang(OMF)
$^3A''$	B3LYP/AVTZ(-PP)	-394.3749381	1.835, 1.891, 1.464, 112.5, 176.5
$^3A''$	BP86/AVTZ(-PP)	-394.4989477	1.783, 1.889, 1.597, 109.9, 187.3
$^3A''$	CCSD(T)/AVTZ(-PP)	-393.3798976	1.830, 1.884, 1.475, 108.9, 176.8
$^3A'$	B3LYP/AVTZ(-PP)	-394.3473293	1.882, 1.898, 1.441, 113.9, 186.0
$^3A'$	BP86/AVTZ(-PP)	-394.4667617	1.851, 1.898, 1.517, 115.8, 191.8
$^3A'$	CCSD(T)/AVTZ(-PP)	Converged to $^3A''$	

OPtF$_3$, C_{2v}

Electronic State	Method	Total energy	r(MO), r(MF*2), r(MF'), ang(OMF*2)
$^4A_1$	B3LYP/AVTZ(-PP)	-494.296374	1.791, 1.859*2, 1.888, 92.0
$^4A_1$	BP86/AVTZ(-PP)	-494.4282967	1.796, 1.871*2, 1.902, 92.1
$^4A_1$	CCSD(T)/AVTZ(-PP)	-493.1555755	1.784, 1.845*2, 1.878, 92.0

OPtF$_4$, C_{4v}

Electronic State	Method	Total energy	r(MO), r(MF*4), ang(OMF)
$^3A_2$	B3LYP/AVTZ(-PP)	-594.1203162	1.736, 1.889, 99.1
$^3A_2$	BP86/AVTZ(-PP)	-594.2632682	1.759, 1.901, 99.4

Table S4.2. Computed harmonic frequencies (cm^{-1}) for $ONiF_n$ (n = 1, 2).

NiOF (X^{2}A', C_s), B3LYP/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	829.22(64)	829.21(64)	829.20(64)	804.91(63)	804.90(63)	804.89(63)	A'
	559.19(23)	557.16(23)	555.26(23)	534.51(21)	532.38(21)	530.38(21)	A'
	151.67(8)	151.11(8)	150.59(8)	149.94(7)	149.40(7)	148.89(7)	A'

NiOF (X^{2}A', C_s), BP86/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	665.94(74)	664.10(74)	662.39(75)	642.52(78)	640.70(79)	639.02(80)	A'
	555.38(82)	554.91(81)	554.45(80)	534.63(71)	534.03(70)	533.44(69)	A'
	150.71(7)	150.14(7)	149.59(7)	148.66(7)	148.10(7)	147.57(7)	A'

ONiF (X$^4\Sigma^-$, $C_{\infty v}$), B3LYP/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	868.52(62)	863.93(60)	859.64(58)	839.48(72)	834.51(70)	829.85(68)	∑
	654.67(71)	654.01(72)	653.35(72)	645.34(61)	644.96(62)	644.58(62)	∑
	162.82(36)*2	161.80(35)*2	160.85(35)*2	159.47(35)*2	158.44(34)*2	157.46(34)*2	∏

ONiF (X$^4\Sigma^-$, $C_{\infty v}$), BP86/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	891.25(74)	886.75(72)	882.53(70)	859.46(80)	854.59(77)	850.01(76)	∑
	647.68(49)	646.88(49)	646.09(50)	639.93(42)	639.40(42)	638.87(43)	∑
	151.57(36)	150.63(27)	149.74(26)	148.45(26)	147.49(26)	146.59(25)	∏

ONiF ($X^4\Sigma^-$, $C_{\infty v}$), CCSD(T)/AVTZ

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
	741.46	736.85	733.81	729.23	∑
	570.90	570.85	549.62	549.47	∑
	127.75	127.22	124.89	124.35	∏

ONiF ($X^4\Sigma^-$, $C_{\infty v}$), CCSD(T)/AVQZ

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
	748.00	743.48	742.71	738.30	∑
	606.58	606.43	582.06	581.74	∑
	174.36	173.03	171.41	170.08	∏

$ONiF_2$ (X^3A_2, C_{2v}), B3LYP/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	860.95(4)	857.84(3)	854.94(3)	822.78(4)	819.47(4)	816.38(4)	A_1
	746.90(159)	742.16(157)	737.70(155)	746.90(159)	742.16(157)	737.69(155)	B_2
	628.11(18)	627.76(18)	627.43(18)	627.23(18)	626.94(18)	626.66(18)	A_1
	220.85(26)	219.08(26)	217.42(25)	219.63(26)	217.85(25)	216.17(25)	B_1
	187.55(1)	187.23(1)	186.92(1)	181.74(7)	181.06(7)	180.43(0)	B_2
	182.36(7)	181.64(7)	180.96(7)	181.08(0)	180.75(0)	180.40(7)	A_1

ONiF$_2$ (X^{3}A$_2$, C_{2v}), BP86/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	863.58(15)	860.36(14)	857.35(14)	822.26(14)	822.26(14)	819.06(14)	A_1
	716.49(122)	712.02(121)	707.82(119)	712.02(121)	712.02(121)	707.81(119)	B_2
	611.85(12)	611.51(12)	611.18(12)	610.61(11)	610.61(11)	610.33(11)	A_1
	209.82(19)	208.13(19)	206.54(18)	206.78(18)	206.78(18)	205.18(18)	B_1
	183.45(6)	182.76(6)	182.09(6)	182.11(6)	182.11(6)	181.48(6)	A_1
	159.88(2)	159.59(2)	159.31(2)	154.12(2)	154.12(2)	153.83(2)	B_2

ONiF$_2$ (X^{3}A$_2$, C_{2v}), CCSD(T)/AVDZ

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
	903.53	900.22	863.72	860.19	A_1
	778.44	773.61	778.44	773.61	B_2
	652.01	651.63	650.92	650.61	A_1
	257.31	254.63	256.58	253.92	B_2
	224.69	224.29	216.11	215.70	A_1
	214.60	213.82	213.92	213.18	B_1

ONiF$_2$ (X^{3}A$_2$, C_{2v}), CCSD(T)/AVTZ

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
	915.23	911.84	874.95	871.34	A_1
	781.30	776.33	781.29	776.33	B_2
	654.43	653.99	653.46	653.09	A_1
	226.57	224.67	224.98	223.07	B_2
	219.32	218.52	218.59	217.82	A_1
	185.26	185.03	179.08	178.86	B_1

ONiF$_2$ (X^{3}A$_2$, C_{2v}), CCSD(T)/AVDZ-DK

16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
914.90	911.45	875.01	871.34	A$_1$
781.60	776.65	781.60	776.66	B$_2$
662.00	661.65	660.74	660.46	A$_1$
229.77	227.84	228.53	226.60	B$_2$
215.26	214.33	214.39	213.50	A$_1$
180.52	180.28	174.05	173.81	B$_1$

ONiF$_2$ (X^{3}A$_2$, C_{2v}), CCSD(T)/AVTZ-DK

16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
928.12	924.67	887.28	883.62	A$_1$
788.10	783.06	788.10	783.05	B$_2$
674.97	674.57	674.04	673.71	A$_1$
233.16	231.22	232.76	230.84	B$_2$
184.43	184.1	178.81	178.31	A$_1$
179.37	178.84	177.92	177.60	B$_1$

ONiF$_2$ (^{5}A$_1$, C_{2v}), B3LYP/AVTZ

16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	sym.
724.06(128)	719.83(127)	715.85(127)	724.06(128)	719.82(127)	715.84(125)	B$_2$
660.00(20)	657.04(20)	654.26(19)	643.99(37)	641.18(37)	638.57(38)	A$_1$
612.45(33)	612.44(33)	612.43(33)	598.61(16)	598.35(15)	598.08(14)	A$_1$
187.91(2)	187.49(2)	187.09(2)	181.89(2)	181.46(2)	181.04(2)	B$_2$
151.19(5)	150.65(5)	150.13(5)	150.78(5)	150.26(5)	149.76(5)	A$_1$
132.90(35)	131.83(34)	130.82(34)	131.77(35)	130.69(34)	129.67(34)	B$_1$

ONiF$_2$ (^{5}A$_1$, C_{2v}), BP86/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	sym.
	726.68(2)	724.02(2)	721.54(2)	695.16(3)	692.25(3)	689.53(3)	A$_1$
	677.38(67)	673.52(66)	669.88(65)	677.37(67)	673.51(66)	669.87(65)	B$_2$
	587.83(20)	587.35(20)	586.88(20)	585.92(19)	585.58(19)	585.25(19)	A$_1$
	179.76(2)	179.33(2)	178.92(2)	173.96(2)	173.52(2)	173.09(2)	B$_2$
	143.45(5)	142.93(5)	142.43(5)	143.08(5)	142.58(5)	142.10(5)	A$_1$
	109.25(26)	108.37(26)	107.53(26)	108.18(26)	107.29(26)	106.45(25)	B$_1$

ONiF$_2$ (^{5}A$_1$, C_{2v}), CCSD(T)/AVDZ

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
	747.83	743.46	747.83	743.46	B$_2$
	703.44	700.57	681.22	678.25	A$_1$
	597.45	597.43	588.08	588.06	A$_1$
	172.23	171.78	166.80	166.30	B$_2$
	138.03	137.17	137.52	136.68	A$_1$
	130.97	129.87	131.41	130.31	B$_1$

ONiF$_2$ (^{5}A$_1$, C_{2v}), CCSD(T)/AVDZ-DK

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	Sym.
	752.73	748.25	752.73	748.25	B$_2$
	735.02	731.95	710.33	707.08	A$_1$
	628.27	628.20	619.77	619.77	A$_1$
	194.49	194.07	188.08	187.65	B$_2$
	161.98	161.40	161.62	161.05	A$_1$
	141.50	140.30	140.40	139.20	B$_1$

ONiF$_2$ ($^5A_1$, C_{2v}), CCSD(T)/AVTZ-DK

	16O/58Ni	16O/60Ni	18O/58Ni	18O/60Ni	sym.
	752.68	748.28	752.68	748.28	B_2
	750.19	747.09	723.27	719.95	A_1
	633.25	633.12	626.20	626.19	A_1
	201.94	201.58	196.05	195.66	B_2
	159.22	158.39	158.71	157.90	A_1
	147.83	146.16	147.58	145.92	B_1

FONiF ($^3A''$, C_s), B3LYP/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	902.37(31)	902.27(32)	902.19(32)	875.41(31)	875.32(31)	875.23(32)	A′
	742.00(199)	737.36(196)	732.99(193)	734.58(195)	729.98(192)	725.65(189)	A′
	587.65(0)	587.60(0)	587.56(0)	566.50(0)	566.33(0)	566.16(0)	A′
	190.07(28)	188.69(28)	187.38(27)	188.41(28)	187.02(27)	185.70(27)	A′
	123.65(26)	122.84(26)	122.09(26)	121.54(26)	120.72(26)	119.95(25)	A″
	87.68(4)	87.53(4)	87.39(4)	87.32(4)	87.18(4)	87.04(4)	A′

FONiF ($^3A''$, C_s), CCSD(T)/AVTZ

	16O/58Ni	16O/60Ni	16O/62Ni	18O/58Ni	18O/60Ni	18O/62Ni	Sym.
	810.28	810.09	809.94	787.00	786.76	786.57	A′
	749.69	745.1	740.77	743.07	738.58	734.34	A′
	577.89	577.79	577.68	556.18	555.93	555.69	A′
	180.15	178.93	177.78	178.62	177.37	176.22	A′
	125.55	124.85	124.28	124.54	124.28	124.03	A″
	124.8	124.54	124.19	122.25	121.53	120.85	A′

Table S4.3. Computed harmonic frequencies (cm^{-1}) for OPdF$_n$ (n = 1-4).

PdOF (^{2}A', C_s), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	869.68(89)	869.68(89)	869.68(89)	869.68(89)	869.68(89)	843.49(86)	843.49(86)	843.49(86)	843.49(86)	843.49(86)	A'
	509.42(12)	509.10(12)	508.79(12)	508.19(12)	507.58(12)	484.50(11)	484.17(11)	483.84(11)	483.20(11)	482.56(11)	A'
	180.78(5)	180.65(5)	180.52(5)	180.27(5)	180.02(5)	178.94(5)	178.81(5)	178.69(5)	178.44(5)	178.19(5)	A'

PdOF (^{2}A', C_s), BP86/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	733.74(131)	733.72(131)	733.71(131)	733.68(131)	733.65(131)	712.40(125)	712.39(125)	712.37(125)	712.34(125)	712.31(125)	A'
	520.74(4)	520.43(4)	520.12(4)	519.52(4)	518.91(4)	494.80(4)	494.47(4)	494.14(4)	493.51(4)	492.87(4)	A'
	181.58(6)	181.44(6)	181.32(6)	181.06(6)	181.81(6)	179.58(6)	179.45(6)	179.32(6)	179.08(6)	178.82(6)	A'

OPdF (X$^4\Sigma^-$, $C_{\infty v}$), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	778.82(33)	777.54(32)	778.17(32)	776.30(31)	775.06(31)	743.92(40)	739.72(37)	742.48(39)	741.11(38)	739.72(37)	∑
	602.27(95)	601.82(96)	602.04(96)	601.39(96)	600.95(96)	598.65(88)	597.66(89)	598.32(88)	597.99(89)	597.66(89)	∑
	160.54(17)	160.16(17)	160.35(17)	159.80(17)	159.43(17)	156.62(16)	155.48(16)	156.24(16)	155.86(16)	155.48(16)	∏

OPdF (X$^4\Sigma^-$, $C_{\infty v}$), BP86/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	791.40(43)	790.75(43)	790.12(42)	788.88(41)	787.64(41)	755.56(47)	754.84(46)	754.13(46)	752.76(45)	751.39(44)	∑
	595.00(65)	594.77(65)	594.55(65)	594.11(65)	593.65(65)	591.73(59)	591.55(59)	591.38(59)	591.03(60)	590.67(60)	∑
	153.34(13)	153.16(13)	152.98(13)	152.63(13)	152.28(13)	149.61(13)	149.42(13)	149.24(13)	148.88(12)	148.52(12)	∏

OPdF (X$^4\Sigma^-$, $C_{\infty v}$), CCSD(T)/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	774.18	773.52	772.88	771.63	770.43	739.93	739.19	738.47	737.06	735.72	∑ (Pd-O)
	606.64	606.42	606.21	605.79	605.38	602.64	602.48	602.33	602.03	601.73	∑ (Pd-F)
	171.73	171.53	171.33	170.94	170.56	167.54	167.33	167.13	166.73	166.34	∏

OPdF$_2$ (X^{3}A$_2$, C_{2v}), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	766.78(3)	766.35(3)	765.93(3)	765.12(3)	764.30(3)	728.75(3)	728.31(3)	727.87(3)	726.17(3)	726.17(3)	A$_1$
	643.38(166)	642.60(165)	641.83(165)	640.32(164)	638.80(163)	643.38(166)	642.60(165)	641.83(165)	638.80(163)	638.80(163)	B$_2$
	575.41(21)	575.34(21)	575.26(21)	575.12(21)	574.97(21)	575.24(21)	575.16(21)	575.08(21)	574.76(21)	574.76(21)	A$_1$
	197.72(17)	197.40(17)	197.09(17)	196.50(17)	195.88(16)	196.75(17)	196.43(17)	196.12(16)	194.91(16)	194.91(16)	B$_1$
	167.04(10)	166.88(10)	166.73(10)	166.42(9)	166.11(9)	166.78(10)	166.62(10)	166.47(9)	165.88(9)	165.88(9)	A$_1$
	162.99(2)	162.93(2)	162.86(2)	162.74(2)	162.61(2)	156.93(2)	156.86(2)	156.80(2)	156.53(2)	156.53(2)	B$_2$

OPdF$_2$ (X^{3}A$_2$, C_{2v}), BP86/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	sym.
	783.52(8)	783.06(8)	782.61(8)	781.72(8)	780.83(8)	744.48(8)	743.99(8)	743.52(8)	742.58(7)	741.64(7)	A$_1$
	621.69(132)	620.94(132)	620.21(131)	618.79(131)	617.35(130)	621.68(132)	620.94(132)	620.21(131)	618.78(131)	617.34(130)	B$_2$
	560.72(14)	560.66(14)	560.60(14)	560.49(14)	560.38(14)	560.72(14)	560.66(14)	560.60(14)	560.49(14)	560.37(14)	A$_1$
	189.80(12)	189.50(12)	189.20(12)	188.62(12)	188.03(12)	188.73(12)	188.42(12)	188.12(12)	187.54(12)	186.95(12)	B$_1$
	158.30(8)	158.16(8)	158.01(8)	157.72(8)	157.43(8)	158.05(8)	157.90(8)	157.76(8)	157.49(8)	157.20(8)	A$_1$
	135.68(4)	135.62(4)	135.56(4)	135.45(4)	135.34(4)	130.63(4)	130.57(4)	130.52(4)	130.40(4)	130.28(4)	B$_2$

OPdF$_2$ (X^{3}A$_2$, C_{2v}), CCSD(T)/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	828.47	827.99	827.51	826.58	825.69	787.23	786.71	786.21	785.23	784.29	A$_1$
	667.66	666.85	666.06	664.51	663.02	667.65	666.84	666.05	664.51	663.01	B$_2$
	601.53	601.48	601.44	601.36	601.28	601.50	601.46	601.41	601.33	601.25	A$_1$
	215.27	214.93	214.59	213.92	213.28	214.85	214.5	214.16	213.50	212.87	B$_1$
	192.94	192.72	192.49	192.05	191.63	192.58	192.35	192.14	191.71	191.30	A$_1$
	185.77	185.64	185.51	185.26	185.01	179.29	179.16	179.02	178.76	178.50	B$_2$

OPdF$_2$ (^{5}A$_1$, C_{2v}), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	614.83(112)	614.12(112)	613.43(112)	612.07(112)	610.70(112)	614.82(112)	614.11(112)	613.41(112)	612.06(112)	610.69(112)	B_2
	578.51(8)	578.38(8)	578.24(8)	577.99(8)	577.74(8)	558.15(14)	558.09(14)	558.03(14)	557.93(14)	557.82(14)	A_1
	524.02(16)	523.81(16)	523.60(16)	523.19(16)	522.77(16)	515.65(10)	515.35(10)	515.05(10)	514.46(10)	513.86(10)	A_1
	138.11(1)	138.04(1)	137.98(1)	137.85(1)	137.72(1)	133.24(1)	133.17(1)	133.10(1)	132.97(1)	132.84(1)	B_2
	103.27(4)	103.17(4)	103.07(4)	102.87(4)	102.67(4)	103.19(4)	103.09(4)	102.99(4)	102.80(4)	102.60(4)	B_1
	17.59(21)	17.57(21)	17.54(21)	17.49(21)	17.44(21)	17.57(21)	17.54(21)	17.51(21)	17.45(21)	17.41(21)	A_1

OPdF$_2$ (^{5}A$_1$, C_{2v}), BP86/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	615.18(0)	614.92(0)	614.66(0)	614.16(0)	613.65(0)	584.83(0)	584.57(0)	584.32(0)	583.82(0)	583.32(0)	A_1
	571.31(63)	570.68(63)	570.06(62)	568.85(62)	567.63(62)	571.28(62)	570.65(62)	570.03(62)	568.82(62)	567.60(62)	B_2
	503.02(13)	502.90(13)	502.78(13)	502.55(13)	502.32(13)	502.35(13)	502.21(13)	502.07(13)	501.80(13)	501.53(13)	A_1
	125.06(1)	125.00(1)	124.93(1)	124.81(1)	124.68(1)	120.70(1)	120.64(1)	120.57(1)	120.44(1)	120.31(1)	B_2
	90.32(4)	90.23(4)	90.15(4)	89.98(4)	89.81(4)	90.25(4)	90.16(4)	90.08(4)	89.91(4)	89.74(4)	A_1
	20.00(16)	19.97(16)	19.94(16)	19.88(16)	19.82(16)	20.04(16)	20.01(16)	19.97(16)	19.91(16)	19.85(15)	B_1

FOPdF (^{3}A', C_s), CCSD(T)/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	822.01	822.01	822.00	821.98	821.97	797.26	797.24	797.23	797.22	797.21	A′
	634.01	633.36	632.74	631.51	630.34	632.48	631.86	631.25	630.07	628.94	A′
	523.27	523.12	522.98	522.68	522.39	499.16	498.95	498.76	498.39	498.02	A′
	225.41	225.26	225.11	224.82	224.54	223.64	223.51	223.36	223.07	222.79	A′
	108.52	108.39	108.27	108.03	107.79	108.18	108.06	107.94	107.69	107.46	A′
	56.44	56.33	56.23	56.02	55.82	56.31	56.20	56.09	55.88	55.68	A″

FOPdF (^{3}A", C_s), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	878.53(120)	878.53(120)	878.52(120)	878.52(120)	878.51(121)	851.43(115)	851.43(115)	851.43(115)	851.42(115)	851.42(115)	A′
	638.24(149)	637.48(149)	636.73(148)	635.27(148)	633.80(147)	630.90(154)	630.16(153)	629.44(153)	628.02(152)	628.02(152)	A′
	559.94(10)	559.93(9)	559.92(9)	559.89(9)	559.86(9)	538.53(3)	538.48(3)	538.43(3)	538.33(2)	538.33(2)	A′
	272.14(6)	271.84(6)	271.53(6)	270.95(6)	270.35(6)	268.76(6)	268.45(6)	268.14(6)	267.55(6)	267.44(6)	A′
	120.86(6)	120.77(6)	120.68(6)	120.51(6)	120.33(6)	120.76(6)	120.67(6)	120.59(6)	120.41(6)	120.41(6)	A″
	114.81(13)	114.66(13)	114.52(13)	114.24(13)	113.95(13)	112.52(13)	112.37(13)	112.22(13)	111.93(13)	111.93(13)	A′

FOPdF (^{3}A", C_s), CCSD(T)/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	859.89	859.87	859.85	859.82	859.78	832.25	832.23	832.22	832.18	832.15	A′
	643.17	642.38	641.61	640.09	638.63	634.60	633.82	633.06	631.59	630.18	A′
	586.87	586.86	586.85	586.84	586.83	566.35	566.29	566.25	566.16	566.08	A′
	290.68	290.40	290.13	289.61	289.11	286.97	286.68	286.41	285.88	285.37	A′
	158.02	157.85	157.69	157.36	157.05	157.68	157.58	157.42	157.10	156.79	A″
	141.10	140.92	140.74	140.39	140.05	137.86	137.68	137.49	137.14	136.79	A′

$OPdF_3$ (X^4A_1, C_{2v}), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	681.81(25)	680.96(25)	680.12(25)	678.48(25)	676.83(24)	679.42(86)	678.55(86)	677.69(86)	677.02(86)	674.34(85)	A_1
	679.43(86)	678.56(86)	677.70(86)	676.03(86)	674.35(85)	671.30(41)	670.45(41)	669.62(41)	668.01(41)	666.38(41)	B_2
	619.40(36)	619.40(36)	619.40(36)	619.40(36)	619.39(36)	604.73(16)	604.71(16)	604.69(16)	604.65(16)	604.61(16)	A_1
	565.35(15)	565.35(15)	565.35(15)	565.35(15)	565.35(15)	558.49(19)	558.48(19)	558.47(19)	558.44(19)	558.42(19)	A_1
	265.14(1)	264.95(1)	264.76(1)	264.40(1)	264.02(1)	264.70(1)	264.52(1)	264.34(1)	263.98(1)	263.62(1)	A_1
	255.03(0)	255.03(0)	255.03(0)	255.03(0)	255.02(0)	253.54(1)	253.52(1)	253.50(1)	253.46(1)	253.43(1)	B_2
	243.46(3)	243.30(3)	243.14(3)	242.82(3)	242.50(3)	235.34(3)	235.19(3)	235.04(3)	234.74(3)	234.44(3)	B_2
	203.01(15)	202.65(15)	202.31(15)	201.63(15)	200.94(15)	199.48(15)	199.12(15)	198.77(15)	198.07(15)	197.38(15)	B_1
	51.34(3)	51.33(3)	51.32(3)	51.30(3)	51.27(3)	50.96(3)	50.95(3)	50.94(3)	50.92(3)	50.90(3)	B_1

$OPdF_3$ (X^4A_1, C_{2v}), BP86/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	728.28(13)	727.59(13)	726.91(13)	725.60(12)	724.28(12)	698.96(19)	698.17(18)	697.39(18)	695.89(18)	694.37(17)	A_1
	639.58(62)	638.78(62)	638.00(62)	636.49(62)	634.95(61)	639.55(62)	638.76(62)	637.98(62)	636.46(62)	634.93(61)	B_2
	603.99(37)	603.81(37)	603.63(37)	603.27(37)	602.90(38)	599.09(32)	598.99(32)	598.88(32)	598.67(32)	598.45(32)	A_1
	531.99(3)	531.99(3)	531.99(3)	531.99(3)	531.98(3)	530.76(3)	530.76(3)	530.76(3)	530.78(3)	530.76(3)	A_1
	259.17(0)	259.16(0)	259.15(0)	259.12(0)	259.10(0)	255.83(1)	255.65(1)	255.48(1)	255.14(1)	254.79(1)	A_1
	256.30(1)	256.11(1)	255.93(1)	255.58(1)	255.22(1)	253.55(0)	253.54(0)	253.54(0)	253.53(0)	253.53(1)	B_2
	229.74(5)	229.58(5)	229.43(5)	229.13(5)	228.83(5)	225.61(5)	225.44(5)	225.28(5)	224.95(5)	224.62(5)	B_2
	207.70(12)	207.32(12)	206.96(12)	206.23(12)	205.50(12)	204.33(12)	203.95(12)	203.57(12)	202.84(12)	202.09(12)	B_1
	60.84(1)	60.83(1)	60.82(1)	60.81(1)	60.79(1)	60.30(1)	60.29(1)	60.29(1)	60.27(1)	60.26(1)	B_1

$OPdF_3$ (X^4A_1, C_{2v}), CCSD(T)/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	729.68	728.73	727.80	725.99	724.24	729.67	728.72	727.79	725.98	724.23	B_2
	685.51	684.76	684.02	682.60	681.23	682.59	681.88	681.18	679.83	678.53	A_1
	627.17	627.13	627.09	627.02	626.95	625.64	625.60	625.56	625.47	625.39	A_1
	572.60	572.56	572.51	572.42	572.33	547.16	547.06	546.97	546.78	546.59	A_1
	275.09	274.88	274.68	274.27	273.87	274.75	274.54	274.34	273.95	273.56	A_1
	261.31	261.30	261.28	261.26	261.24	260.58	260.56	260.54	260.50	260.46	B_2
	242.21	242.05	241.89	241.58	241.27	233.44	233.28	233.13	232.82	232.53	B_2
	203.01	202.66	202.32	201.64	201.00	199.18	198.82	198.47	197.79	197.13	B_1
	48.30	48.27	48.25	48.19	48.14	47.91	47.88	47.85	47.80	47.75	B_1

$OPdF_4$ ($^3A_2$, C_{4v}), B3LYP/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	834.46(1)	833.91(1)	833.36(1)	832.29(1)	831.21(1)	793.73(0)	793.14(0)	792.55(0)	791.41(0)	790.27(0)	A_1
	669.77(125)	668.87(125)	667.99(125)	666.27(125)	664.54(125)	669.76(125)	668.86(125)	667.98(125)	666.27(125)	664.54(125)	E
	600.40(9)	600.37(9)	600.33(9)	600.25(9)	600.18(9)	600.00(9)	599.97(9)	599.94(9)	599.88(9)	599.81(9)	A_1
	554.25(0)	554.25(0)	554.25(0)	554.25(0)	554.25(0)	554.25(0)	554.25(0)	554.25(0)	554.25(0)	554.25(0)	B_2
	276.36(2)	276.13(2)	275.90(2)	275.45(2)	274.98(2)	275.16(2)	274.93(2)	274.70(2)	274.25(2)	273.79(2)	E
	240.66(7)	240.30(7)	239.94(7)	239.24(7)	238.53(7)	239.89(7)	239.54(7)	239.19(7)	238.51(7)	237.82(7)	A_1
	233.24(0)	233.24(0)	233.24(0)	233.24(0)	233.24(0)	233.24(0)	233.24(0)	233.24(0)	233.24(0)	233.24(0)	B_1
	183.47(0)	183.47(0)	183.45(0)	183.43(0)	183.41(0)	177.31(0)	177.29(0)	177.28(0)	177.25(0)	177.22(0)	E
	132.23(0)	132.23(0)	132.23(0)	132.23(0)	132.23(0)	132.23(0)	132.23(0)	132.23(0)	132.23(0)	132.23(0)	B_2

$OPdF_4$ ($^3A_2$, C_{4v}), BP86/AVTZ(-PP)

	16O/104Pd	16O/105Pd	16O/106Pd	16O/108Pd	16O/110Pd	18O/104Pd	18O/105Pd	18O/106Pd	18O/108Pd	18O/110Pd	Sym.
	798.40(2)	797.86(2)	797.33(2)	796.30(2)	796.30(2)	759.44(2)	758.86(2)	758.30(2)	757.20(2)	756.09(2)	A_1
	642.61(95)	641.75(95)	640.91(94)	639.28(93)	639.28(93)	642.60(95)	641.75(95)	640.91(95)	639.28(95)	637.63(95)	E
	577.46(6)	577.42(6)	577.38(6)	577.31(6)	577.31(6)	577.13(6)	577.10(6)	577.07(6)	577.00(6)	576.94(6)	A_1
	550.64(0)	550.64(0)	550.64(0)	550.64(0)	550.64(0)	550.64(0)	550.64(0)	550.64(0)	550.64(0)	550.64(0)	B_2
	267.83(2)	267.59(2)	267.37(2)	266.92(2)	266.92(2)	266.51(2)	266.28(2)	266.06(2)	265.61(2)	265.16(2)	E
	235.06(7)	234.71(7)	234.36(7)	233.68(7)	233.68(7)	234.28(7)	233.93(7)	233.60(7)	232.94(7)	232.27(7)	A_1
	224.05(0)	224.05(0)	224.05(0)	224.05(0)	224.05(0)	224.05(0)	224.05(0)	224.05(0)	224.05(0)	224.05(0)	B_1
	179.46(0)	179.45(0)	179.45(0)	179.43(0)	179.43(0)	173.58(0)	173.57(0)	173.56(0)	173.53(0)	173.50(0)	E
	146.94(0)	146.94(0)	146.94(0)	146.94(0)	146.94(0)	146.94(0)	146.94(0)	146.94(0)	146.94(0)	146.94(0)	B_2

Table S4.4. Computed harmonic frequencies (cm^{-1}) for OPtF$_n$ (n = 1-4).

PtOF (^{2}A', C_s), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	856.91(92)	856.91(92)	856.91(92)	856.91(92)	831.16(89)	831.16(89)	831.16(89)	831.16(89)	A'
	574.48(12)	574.39(12)	574.30(12)	574.12(12)	544.30(10)	544.20(10)	544.11(10)	543.92(10)	A'
	242.48(6)	242.42(6)	242.35(6)	242.22(6)	239.97(6)	239.91(6)	239.84(6)	239.71(6)	A'

PtOF (^{2}A', C_s), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	783.18(122)	783.18(122)	783.18(122)	783.17(122)	760.12(117)	760.12(117)	760.12(117)	760.11(117)	A'
	595.41(4)	595.31(4)	595.21(4)	595.01(4)	563.79(4)	563.68(4)	563.57(4)	563.36(4)	A'
	228.25(6)	228.20(6)	228.14(6)	228.02(6)	225.84(6)	225.78(6)	225.72(6)	225.60(6)	A'

PtOF (^{2}A", C_s), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	702.01(150)	701.98(150)	701.96(150)	701.91(150)	680.70(146)	680.68(146)	680.65(146)	680.60(146)	A'
	611.01(25)	610.93(25)	610.84(25)	610.67(25)	579.06(21)	578.97(21)	578.87(21)	578.69(21)	A'
	259.76(9)	259.70(9)	259.63(9)	259.50(9)	256.65(9)	256.58(9)	256.52(9)	256.39(9)	A'

PtOF (^{2}A", C_s), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	737.28(10)	737.14(10)	737.00(10)	736.72(10)	699.17(8)	699.02(8)	698.88(8)	698.58(8)	A'
	544.73(163)	544.73(163)	544.73(163)	544.73(163)	527.16(156)	527.16(156)	527.16(156)	527.16(156)	A'
	238.95(13)	238.90(13)	238.84(13)	238.72(13)	236.15(11)	236.09(11)	236.03(11)	235.91(11)	A'

OPtF ($X^4\Sigma^-$, $C_{\infty v}$), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	852.60(24)	852.44(23)	852.28(23)	851.96(23)	807.51(23)	807.33(23)	807.16(23)	806.82(23)	∑
	629.76(115)	629.64(115)	629.51(115)	629.26(115)	629.56(114)	629.43(114)	629.31(114)	629.07(114)	∑
	171.10(11)	171.03(11)	170.97(11)	170.84(11)	166.32(10)	166.25(10)	166.18(10)	166.05(10)	∏

OPtF ($X^4\Sigma^-$, $C_{\infty v}$), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	844.04(34)	843.87(34)	843.71(34)	843.39(34)	799.47(33)	799.29(33)	799.11(33)	798.77(32)	∑
	619.99(90)	619.87(90)	619.74(90)	619.50(90)	619.73(88)	619.61(89)	619.50(89)	619.27(89)	∑
	156.83(9)	156.77(9)	156.71(9)	156.59(9)	152.46(9)	152.40(8)	152.34(8)	152.22(8)	∏

OPtF ($X^4\Sigma^-$, $C_{\infty v}$), CCSD(T)/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	848.51	848.34	848.18	847.86	803.69	803.51	803.33	802.99	∑
	640.46	640.33	640.21	639.96	640.20	640.08	639.96	639.72	∑
	180.50	180.43	180.36	180.22	175.38	175.31	175.24	175.10	∏

$OPtF_2$ (X^3A_2, C_{2v}), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	877.85(4)	877.69(4)	877.52(4)	877.20(4)	831.63(3)	831.46(3)	831.29(3)	830.95(3)	A_1
	629.19(160)	628.94(160)	628.70(160)	628.23(160)	629.16(160)	628.92(160)	628.68(160)	628.20(160)	B_2
	612.64(16)	612.62(16)	612.60(16)	612.57(16)	612.56(16)	612.54(16)	612.52(16)	612.48(16)	A_1
	208.06(9)	207.95(9)	207.84(9)	207.62(9)	206.91(9)	206.80(9)	206.69(9)	206.47(9)	B_1
	170.30(7)	170.24(7)	170.18(7)	170.07(7)	170.17(7)	170.11(7)	170.05(7)	169.94(7)	A_1
	100.21(7)	100.19(7)	100.18(7)	100.14(7)	96.28(7)	96.27(7)	96.25(7)	96.21(6)	B_2

OPtF$_2$ (X^{3}A$_2$, C_{2v}), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	859.92(6)	859.75(6)	859.59(6)	859.27(6)	814.55(5)	814.38(5)	814.21(5)	813.87(5)	A$_1$
	612.08(138)	611.85(138)	611.62(138)	611.17(138)	612.02(139)	611.79(139)	611.56(139)	611.11(139)	B$_2$
	599.47(12)	599.45(12)	599.43(12)	599.40(12)	599.45(12)	599.43(12)	599.41(12)	599.38(12)	A$_1$
	202.44(6)	202.33(6)	202.23(6)	202.01(6)	201.26(6)	201.15(6)	201.04(6)	200.82(6)	B$_1$
	163.97(5)	163.92(5)	163.86(5)	163.75(5)	163.85(5)	163.79(5)	163.74(5)	163.63(5)	A$_1$
	30.43(11)	30.41(11)	30.42(11)	30.40(11)	29.19(10)	29.18(10)	29.18(10)	29.17(10)	B$_2$

OPtF$_2$ (X^{3}A$_2$, C_{2v}), CCSD(T)/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	870.92	870.76	870.6	870.28	825.21	825.03	824.86	824.53	A$_1$
	652.45	652.19	651.93	651.43	652.44	652.18	651.93	651.42	B$_2$
	626.98	626.96	626.94	626.90	626.82	626.80	626.77	626.73	A$_1$
	233.28	233.15	233.03	232.79	232.17	232.05	231.92	231.68	B$_1$
	173.85	173.8	173.74	173.63	173.71	173.66	173.6	173.49	A$_1$
	140.81	140.79	140.76	140.72	135.11	135.09	135.06	135.02	B$_2$

OPtF$_2$ (^{5}A$_1$, C_{2v}), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	647.67(137)	647.41(137)	647.16(137)	646.66(137)	647.65(137)	647.39(137)	647.14(137)	646.64(137)	B$_2$
	613.39(6)	613.36(6)	613.33(6)	613.26(6)	599.58(6)	599.56(6)	599.54(6)	599.51(6)	A$_1$
	534.86(3)	534.80(3)	534.74(3)	534.61(3)	517.99(3)	517.90(3)	517.82(3)	517.66(3)	A$_1$
	163.28(1)	163.25(1)	163.23(1)	163.18(1)	157.25(1)	157.23(1)	157.20(1)	157.15(1)	B$_2$
	146.62(1)	146.57(1)	146.51(1)	146.40(1)	146.60(1)	146.54(1)	146.49(1)	146.38(1)	A$_1$
	126.97(9)	126.90(9)	126.84(9)	126.71(9)	126.59(9)	126.52(9)	126.46(9)	126.33(9)	B$_1$

$OPtF_2$ ($^5A_1$, C_{2v}), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	628.27(98)	628.02(98)	627.78(98)	627.30(98)	628.24(98)	628.00(98)	627.75(98)	627.27(98)	B_2
	615.01(0)	614.95(0)	614.89(0)	614.77(0)	593.89(19)	593.85(19)	593.80(19)	593.72(19)	A_1
	532.10(3)	532.06(3)	532.02(3)	531.95(3)	521.62(2)	521.56(2)	521.50(2)	521.38(2)	A_1
	160.51(2)	160.49(2)	160.46(2)	160.41(2)	154.58(2)	154.56(2)	154.53(2)	154.48(2)	B_2
	143.10(1)	143.05(1)	142.99(1)	142.88(1)	143.08(1)	143.02(1)	142.97(1)	142.86(1)	A_1
	129.80(6)	129.73(6)	129.67(6)	129.54(6)	129.41(6)	129.35(6)	129.28(6)	129.15(6)	B_1

$OPtF_2$ ($^5A_1$, C_{2v}), CCSD(T)/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	673.37	673.10	672.84	672.32	673.35	673.08	672.82	672.30	B_2
	625.69	625.68	625.66	625.64	620.45	620.45	620.45	620.44	A_1
	566.46	566.38	566.29	566.13	540.74	540.64	540.55	540.35	A_1
	180.72	180.68	180.65	180.59	174.16	174.13	174.09	174.03	B_2
	158.86	158.79	158.73	158.61	158.83	158.77	158.71	158.59	A_1
	130.76	130.69	130.62	130.48	130.53	130.46	130.39	130.25	B_1

FOPtF ($^3A'$, C_s), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	824.21(143)	824.21(143)	824.21(143)	824.21(143)	798.77(134)	798.77(134)	798.77(134)	798.77(134)	A'
	664.66(61)	664.42(61)	664.18(60)	663.71(60)	650.93(93)	650.69(93)	650.44(93)	649.96(93)	A'
	617.21(52)	617.19(52)	617.18(52)	617.15(53)	597.06(20)	597.04(20)	597.03(20)	597.00(20)	A'
	307.64(2)	307.54(2)	307.44(2)	307.23(2)	303.53(1)	303.43(1)	303.32(1)	303.12(1)	A'
	128.48(4)	128.44(4)	128.40(4)	128.32(4)	128.46(4)	128.42(4)	128.38(4)	128.29(4)	A'
	120.57(6)	120.52(6)	120.46(6)	120.36(6)	118.17(6)	118.12(6)	118.06(6)	117.95(6)	A''

FOPtF (^{3}A', C_s), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	678.89(22)	678.72(22)	678.57(22)	678.24(22)	650.95(36)	650.73(36)	650.52(36)	650.10(36)	A′
	630.51(4)	630.43(4)	630.34(4)	630.17(4)	623.72(2)	623.68(2)	623.63(2)	623.54(2)	A′
	570.05(251)	570.05(251)	570.04(251)	570.03(251)	551.21(227)	551.21(227)	551.21(227)	551.20(227)	A′
	308.62(2)	308.52(2)	308.42(2)	308.21(2)	304.66(2)	304.55(2)	304.45(2)	304.24(2)	A′
	116.28(3)	116.24(3)	116.20(3)	116.13(3)	116.24(3)	116.21(3)	116.17(3)	116.10(3)	A′
	56.25(5)	56.23(5)	56.20(5)	56.15(5)	55.45(5)	55.42(5)	55.40(5)	55.34(5)	A″

FOPtF (^{3}A", C_s), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	722.42(141)	722.42(141)	722.42(141)	722.42(141)	702.88(128)	702.88(128)	702.88(128)	702.88(128)	A′
	648.39(129)	648.13(129)	647.87(128)	647.36(128)	641.92(160)	641.69(160)	641.47(160)	641.04(160)	A′
	618.24(36)	618.23(36)	618.23(36)	618.23(36)	591.60(9)	591.56(9)	591.51(9)	591.42(9)	A′
	215.73(4)	215.65(4)	215.58(4)	215.42(4)	212.00(4)	211.92(4)	211.84(4)	211.69(4)	A′
	149.64(6)	149.57(6)	149.51(6)	149.39(6)	146.22(6)	146.15(6)	146.09(6)	145.97(6)	A″
	132.49(4)	132.45(4)	132.41(4)	132.34(4)	132.46(4)	132.42(4)	132.39(4)	132.31(4)	A′

FOPtF (^{3}A", C_s), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	725.71(16)	725.53(16)	725.36(16)	725.03(16)	690.57(22)	690.37(22)	690.17(22)	689.78(22)	A′
	635.43(60)	635.32(60)	635.21(60)	634.99(60)	634.11(58)	634.01(58)	633.93(58)	633.75(58)	A′
	480.47(220)	480.47(220)	480.47(220)	480.47(220)	466.36(206)	466.36(206)	466.36(206)	466.36(206)	A′
	160.40(7)	160.33(7)	160.26(7)	160.13(7)	157.80(7)	157.73(7)	157.66(7)	157.52(7)	A′
	152.89(5)	152.82(5)	152.76(5)	152.62(5)	149.71(4)	149.65(4)	149.58(4)	149.44(4)	A″
	103.29(2)	103.26(2)	103.24(2)	103.20(2)	103.09(2)	103.06(2)	103.04(2)	103.00(2)	A′

FOPtF (^{3}A", C_s), CCSD(T)/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	762.23	762.22	762.22	762.22	737.79	737.78	737.79	737.79	A′
	689.28	689.09	688.93	688.57	660.74	660.48	660.22	659.72	A′
	645.87	645.79	645.7	645.54	637.95	637.95	637.95	637.94	A′
	306.15	306.04	305.92	305.69	302.01	301.9	301.78	301.54	A′
	194.33	194.29	194.24	194.14	186.69	186.65	186.6	186.48	A″
	141.53	141.49	141.44	141.37	141.5	141.47	141.45	141.39	A′

$OPtF_3$ (X^4A_1, C_{2v}), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	781.15(1)	780.98(1)	780.81(1)	780.48(1)	740.70(2)	740.51(2)	740.31(2)	739.93(2)	A_1
	691.34(119)	691.05(118)	690.77(118)	690.21(118)	691.33(119)	691.04(118)	690.76(118)	690.20(118)	B_2
	661.68(60)	661.60(60)	661.51(60)	661.34(59)	661.33(58)	661.25(58)	661.17(58)	661.03(57)	A_1
	629.98(27)	629.95(27)	629.91(27)	629.84(27)	629.49(27)	629.46(27)	629.43(28)	629.37(28)	A_1
	278.92(1)	278.90(1)	278.88(1)	278.84(1)	278.35(2)	278.27(2)	278.20(2)	278.04(2)	A_1
	278.58(2)	278.49(2)	278.41(2)	278.25(2)	269.98(1)	269.97(1)	269.96(1)	269.93(1)	B_2
	244.68(5)	244.63(5)	244.57(5)	244.47(5)	242.36(5)	242.29(5)	242.23(5)	242.11(5)	B_2
	218.37(10)	218.23(10)	218.10(10)	217.83(10)	213.90(10)	213.76(10)	213.62(10)	213.35(10)	B_1
	119.91(1)	119.90(1)	119.89(1)	119.88(1)	119.03(1)	119.03(1)	119.02(1)	119.01(1)	B_1

$OPtF_3$ (X^4A_1, C_{2v}), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	785.84(9)	785.66(9)	785.49(9)	785.16(9)	745.16(10)	744.97(10)	744.78(10)	744.41(10)	A_1
	663.46(87)	663.18(87)	662.91(87)	662.38(87)	663.44(87)	663.17(87)	662.90(87)	662.37(87)	B_2
	632.12(44)	632.04(44)	631.95(44)	631.78(44)	631.89(43)	631.81(43)	631.73(43)	631.57(43)	A_1
	601.94(19)	601.91(19)	601.88(19)	601.82(19)	601.35(19)	601.32(19)	601.30(19)	601.25(19)	A_1
	272.97(2)	272.95(2)	272.93(2)	272.90(2)	268.42(2)	268.33(2)	268.26(2)	268.11(2)	A_1
	268.63(2)	268.55(2)	268.47(2)	268.31(2)	264.20(1)	264.19(1)	264.17(1)	264.15(1)	B_2
	232.26(5)	232.20(5)	232.15(5)	232.05(5)	230.06(6)	230.00(6)	229.94(6)	229.83(6)	B_2
	213.11(7)	212.97(7)	212.83(7)	212.56(7)	209.10(7)	208.95(7)	208.81(7)	208.53(7)	B_1
	119.46(0)	119.45(0)	119.45(0)	119.44(0)	118.37(0)	118.37(0)	118.37(0)	118.36(0)	B_1

$OPtF_3$ (X^4A_1, C_{2v}), CCSD(T)/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	805.99	805.81	805.63	805.28	764.38	764.17	763.97	763.56	A_1 (Pt-O)
	722.11	721.80	721.50	720.90	722.09	721.79	721.49	720.89	B_2 (Pt-F)
	683.97	683.91	683.85	683.73	683.63	683.58	683.53	683.43	A_1
	656.07	656.01	655.94	655.82	655.44	655.39	655.33	655.22	A_1
	284.46	284.38	284.30	284.13	284.23	284.14	284.06	283.90	A_1
	282.89	282.87	282.85	282.80	273.59	273.58	273.57	273.54	B_2
	249.90	249.85	249.80	249.70	247.76	247.70	247.64	247.52	B_2
	220.75	220.61	220.48	220.22	216.05	215.91	215.77	215.50	B_1
	117.34	117.33	117.32	117.30	116.57	116.56	116.55	116.53	B_1

OPtF$_4$ (^{3}A$_2$, C_{4v}), B3LYP/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	897.22(0)	897.04(0)	897.04(0)	896.50(0)	850.05(0)	849.85(0)	849.66(0)	849.28(0)	A$_1$
	659.46(135)	659.18(135)	659.18(135)	658.34(134)	659.44(135)	659.15(135)	658.87(135)	658.31(135)	E
	635.77(12)	635.76(12)	635.76(12)	635.71(12)	635.73(12)	635.72(12)	635.70(12)	635.67(12)	A$_1$
	604.33(0)	604.33(0)	604.33(0)	604.33(0)	604.33(0)	604.33(0)	604.33(0)	604.33(0)	B$_2$
	270.48(3)	270.38(3)	270.38(3)	270.11(3)	269.58(3)	269.49(3)	269.39(3)	269.21(3)	E
	228.56(8)	228.42(8)	228.42(8)	228.02(8)	228.23(8)	228.09(8)	227.96(8)	227.70(8)	A$_1$
	214.77(0)	214.77(0)	214.77(0)	214.77(0)	214.77(0)	214.77(0)	214.77(0)	214.77(0)	B$_1$
	160.51(0)	160.51(0)	160.51(0)	160.51(0)	160.51(0)	160.51(0)	160.51(0)	160.51(0)	B$_2$
	159.11(1)	159.10(1)	159.09(1)	159.08(1)	153.39(1)	153.38(1)	153.37(1)	153.35(1)	E

OPtF$_4$ (^{3}A$_2$, C_{4v}), BP86/AVTZ(-PP)

	16O/194Pt	16O/195Pt	16O/196Pt	16O/198Pt	18O/194Pt	18O/195Pt	18O/196Pt	18O/198Pt	Sym.
	844.93(1)	844.76(1)	844.59(1)	844.25(1)	800.48(1)	800.30(1)	800.12(1)	799.76(1)	A$_1$
	636.04(109)	636.77(109)	635.50(109)	634.97(109)	636.01(109)	635.74(109)	635.47(109)	634.94(109)	E
	612.37(8)	612.36(8)	612.34(8)	612.31(8)	612.33(8)	612.32(8)	612.31(8)	612.28(8)	A$_1$
	591.69(0)	591.69(0)	591.69(0)	591.69(0)	591.69(0)	591.69(0)	591.69(0)	591.69(0)	B$_2$
	260.40(3)	260.31(3)	260.22(3)	260.04(3)	259.53(3)	259.43(3)	259.34(3)	259.16(3)	E
	221.14(7)	221.01(7)	220.88(7)	220.62(7)	220.83(6)	220.70(6)	220.57(6)	220.32(6)	A$_1$
	203.00(0)	203.00(0)	203.00(0)	203.00(0)	203.00(0)	203.00(0)	203.00(0)	203.00(0)	B$_1$
	157.30(0)	157.30(0)	157.30(0)	157.30(0)	157.30(0)	157.30(0)	157.30(0)	157.30(0)	B$_2$
	148.05(2)	148.04(2)	148.04(2)	148.02(2)	142.77(2)	142.76(2)	142.75(2)	142.74(2)	E

Table S4.5. Structural parameters (bond lengths r in Å, angles in deg) and computed harmonic frequencies (cm^{-1}) for OCuF ($^3\Sigma^-$; $C_{\infty v}$) and OCuF$_2$ ($^2B_2$, $^4A_2$; C_{2v}).

OCuF, $C_{\infty v}$

Electronic State	Method	Total energy	r(MO), r(MF), ang(FMF)	T_1 parameters
$^3\Sigma^-$	CCSD(T)/VTZ-DK	-1828.560199	1.666, 1.705, 180.0	0.079
$^3\Sigma^-$	CCSD(T)/(A)VTZ-DK	-1828.584090	1.668, 1.712, 180.0	0.081

OCuF ($^3\Sigma^-$, $C_{\infty v}$), CCSD(T)/VTZ-DK

	16O/63Cu	**16O/65Cu**	**18O/63Cu**	**18O/65Cu**	**Sym.**
	858.50	854.05	835.78	831.09	Σ (Cu-O)
	660.28	660.05	645.86	645.80	Σ (Cu-F)
	157.26	156.40	154.09	153.22	Π

OCuF ($^3\Sigma^-$, $C_{\infty v}$), CCSD(T)/(A)VTZ-DK

	16O/63Cu	**16O/65Cu**	**18O/63Cu**	**18O/65Cu**	**Sym.**
	852.99	848.64	829.16	824.55	Σ (Cu-O)
	650.98	650.71	637.73	637.63	Σ (Cu-F)
	155.45	154.60	152.31	151.44	Π

$OCuF_2$, C_{2v}

Electronic State	Method	Total energy	r(MO), r(MF), ang(OMF)	T_1 parameters
$^2B_2$	B3LYP/AVTZ-PP	-472.2710581	1.759, 1.713, 97.0	
$^2B_2$	CCSD(T)/AVDZ-PP	-470.913789	1.820, 1.717, 95.2	0.051
$^2B_2$	CCSD(T)/AVTZ-PP	-471.2119437	1.771, 1.704, 95.8	
$^2B_2$	CCSD(T)/VTZ-DK	-1928.328104	1.773, 1.702, 96.15	0.050
$^2B_2$	CCSD(T)/(A)VTZ-DK	-1927.3649490	1.778, 1.707, 95.7	0.050
$^2B_2$	CCSD(T)/AVTZ-DK	-1928.3785992	1.779, 1.707, 95.7	0.051
$^4A_2$-2	CCSD(T)/AVDZ-PP	-470.9125929	2.087, 1.746, 94.8	0.029
$^4A_2$-2	CCSD(T)/AVTZ-PP	-471.2054971	2.00, 1.735, 95.6	
$^4A_2$-2	CCSD(T)/VTZ-DK	-1928.320343	2.045, 1.732, 95.6	0.027
$^4A_2$-2	CCSD(T)/(A)VTZ-DK	-1928.3574495	2.026, 1.739, 95.1	0.027
$^4A_2$-2	CCSD(T)/AVTZ-DK	-1928.3707900	2.025, 1.737, 95.2	0.028
$^4A_2$-1	B3LYP/AVTZ-PP	-472.2736039	1.725, 1.740, 115.2	
$^4A_2$-1	CCSD(T)/AVDZ-PP	-469.818636	1.815, 1.755, 107.2	0.104
$^4A_2$-1	CCSD(T)/VTZ-DK	-1928.31093	1.699, 1.727, 114.2	0.053
$^4A_2$-1	CCSD(T)/AVTZ-DK	-1928.360589	1.700, 1.732, 114.0	0.053

$OCuF_2$ ($^2B_2$, C_{2v}), B3LYP/AVTZ(-PP)

	16O/63Cu	**16O/65Cu**	**18O/63Cu**	**18O/65Cu**	**Sym.**
	762.35(132)	757.98(131)	762.35(132)	757.98(131)	B_2
	621.81(5)	621.55(5)	621.34(5)	621.11(5)	A_1
	508.15(6)	506.77(6)	485.22(6)	483.72(6)	A_1
	204.92(31)	203.58(31)	204.70(31)	203.36(31)	B_1
	200.84(19)	200.04(18)	200.12(19)	199.35(18)	A_1
	169.93(0)	169.72(0)	164.12(0)	163.91(0)	B_2

$OCuF_2$ ($^2B_2$, C_{2v}), CCSD(T)/AVTZ(-PP)

	16O/63Cu	16O/65Cu	18O/63Cu	18O/65Cu	Sym.
	788.75	784.22	788.75	784.22	B_2
	641.52	641.39	641.43	641.31	A_1
	510.49	509.05	487.03	485.49	A_1
	216.06	214.67	215.90	214.52	B_1
	203.76	202.92	203.08	202.28	A_1
	160.12	159.93	154.62	154.42	B_2

$OCuF_2$ ($^2B_2$, C_{2v}), CCSD(T)/VTZ-DK

	16O/63Cu	16O/65Cu	18O/63Cu	18O/65Cu	Sym.
	795.47	790.91	795.47	790.91	B_2
	647.38	647.23	647.22	647.08	A_1
	489.22	487.85	466.81	465.34	A_1
	214.91	213.53	214.72	213.33	B_1
	204.24	203.39	203.55	202.74	A_1
	166.34	166.15	160.66	160.47	B_2

$OCuF_2$ ($^2B_2$, C_{2v}), CCSD(T)/(A)VTZ-DK

	16O/63Cu	16O/65Cu	18O/63Cu	18O/65Cu	Sym.
	783.77	779.27	783.77	779.27	B_2
	636.11	635.97	635.97	635.84	A_1
	485.51	484.13	463.32	461.84	A_1
	214.06	212.68	213.96	212.58	B_1
	204.78	203.95	204.06	203.27	A_1
	159.73	159.63	153.87	153.77	B_2

$OCuF_2$ ($^4A_2$-1, C_{2v}), B3LYP/AVTZ(-PP)

	16O/63Cu	16O/65Cu	18O/63Cu	18O/65Cu	Sym.
	681.54(92)	678.23(91)	681.51(92)	678.20(91)	B_2
	636.23(13)	633.79(13)	625.86(23)	623.64(24)	A_1
	580.32(28)	580.29(27)	561.83(18)	561.50(17)	A_1
	185.99(27)	184.66(26)	184.25(27)	182.91(26)	B_1
	154.49(3)	154.14(3)	149.53(2)	149.16(2)	B_2
	130.48(1)	130.05(1)	130.25(1)	129.84(1)	A_1

$OCuF_2$ ($^4A_2$-1, C_{2v}), CCSD(T)/VTZ-DK

	16O/63Cu	16O/65Cu	18O/63Cu	18O/65Cu	Sym.
	729.84	726.46	729.75	726.37	B_2
	688.88	686.47	678.36	676.11	A_1
	602.24	602.15	582.31	581.99	A_1
	229.68	228.41	226.51	225.20	B_1
	205.27	204.33	204.89	203.97	A_1
	180.48	179.47	172.12	171.04	B_2

$OCuF_2$ ($^4A_2$-1, C_{2v}), CCSD(T)/AVTZ-DK

	16O/63Cu	16O/65Cu	18O/63Cu	18O/65Cu	sym.
	728.13	724.28	728.12	724.27	B_2
	681.80	679.33	670.21	667.84	A_1
	577.50	577.44	559.48	559.26	A_1
	276.60	275.85	281.26	280.49	B_1
	205.51	204.03	204.90	203.46	A_1
	197.82	194.89	192.89	189.92	B_2

Part 5. RHF, CI and RCCSD(T) calculations on different spin-states of NiOF

Doublet and quartet spin states of NiOF were investigated by RHF, CI and RCCSD(T). The reference RHF wave function, which was used in subsequent CI and RCCSD(T) calculations, was obtained without the use of symmetry so that the molecular geometry could relax into the ground state. Geometry optimization and normal mode analysis were carried out in the reduced point group C_1 and subsequently checked against the corresponding calculations in point group C_s.

<u>NiOF ^{2}A′:</u>

Table S5.1. Natural orbitals obtained from RHF calculations at the RCCSD(T) optimized geometry using the AVTZ-DK basis set:

```
Orbital  Occupation    Energy     Coefficients
  1.1     2.00000  -308.58650     3 1s    0.99247
  2.1     2.00000   -38.41652     3 1s    0.99250
  3.1     2.00000   -32.89336     3 2py  -0.64119     3 2pz   0.76732
  4.1     2.00000   -32.87945     3 2py   0.76732     3 2pz   0.64119
  5.1     2.00000   -26.27118     2 1s    0.99889
  6.1     2.00000   -20.59022     1 1s    0.99911
  7.1     2.00000    -4.81093     3 1s    0.99716
  8.1     2.00000    -3.13593     3 2py  -0.56594     3 2pz   0.82254
  9.1     2.00000    -3.12709     3 2py   0.82378     3 2pz   0.56628
 10.1     2.00000    -1.52787     1 1s    0.29589     2 1s    0.88995
 11.1     2.00000    -1.17526     1 1s    0.88781     2 1s   -0.38181
 12.1     2.00000    -0.63193     1 2pz   0.35245     2 2py  -0.39800     2 2pz   0.67581
 13.1     2.00000    -0.57832     1 2py  -0.31739     1 2pz  -0.30801     2 2py   0.60951     2 2pz   0.33432
 14.1     2.00000    -0.48917     1 2pz   0.31595     2 2pz  -0.42033     3 3d0   0.68740     3 3d2+  0.49132
 15.1     2.00000    -0.47142     1 2py   0.46824     1 2pz  -0.56587     2 2py  -0.36124     2 2pz   0.26326
 16.1     2.00000    -0.45487     3 3d0   0.40995     3 3d2+ -0.80494     3 3d1-  0.43294
 17.1     1.00000    -0.52990     3 3d0  -0.40940     3 3d1-  0.85403

  1.2     2.00000   -32.87680     3 2px   0.99996
  2.2     2.00000    -3.12435     3 2px   0.99976
  3.2     2.00000    -0.62145     1 2px   0.40698     2 2px   0.81212
  4.2     2.00000    -0.51252     1 2px   0.34778     2 2px  -0.39691     3 3d2-  0.52832     3 3d1+ -0.65186
  5.2     2.00000    -0.45670     3 3d2-  0.80617     3 3d1+  0.60363
  6.2     2.00000    -0.42386     1 2px   0.78485     2 2px  -0.35427     3 3d2- -0.29366     3 3d1+  0.44966
```

Table S5.2. Structural parameters for the ground state ^{2}A′ NiOF.

	RHF			
	Energy (E_h)	r_{O-F} (Å)	r_{Ni-O} (Å)	Angle (°)
VDZ	-1681.01619907	1.4719	1.9387	80.6250
VTZ	-1681.07027174	1.4332	1.9116	90.9838
VQZ	-1681.08699476	1.4322	1.9133	91.1737
AVDZ	-1681.03209432	1.4567	1.9300	85.1923
AVTZ	-1681.07537612	1.4337	1.9157	91.0206
AVQZ	-1681.08850477	1.4318	1.9149	91.2930
VDZ-DK	-1693.33866845	1.4658	1.9196	82.7751
VTZ-DK	-1693.39349250	1.4277	1.8956	93.5108
VQZ-DK	-1693.41086091	1.4268	1.8973	93.7608
AVDZ-DK	-1693.35457670	1.4507	1.9127	87.8951
AVTZ-DK	-1693.39846097	1.4288	1.8998	93.4875

Continued on next page

AVQZ-DK	-1693.41231976	1.4266	1.8989	93.7326

CISD

	Energy (E_h)	r_{O-F} (Å)	r_{Ni-O} (Å)	Angle (°)
VDZ	-1681.63434693	1.4668	1.8691	87.6774
VTZ	-1681.83476495	1.4337	1.8556	95.2490
VQZ	-1681.91133910	1.4294	1.8547	95.8603
AVDZ	-1681.68481586	1.4653	1.8717	89.5951
AVTZ	-1681.85922271	1.4354	1.8584	95.2407
AVQZ	-1681.92164287	1.4299	1.8554	95.4821
VDZ-DK	-1693.95965837	1.4619	1.8508	90.3470
VTZ-DK	-1694.16023487	1.4311	1.8392	96.9859
VQZ-DK	-1694.23744222	1.4272	1.8386	97.4669
AVDZ-DK	-1694.00941967	1.4612	1.8546	92.0489
AVTZ-DK	-1694.18404909	1.4330	1.8420	96.9234
AVQZ-DK	-1694.24756019	1.4275	1.8391	97.1434

RCCSD(T)

	Energy (E_h)	r_{O-F} (Å)	r_{Ni-O} (Å)	Angle (°)
VDZ	-1681.74211777	1.5528	1.8417	78.4392
VTZ	-1681.97707001	1.5008	1.8185	88.6637
VQZ	-1682.06897015	1.4956	1.8162	91.2182
AVDZ	-1681.81019576	1.5570	1.8471	78.0911
AVTZ	-1682.01265799	1.5032	1.8209	90.8299
AVQZ	-1682.08383389	1.4979	1.8174	90.7428
VDZ-DK	-1694.07017279	1.5597	1.8205	77.6751
VTZ-DK	-1694.30550601	1.5208	1.8058	80.2085
VQZ-DK	-1694.39782512	1.4968	1.7960	91.8918
AVDZ-DK	-1694.13748505	1.5642	1.8267	77.0405
AVTZ-DK	-1694.34009773	1.5053	1.8003	91.0270
AVQZ-DK	-1694.41245504	1.5004	1.7972	90.5894

Table S5.3. T_1 parameters for the $^2A'$ state NiOF, RCCSD(T) calculations.

Basis set	T_1
VDZ	0.0413
VTZ	0.0336
VQZ	0.0321
AVDZ	0.0410
AVTZ	0.0337
AVQZ	0.0324
VDZ-DK	0.0485
VTZ-DK	0.0418
VQZ-DK	0.0349
AVDZ-DK	0.0481
AVTZ-DK	0.0368
AVQZ-DK	0.0354

Table S5.4. Harmonic vibrational frequencies for the $^2A'$ $^{58}Ni^{16}OF$ isotopologue.

		RHF			**CISD**			**RCCSD(T)**		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	113.95	501.17	866.18	92.84	555.38	916.90	171.87	520.16	726.65
	I	7.29	37.86	83.45	7.72	38.22	39.51	-	-	-
	I_r	8.74	45.37	100.00	19.55	96.74	100.00	-	-	-
VTZ	ω	109.89	537.88	970.02	124.10	573.05	1001.28	95.48	574.14	804.38
	I	7.30	45.15	69.61	8.33	44.71	41.47	-	-	-
	I_r	10.49	64.86	100.00	18.63	100.00	92.75	-	-	-
VQZ	ω	104.02	535.28	961.71	124.70	573.25	998.98	96.90	573.84	800.00
	I	7.82	44.10	71.89	8.80	43.32	44.40	-	-	-
	I_r	10.88	61.35	100.00	19.82	97.56	100.00	-	-	-
AVDZ	ω	100.58	514.50	891.26	106.44	559.18	924.44	149.13	509.00	727.23
	I	8.41	41.57	85.03	9.66	39.19	49.89	-	-	-
	I_r	9.90	48.89	100.00	19.36	78.56	100.00	-	-	-
AVTZ	ω	107.33	532.09	962.95	122.56	568.94	992.57	94.40	565.10	790.90
	I	8.24	43.44	72.50	9.26	42.02	44.87	-	-	-
	I_r	11.36	59.91	100.00	20.64	93.64	100.00	-	-	-
AVQZ	ω	105.06	532.26	959.90	121.93	571.60	995.67	95.64	569.71	795.07
	I	8.14	43.59	71.89	9.13	42.26	45.34	-	-	-
	I_r	11.32	60.63	100.00	20.14	93.22	100.00	-	-	-
VDZ-DK	ω	97.32	515.36	881.81	96.43	567.86	926.63	196.26	512.15	712.09
	I	6.71	38.17	78.08	7.38	38.39	36.14	-	-	-
	I_r	8.59	48.89	100.00	19.22	100.00	94.12	-	-	-
VTZ-DK	ω	119.44	548.08	986.63	134.65	581.89	1006.47	131.02	555.17	778.73
	I	6.99	45.78	64.67	8.13	44.55	39.62	-	-	-
	I_r	10.81	70.79	100.00	18.26	100.00	88.95	-	-	-
VQZ-DK	ω	115.81	545.22	978.37	137.75	581.89	1003.87	100.71	585.01	792.21
	I	7.51	44.66	66.91	8.60	43.11	42.59	-	-	-
	I_r	11.22	66.74	100.00	19.94	100.00	98.80	-	-	-
AVDZ-DK	ω	99.61	526.79	907.86	117.48	568.56	932.35	150.60	486.92	707.62
	I	7.94	41.91	79.19	9.23	38.92	47.05	-	-	-
	I_r	10.03	52.92	100.00	19.62	82.72	100.00	-	-	-
AVTZ-DK	ω	116.48	541.65	978.09	133.06	577.26	997.29	68.84	573.04	781.01
	I	7.91	43.91	67.82	9.01	41.75	43.05	-	-	-
	I_r	11.66	64.74	100.00	20.94	97.00	100.00	-	-	-
AVQZ-DK	ω	114.10	542.05	975.61	133.64	580.70	1000.66	84.70	580.03	785.76
	I	7.84	44.10	67.27	8.90	42.08	43.52	-	-	-
	I_r	11.66	65.55	100.00	20.46	96.69	100.00	-	-	-

Table S5.5. Harmonic vibrational frequencies for the $^{2}\mathrm{A}'$ $^{58}\mathrm{Ni}^{18}\mathrm{OF}$ isotopologue.

		RHF			**CISD**			**RCCSD(T)**		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	112.85	480.05	841.91	91.84	531.18	890.38	170.77	498.52	705.02
	I	7.11	35.56	82.12	7.42	35.60	39.82	-	-	-
	I_r	8.66	43.30	100.00	18.63	89.42	100.00	-	-	-
VTZ	ω	108.87	514.41	941.69	122.89	547.96	971.54	95.30	548.58	781.14
	I	6.96	41.96	69.32	7.89	41.47	42.04	-	-	-
	I_r	10.04	60.53	100.00	18.77	98.64	100.00	-	-	-
VQZ	ω	103.05	511.92	933.61	123.48	548.18	969.25	96.30	548.34	776.85
	I	7.47	41.01	71.54	8.34	40.20	44.93	-	-	-
	I_r	10.44	57.32	100.00	18.56	89.47	100.00	-	-	-
AVDZ	ω	99.68	492.25	865.77	105.73	534.53	897.46	148.07	487.90	705.23
	I	8.12	38.85	84.02	9.26	36.52	50.08	-	-	-
	I_r	9.67	46.24	100.00	18.50	72.92	100.00	-	-	-
AVTZ	ω	106.34	508.86	934.81	121.37	544.02	963.07	93.75	539.96	768.02
	I	7.87	40.42	72.13	8.80	39.03	45.37	-	-	-
	I_r	10.91	56.04	100.00	19.39	86.04	100.00	-	-	-
AVQZ	ω	104.09	509.02	931.84	120.76	546.58	966.07	95.14	544.41	772.05
	I	7.77	40.55	71.54	8.67	39.25	45.82	-	-	-
	I_r	10.86	56.68	100.00	18.91	85.66	100.00	-	-	-
VDZ-DK	ω	96.39	493.39	857.01	95.54	543.00	899.73	194.59	491.36	690.32
	I	6.54	35.72	77.00	7.05	35.69	36.60	-	-	-
	I_r	8.49	46.39	100.00	19.26	97.51	100.00	-	-	-
VTZ-DK	ω	118.25	524.18	957.61	133.27	556.47	976.46	130.32	531.59	755.46
	I	6.62	42.47	64.59	7.68	41.27	40.27	-	-	-
	I_r	10.25	65.76	100.00	18.60	100.00	97.56	-	-	-
VQZ-DK	ω	114.68	521.44	949.58	136.39	556.48	973.88	100.53	558.95	769.43
	I	7.12	41.46	66.79	8.12	39.97	43.19	-	-	-
	I_r	10.66	62.08	100.00	18.79	92.55	100.00	-	-	-
AVDZ-DK	ω	98.68	503.88	881.74	116.64	543.49	905.04	148.68	467.51	685.79
	I	7.63	39.06	78.46	8.81	36.19	47.36	-	-	-
	I_r	9.73	49.79	100.00	18.61	76.41	100.00	-	-	-
AVTZ-DK	ω	115.32	518.01	949.32	131.70	552.02	967.54	68.62	547.52	758.51
	I	7.52	40.79	67.65	8.53	38.75	43.61	-	-	-
	I_r	11.11	60.30	100.00	19.57	88.85	100.00	-	-	-
AVQZ-DK	ω	112.98	518.40	946.90	132.36	555.32	970.80	85.01	554.23	763.18
	I	7.45	40.96	67.12	8.42	39.04	44.07	-	-	-
	I_r	11.10	61.02	100.00	19.12	88.58	100.00	-	-	-

Table S5.6. Harmonic vibrational frequencies for the ^{2}A′ ^{60}Ni^{16}OF isotopologue.

		RHF			**CISD**			**RCCSD(T)**		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	113.58	499.01	866.10	92.59	553.18	916.86	170.95	518.21	726.36
	I	7.25	37.39	84.22	7.75	37.75	39.88	-	-	-
	I_r	8.61	44.39	100.00	19.43	94.67	100.00	-	-	-
VTZ	ω	109.49	535.80	969.99	123.64	570.89	1001.26	94.68	572.03	804.32
	I	7.34	44.63	70.04	8.37	44.19	41.74	-	-	-
	I_r	10.47	63.72	100.00	18.95	100.00	94.47	-	-	-
VQZ	ω	103.64	533.22	961.67	124.23	571.10	998.96	96.34	571.70	799.96
	I	7.85	43.58	72.32	8.84	42.80	44.68	-	-	-
	I_r	10.86	60.27	100.00	19.79	95.80	100.00	-	-	-
AVDZ	ω	100.23	512.42	891.22	105.91	557.06	924.41	148.42	507.10	726.88
	I	8.42	41.04	85.65	9.69	38.68	50.27	-	-	-
	I_r	9.83	47.92	100.00	19.28	76.95	100.00	-	-	-
AVTZ	ω	106.94	530.04	962.92	122.11	566.80	992.54	93.86	563.01	790.85
	I	8.27	42.91	72.94	9.30	41.50	45.16	-	-	-
	I_r	11.34	58.83	100.00	20.59	91.91	100.00	-	-	-
AVQZ	ω	104.68	530.20	959.87	121.47	569.46	995.65	95.08	567.59	795.02
	I	8.17	43.07	72.32	9.17	41.75	45.62	-	-	-
	I_r	11.29	59.55	100.00	20.09	91.51	100.00	-	-	-
VDZ-DK	ω	96.99	513.19	881.74	96.06	565.67	926.60	195.50	510.35	711.61
	I	6.68	37.72	78.75	7.41	37.94	36.45	-	-	-
	I_r	8.48	47.90	100.00	19.52	100.00	96.06	-	-	-
VTZ-DK	ω	119.02	545.98	986.60	134.14	579.73	1006.45	130.25	553.15	778.45
	I	7.03	45.27	65.04	8.17	44.03	39.87	-	-	-
	I_r	10.80	69.60	100.00	18.57	100.00	90.55	-	-	-
VQZ-DK	ω	115.39	543.15	978.34	137.22	579.73	1003.85	100.02	582.88	792.17
	I	7.54	44.15	67.28	8.63	42.60	42.84	-	-	-
	I_r	11.21	65.61	100.00	20.15	99.44	100.00	-	-	-
AVDZ-DK	ω	99.26	524.70	907.83	116.90	566.42	932.32	150.50	485.08	707.14
	I	7.96	41.40	79.71	9.26	38.42	47.37	-	-	-
	I_r	9.98	51.94	100.00	19.56	81.11	100.00	-	-	-
AVTZ-DK	ω	116.07	539.58	978.06	132.56	575.11	997.26	68.31	570.94	780.93
	I	7.94	43.39	68.20	9.05	41.25	43.30	-	-	-
	I_r	11.65	63.63	100.00	20.89	95.26	100.00	-	-	-
AVQZ-DK	ω	113.69	539.99	975.58	133.12	578.55	1000.63	84.00	577.92	785.71
	I	7.88	43.58	67.64	8.94	41.57	43.77	-	-	-
	I_r	11.64	64.43	100.00	20.42	94.97	100.00	-	-	-

Table S5.7. Harmonic vibrational frequencies for the $^2A'$ $^{60}Ni^{18}OF$ isotopologue.

		RHF			**CISD**			**RCCSD(T)**		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	112.51	477.86	841.89	91.56	528.93	890.37	170.11	496.52	704.79
	I	7.08	35.07	82.09	7.35	35.14	39.81	-	-	-
	I_r	8.63	42.72	100.00	18.45	88.27	100.00	-	-	-
VTZ	ω	108.50	512.27	941.68	122.45	545.74	971.53	94.80	546.41	781.11
	I	6.89	41.43	69.32	7.80	40.96	42.05	-	-	-
	I_r	9.94	59.77	100.00	18.56	97.40	100.00	-	-	-
VQZ	ω	102.70	509.79	933.60	123.04	545.96	969.24	95.88	546.14	776.84
	I	7.39	40.49	71.55	8.25	39.70	44.95	-	-	-
	I_r	10.33	56.59	100.00	18.35	88.32	100.00	-	-	-
AVDZ	ω	99.35	490.12	865.76	105.34	532.34	897.45	147.48	485.93	705.02
	I	8.06	38.33	84.00	9.17	36.03	50.07	-	-	-
	I_r	9.59	45.63	100.00	18.32	71.95	100.00	-	-	-
AVTZ	ω	105.97	506.74	934.80	120.93	541.81	963.06	93.32	537.80	767.99
	I	7.79	39.90	72.13	8.70	38.54	45.38	-	-	-
	I_r	10.80	55.32	100.00	19.18	84.92	100.00	-	-	-
AVQZ	ω	103.73	506.91	931.83	120.32	544.37	966.06	94.73	542.23	772.03
	I	7.69	40.03	71.54	8.57	38.75	45.84	-	-	-
	I_r	10.75	55.95	100.00	18.70	84.55	100.00	-	-	-
VDZ-DK	ω	96.08	491.19	856.99	95.20	540.74	899.72	193.88	489.47	689.96
	I	6.50	35.25	76.98	6.98	35.24	36.60	-	-	-
	I_r	8.44	45.79	100.00	19.06	96.28	100.00	-	-	-
VTZ-DK	ω	117.84	522.03	957.60	132.79	554.23	976.45	129.73	529.50	755.28
	I	6.55	41.96	64.60	7.59	40.77	40.28	-	-	-
	I_r	10.14	64.95	100.00	18.62	100.00	98.80	-	-	-
VQZ-DK	ω	114.28	519.30	949.57	135.90	554.24	973.87	100.19	556.73	769.41
	I	7.05	40.94	66.80	8.03	39.48	43.21	-	-	-
	I_r	10.55	61.30	100.00	18.58	91.36	100.00	-	-	-
AVDZ-DK	ω	98.34	501.74	881.73	116.19	541.28	905.03	148.27	465.61	685.44
	I	7.57	38.55	78.45	8.72	35.72	47.37	-	-	-
	I_r	9.65	49.14	100.00	18.41	75.41	100.00	-	-	-
AVTZ-DK	ω	114.92	515.88	949.30	131.23	549.80	967.53	68.26	545.35	758.46
	I	7.44	40.28	67.66	8.44	38.26	43.63	-	-	-
	I_r	11.00	59.54	100.00	19.35	87.70	100.00	-	-	-
AVQZ-DK	ω	112.59	516.28	946.89	131.87	553.09	970.79	84.71	552.02	763.14
	I	7.37	40.45	67.13	8.33	38.55	44.09	-	-	-
	I_r	10.98	60.25	100.00	18.90	87.44	100.00	-	-	-

NiOF $^4A''$

Table S5.8. Natural orbitals obtained from RHF calculations at the RCCSD(T) optimized geometry using the AVTZ-DK basis set:

```
Orbital  Occupation    Energy     Coefficients
  1.1     2.00000  -308.80642     3 1s     0.99247
  2.1     2.00000   -38.66117     3 1s     0.99245
  3.1     2.00000   -33.12758     3 2py  -0.58920     3 2pz    0.80793
  4.1     2.00000   -33.12280     3 2py   0.80793     3 2pz    0.58920
  5.1     2.00000   -26.32901     2 1s     0.99888
  6.1     2.00000   -20.64359     1 1s     0.99908
  7.1     2.00000    -5.04465     3 1s     0.99859
  8.1     2.00000    -3.35005     3 2py  -0.35879     3 2pz    0.93201
  9.1     2.00000    -3.34894     3 2py   0.93316     3 2pz    0.35951
 10.1     2.00000    -1.59084     1 1s     0.30494     2 1s     0.88324
 11.1     2.00000    -1.23253     1 1s     0.87756     2 1s    -0.39694
 12.1     2.00000    -0.74433     1 2pz   0.25076     2 2pz    0.35762     3 3d0   -0.81412
 13.1     2.00000    -0.72350     3 3d2+ -0.87235     3 3d1- -0.34308
 14.1     2.00000    -0.66559     2 2py   0.36674     2 2pz   -0.63088     3 3d0   -0.50994
 15.1     2.00000    -0.61883     1 2py   0.37901     2 2py   -0.61810     2 2pz   -0.38240
 16.1     2.00000    -0.52264     1 2py   0.40383     1 2pz   -0.68140     2 2py   -0.25399     2 2pz   0.42719
 17.1     1.00000    -0.78405     3 3d2+ -0.34061     3 3d1-  0.92276
 18.1     1.00000    -0.32258     3 1s     1.04537     3 2pz   -0.49760

  1.2     2.00000   -33.12184     3 2px   0.99995
  2.2     2.00000    -3.34607     3 2px   1.00012
  3.2     2.00000    -0.70991     3 3d2-  0.75601     3 3d1+  0.58679
  4.2     2.00000    -0.67339     1 2px   0.37708     2 2px    0.81293
  5.2     2.00000    -0.50422     1 2px  -0.85304     2 2px    0.49348
  6.2     1.00000    -0.79195     3 3d2- -0.59776     3 3d1+  0.78582
```

Table S5.9. Structural parameters for the ground state $^4A''$ NiOF.

	RHF			
	Energy (E_h)	r_{O-F} (Å)	r_{Ni-O} (Å)	Angle (°)
VDZ	-1681.05907783	1.4852	1.9544	74.2008
VTZ	-1681.13182516	1.4568	1.9248	76.5439
VQZ	-1681.13182516	1.4568	1.9248	76.5439
AVDZ	-1681.07548537	1.4803	1.9456	73.9172
AVTZ	-1681.11993081	1.4568	1.9263	76.8326
AVQZ	-1681.13313708	1.4565	1.9265	76.5754
VDZ-DK	-1693.39330186	1.4788	1.9401	75.8212
VTZ-DK	-1693.44983754	1.4315	1.8948	85.8539
VQZ-DK	-1693.46724156	1.4488	1.9097	79.1091
AVDZ-DK	-1693.40960519	1.4751	1.9332	75.3069
AVTZ-DK	-1693.45456857	1.4482	1.9105	79.7142
AVQZ-DK	-1693.46850867	1.4486	1.9114	79.1200

CISD

	Energy (E_h)	r_{O-F} (Å)	r_{Ni-O} (Å)	Angle (°)
VDZ	-1681.62492561	1.4673	1.8722	83.6009
VTZ	-1681.82533202	1.4322	1.8535	90.3936
VQZ	-1681.89933008	1.4320	1.8546	88.1748
AVDZ	-1681.67501299	1.4741	1.8802	80.3277
AVTZ	-1681.84776122	1.4397	1.8607	86.7096
AVQZ	-1681.90876430	1.4352	1.8583	86.3008
VDZ-DK	-1693.96189498	1.4628	1.8612	85.9235
VTZ-DK	-1694.16234109	1.4284	1.8442	93.0621
VQZ-DK	-1694.23706507	1.4265	1.8443	91.7808
AVDZ-DK	-1694.01120240	1.4704	1.8697	82.2522
AVTZ-DK	-1694.18422819	1.4341	1.8498	90.2944
AVQZ-DK	-1694.24633363	1.4291	1.8470	90.1075

RCCSD(T)

	Energy (E_h)	r_{O-F} (Å)	r_{Ni-O} (Å)	Angle (°)
VDZ	-1681.71875300	1.5203	1.8423	82.7658
VTZ	-1681.94961709	1.4842	1.8271	86.3947
VQZ	-1682.03711523	1.4858	1.8290	84.5869
AVDZ	-1681.78354788	1.5273	1.8538	80.1486
AVTZ	-1681.98138731	1.4930	1.8353	84.2061
AVQZ	-1682.05035092	1.4884	1.8324	83.6962
VDZ-DK	-1694.05656202	1.5214	1.8353	83.4465
VTZ-DK	-1694.28785683	1.4841	1.8197	87.5802
VQZ-DK	-1694.37606864	1.4858	1.8218	85.7092
AVDZ-DK	-1694.12072091	1.5281	1.8471	80.8444
AVTZ-DK	-1694.31896261	1.4929	1.8277	85.4043
AVQZ-DK	-1694.38912605	1.4887	1.8250	84.6818

Table S5.10. T_1 parameters for RCCSD(T) calculations, ^{4}A″ NiOF.

Basis set	T_1
VDZ	0.0367
VTZ	0.0339
VQZ	0.0334
AVQZ	0.0337
AVDZ	0.0362
AVTZ	0.0344
VDZ-DK	0.0359
VTZ-DK	0.0331
VQZ-DK	0.0327
AVDZ-DK	0.0357
AVTZ-DK	0.0337
AVQZ-DK	0.0330

Table S5.11. Harmonic vibrational frequencies for the ^{4}A″ ^{58}Ni^{16}OF isotopologue.

		RHF			**CISD**			**RCCSD(T)**		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	166.37	491.88	838.96	106.15	573.92	921.54	139.88	560.69	755.39
	I	6.75	76.29	57.74	8.69	80.20	19.50	-	-	-
	I_r	8.85	100.00	75.68	10.83	100.00	24.32	-	-	-
VTZ	ω	95.18	540.69	932.79	301.94	639.80	1056.47	102.25	585.35	838.05
	I	9.19	85.86	53.17	9.11	91.17	22.03	-	-	-
	I_r	10.71	100.00	61.92	10.00	100.00	24.16	-	-	-
VQZ	ω	134.75	525.99	897.83	78.81	590.77	999.61	102.38	581.30	828.85
	I	10.28	86.07	59.30	7.96	92.67	26.16	-	-	-
	I_r	11.94	100.00	68.89	8.59	100.00	28.23	-	-	-
AVDZ	ω	173.90	500.37	840.06	132.70	558.11	914.75	153.92	551.54	767.80
	I	9.48	86.20	65.04	11.91	86.24	30.89	-	-	-
	I_r	11.00	100.00	75.45	13.81	100.00	35.82	-	-	-
AVTZ	ω	130.33	524.46	903.48	85.39	582.66	989.87	109.14	572.60	821.99
	I	10.54	85.65	58.22	9.09	90.27	26.73	-	-	-
	I_r	12.31	100.00	67.97	10.07	100.00	29.61	-	-	-
AVQZ	ω	135.59	523.09	896.52	89.23	585.54	990.86	112.12	574.82	824.13
	I	10.37	85.61	58.74	9.33	89.90	27.79	-	-	-
	I_r	12.11	100.00	68.62	10.38	100.00	30.91	-	-	-
VDZ-DK	ω	143.82	501.38	855.53	107.27	573.26	932.07	137.04	564.33	754.88
	I	6.74	77.98	55.99	6.58	83.19	18.61	-	-	-
	I_r	8.64	100.00	71.80	7.91	100.00	22.37	-	-	-
VTZ-DK	ω	57.27	564.57	982.63	99.50	596.59	1021.30	96.66	589.99	837.96
	I	6.68	91.39	44.64	4.80	96.63	20.71	-	-	-
	I_r	7.31	100.00	48.84	4.97	100.00	21.43	-	-	-
VQZ-DK	ω	97.34	540.23	921.24	87.65	596.58	1013.79	94.10	586.29	829.40
	I	9.79	87.97	56.29	6.07	95.79	24.03	-	-	-
	I_r	11.13	100.00	63.99	6.34	100.00	25.09	-	-	-
AVDZ-DK	ω	153.11	509.28	854.19	113.95	566.49	922.79	141.03	552.63	765.00
	I	9.57	87.30	63.90	11.02	87.62	30.01	-	-	-
	I_r	10.96	100.00	73.19	12.58	100.00	34.25	-	-	-
AVTZ-DK	ω	90.59	539.67	929.15	87.16	590.51	1003.70	100.60	577.11	822.54
	I	9.93	87.66	54.89	7.17	93.25	24.70	-	-	-
	I_r	11.33	100.00	62.62	7.69	100.00	26.49	-	-	-
AVQZ-DK	ω	99.54	537.24	919.77	81.89	592.64	1005.38	101.73	579.68	824.11
	I	9.93	87.45	55.89	7.15	93.24	25.52	-	-	-
	I_r	11.36	100.00	63.91	7.67	100.00	27.37	-	-	-

Table S5.12. Harmonic vibrational frequencies for the $^{4}A''$ $^{58}Ni^{18}OF$ isotopologue.

		RHF			**CISD**			**RCCSD(T)**		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	164.30	472.86	816.43	105.26	548.60	895.11	138.59	536.59	733.78
	I	6.40	72.13	56.16	8.44	74.53	19.41	-	-	-
	I_r	8.87	100.00	77.87	11.32	100.00	26.04	-	-	-
VTZ	ω	94.28	518.02	906.61	304.23	609.69	1025.28	101.33	559.84	813.72
	I	8.94	80.26	51.88	8.61	84.43	22.01	-	-	-
	I_r	11.14	100.00	64.64	10.20	100.00	26.07	-	-	-
VQZ	ω	133.40	504.49	872.94	78.18	565.05	970.37	101.50	556.08	804.87
	I	9.92	80.82	57.78	7.75	85.89	25.96	-	-	-
	I_r	12.27	100.00	71.49	9.03	100.00	30.23	-	-	-
AVDZ	ω	171.90	480.73	817.26	131.55	534.36	888.48	152.73	528.00	745.61
	I	8.99	81.43	63.31	11.56	80.49	30.44	-	-	-
	I_r	11.05	100.00	77.75	14.36	100.00	37.82	-	-	-
AVTZ	ω	129.04	502.96	878.35	84.67	557.34	961.00	108.21	547.76	798.19
	I	10.19	80.41	56.76	8.85	83.78	26.49	-	-	-
	I_r	12.67	100.00	70.58	10.57	100.00	31.62	-	-	-
AVQZ	ω	134.23	501.71	871.65	88.76	560.06	961.99	111.10	549.95	800.29
	I	10.00	80.39	57.25	9.09	83.45	27.51	-	-	-
	I_r	12.44	100.00	71.22	10.89	100.00	32.96	-	-	-
VDZ-DK	ω	142.11	481.52	832.35	106.27	548.48	905.18	135.81	539.98	733.26
	I	6.45	73.43	54.51	6.39	77.18	18.58	-	-	-
	I_r	8.79	100.00	74.22	8.28	100.00	24.07	-	-	-
VTZ-DK	ω	56.72	540.28	954.46	98.51	570.64	991.01	95.73	564.21	813.62
	I	6.52	84.82	43.76	4.65	89.28	20.77	-	-	-
	I_r	7.68	100.00	51.59	5.21	100.00	23.26	-	-	-
VQZ-DK	ω	96.39	517.66	895.47	86.83	570.61	983.86	93.29	560.72	805.38
	I	9.51	82.26	54.91	5.90	88.60	23.97	-	-	-
	I_r	11.56	100.00	66.75	6.66	100.00	27.05	-	-	-
AVDZ-DK	ω	151.44	488.89	830.86	112.96	542.14	896.22	139.78	529.00	742.90
	I	9.16	82.21	62.22	10.72	81.59	29.61	-	-	-
	I_r	11.14	100.00	75.69	13.13	100.00	36.29	-	-	-
AVTZ-DK	ω	89.72	517.04	903.07	86.33	564.76	974.19	99.69	551.95	798.71
	I	9.66	81.93	53.58	6.97	86.35	24.59	-	-	-
	I_r	11.79	100.00	65.39	8.07	100.00	28.48	-	-	-
AVQZ-DK	ω	98.61	514.80	894.03	81.08	566.83	975.84	100.81	554.48	800.27
	I	9.65	81.79	54.53	6.96	86.34	25.38	-	-	-
	I_r	11.79	100.00	66.67	8.06	100.00	29.39	-	-	-

Table S5.13. Harmonic vibrational frequencies for the $^{4}A''$ ^{60}Ni^{16}OF isotopologue.

		RHF			CISD			RCCSD(T)		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	165.91	489.42	838.83	105.58	571.83	921.47	139.38	558.40	755.32
	I	6.74	75.15	58.10	8.66	79.22	19.62	-	-	-
	I_r	8.97	100.00	77.31	10.93	100.00	24.77	-	-	-
VTZ	ω	94.88	538.32	932.71	298.75	637.98	1056.32	101.86	583.03	838.01
	I	9.16	84.70	53.42	9.23	90.01	22.12	-	-	-
	I_r	10.82	100.00	63.07	10.26	100.00	24.57	-	-	-
VQZ	ω	134.33	523.57	897.74	78.52	588.45	999.57	101.99	578.96	828.81
	I	10.26	84.84	59.59	7.93	91.60	26.28	-	-	-
	I_r	12.09	100.00	70.23	8.66	100.00	28.69	-	-	-
AVDZ	ω	173.40	497.92	839.93	132.24	555.74	914.68	153.28	549.26	767.70
	I	9.48	84.90	65.39	11.88	85.10	31.04	-	-	-
	I_r	11.16	100.00	77.01	13.96	100.00	36.48	-	-	-
AVTZ	ω	129.93	522.06	903.38	85.09	580.33	989.83	108.71	570.30	821.94
	I	10.52	84.44	58.51	9.05	89.19	26.85	-	-	-
	I_r	12.46	100.00	69.30	10.15	100.00	30.11	-	-	-
AVQZ	ω	135.17	520.68	896.42	88.77	583.22	990.81	111.74	572.49	824.08
	I	10.35	84.39	59.03	9.30	88.81	27.92	-	-	-
	I_r	12.27	100.00	69.96	10.47	100.00	31.44	-	-	-
VDZ-DK	ω	143.41	498.95	855.42	106.89	570.93	932.03	136.52	562.05	754.81
	I	6.72	76.85	56.32	6.56	82.21	18.72	-	-	-
	I_r	8.74	100.00	73.29	7.98	100.00	22.77	-	-	-
VTZ-DK	ω	57.08	562.27	982.58	99.15	594.31	1021.27	96.33	587.67	837.93
	I	6.65	90.31	44.83	4.78	95.61	20.82	-	-	-
	I_r	7.36	100.00	49.65	5.00	100.00	21.77	-	-	-
VQZ-DK	ω	97.04	537.84	921.16	87.35	594.27	1013.76	93.73	583.97	829.36
	I	9.76	86.77	56.55	6.04	94.74	24.14	-	-	-
	I_r	11.24	100.00	65.18	6.38	100.00	25.48	-	-	-
AVDZ-DK	ω	152.65	506.86	854.07	113.55	564.14	922.73	140.52	550.36	764.91
	I	9.56	86.02	64.23	10.99	86.49	30.15	-	-	-
	I_r	11.11	100.00	74.67	12.70	100.00	34.86	-	-	-
AVTZ-DK	ω	90.30	537.31	929.08	86.85	588.22	1003.67	100.23	574.82	822.50
	I	9.90	86.47	55.15	7.14	92.19	24.82	-	-	-
	I_r	11.45	100.00	63.78	7.74	100.00	26.92	-	-	-
AVQZ-DK	ω	99.20	534.87	919.69	81.64	590.32	1005.34	101.37	577.36	824.06
	I	9.90	86.26	56.15	7.12	92.19	25.64	-	-	-
	I_r	11.48	100.00	65.10	7.73	100.00	27.81	-	-	-

Table S5.14. Harmonic vibrational frequencies for the $^4A''$ ^{60}Ni^{18}OF isotopologue.

		RHF			CISD			RCCSD(T)		
		$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$	$1A'$	$2A'$	$3A'$
VDZ	ω	163.88	470.41	816.38	104.87	546.37	895.11	138.10	534.25	733.75
	I	6.39	71.15	56.12	8.39	73.62	19.40	-	-	-
	I_r	8.99	100.00	78.87	11.40	100.00	26.35	-	-	-
VTZ	ω	93.99	515.63	906.59	302.84	607.74	1025.26	100.97	557.46	813.72
	I	8.89	79.23	51.86	8.64	83.39	22.01	-	-	-
	I_r	11.22	100.00	65.45	10.36	100.00	26.39	-	-	-
VQZ	ω	133.01	502.06	872.91	77.94	562.66	970.36	101.15	553.69	804.86
	I	9.87	79.75	57.74	7.70	84.89	25.97	-	-	-
	I_r	12.38	100.00	72.40	9.07	100.00	30.60	-	-	-
AVDZ	ω	171.44	478.29	817.21	131.12	531.97	888.46	152.18	525.69	745.58
	I	8.97	80.32	63.26	11.49	79.46	30.42	-	-	-
	I_r	11.17	100.00	78.76	14.46	100.00	38.28	-	-	-
AVTZ	ω	128.66	500.55	878.32	84.38	554.97	960.99	107.83	545.40	798.18
	I	10.13	79.34	56.72	8.79	82.78	26.49	-	-	-
	I_r	12.77	100.00	71.49	10.62	100.00	32.01	-	-	-
AVQZ	ω	133.84	499.29	871.62	88.43	557.68	961.98	110.71	547.58	800.28
	I	9.95	79.33	57.22	9.02	82.44	27.51	-	-	-
	I_r	12.55	100.00	72.13	10.94	100.00	33.37	-	-	-
VDZ-DK	ω	141.72	479.10	832.31	105.91	546.11	905.17	135.32	537.64	733.23
	I	6.44	72.46	54.47	6.35	76.27	18.57	-	-	-
	I_r	8.89	100.00	75.17	8.32	100.00	24.35	-	-	-
VTZ-DK	ω	56.54	537.93	954.44	98.16	568.29	991.00	95.40	561.84	813.62
	I	6.47	83.82	43.76	4.62	88.30	20.79	-	-	-
	I_r	7.72	100.00	52.21	5.24	100.00	23.54	-	-	-
VQZ-DK	ω	96.09	515.25	895.44	86.54	568.24	983.84	92.96	558.34	805.37
	I	9.45	81.21	54.88	5.86	87.61	23.99	-	-	-
	I_r	11.64	100.00	67.58	6.69	100.00	27.38	-	-	-
AVDZ-DK	ω	151.01	486.47	830.82	112.58	539.76	896.21	139.29	526.69	742.86
	I	9.13	81.11	62.18	10.65	80.57	29.59	-	-	-
	I_r	11.25	100.00	76.66	13.21	100.00	36.73	-	-	-
AVTZ-DK	ω	89.45	514.65	903.05	86.03	562.41	974.17	99.34	549.61	798.70
	I	9.60	80.88	53.55	6.92	85.36	24.61	-	-	-
	I_r	11.87	100.00	66.21	8.11	100.00	28.83	-	-	-
AVQZ-DK	ω	98.31	512.41	894.01	80.81	564.45	975.83	100.45	552.11	800.26
	I	9.59	80.74	54.50	6.91	85.35	25.39	-	-	-
	I_r	11.88	100.00	67.50	8.10	100.00	29.75	-	-	-

Part 6. CASSCF, MRCI, and CASPT2 calculations on ONiF ($^4\Sigma^-$; $C_{\infty v}$)

The $^4\Sigma^-$ electronic state of ONiF was investigated by CASSCF, MRCI and CASPT2. The CASSCF wave function, which served as reference for MRCI and CASPT2, included 13 electrons and 8 orbitals in the active space (13,8). Geometry optimization and normal mode analysis were carried out in the reduced point group C_1. To confirm the electronic state the results were checked against the calculation carried out in point group C_{2v}.

Table S6.1. Natural orbitals obtained from CASSCF(13,8) calculations at the CASPT2 optimized geometry using the AVTZ-DK basis set:

```
Orbital  Occupation    Energy     Coefficients
  1.1     2.00000  -308.78744     1 1s    0.99247
  2.1     2.00000   -38.64571     1 1s    0.99255
  3.1     2.00000   -33.12252     1 2pz   0.99996
  4.1     2.00000   -26.24934     2 1s    0.99886
  5.1     2.00000   -20.59961     3 1s    0.99874
  6.1     2.00000    -5.02786     1 1s    0.99654
  7.1     2.00000    -3.34497     1 2pz   0.99310
  8.1     2.00000    -1.50483     2 1s    0.94523
  9.1     2.00000    -1.26295     3 1s    0.93581
 10.1     2.00000    -0.63201     2 2pz   0.88617
 11.1     1.96554    -0.65265     1 3d2+ -1.00205
 12.1     1.90504    -0.58280     1 3d0  -0.41579     3 2pz  -0.82033
 13.1     1.15226    -0.28733     1 3d0  -0.85792     3 2pz   0.36323

  1.2     2.00000   -33.10183     1 2px   0.99996
  2.2     2.00000    -3.32998     1 2px   0.99971
  3.2     2.00000    -0.59508     2 2px  -0.91612
  4.2     1.81586    -0.54268     1 3d1+ -0.58700     3 2px   0.68889
  5.2     1.18995    -0.30176     1 3d1+  0.80720     3 2px   0.59688

  1.3     2.00000   -33.10183     1 2py   0.99996
  2.3     2.00000    -3.32998     1 2py   0.99971
  3.3     2.00000    -0.59508     2 2py  -0.91612
  4.3     1.81586    -0.54268     1 3d1- -0.58700     3 2py   0.68889
  5.3     1.18995    -0.30176     1 3d1-  0.80720     3 2py   0.59688

  1.4     1.96554    -0.65265     1 3d2-  1.00205
```

Table S6.2. CI vector at the geometry optimized at the CASPT2 level using the AVTZ-DK basis set. The most significantly contributing electronic configuration: $1\delta^4 12\sigma^2 4\pi^4 5\pi^2 13\sigma^1$

```
22a 2a 2a 2       0.8586477
22a a2 a2 2      -0.3116725
2a2 2a a2 2       0.1801057
2a2 a2 2a 2       0.1801057
2a2 a2 a2 2      -0.1432929
222 22 aa a       0.1196932
a22 2a a2 2       0.1196932
222 aa 22 a      -0.1196932
a22 a2 2a 2      -0.1196932
2a2 2a 2a 2      -0.0794179
22a a2 2a 2       0.0733333
22a 2a a2 2       0.0733333
aa2 22 22 a       0.0569154
a2a 22 22 a      -0.0506701
```

Table S6.3. Structural parameters for the ground state $^4\Sigma^-$ ONiF.

CASSCF

	Energy ($\mathrm{E_h}$)	r_{Ni-F} (Å)	r_{Ni-O} (Å)
VDZ	-1681.20840904	1.7657	1.7381
VTZ	-1681.26345515	1.7588	1.7355
VQZ	-1681.28171132	1.7603	1.7370
AVDZ	-1681.22794757	1.7679	1.7428
AVTZ	-1681.26985356	1.7618	1.7386
AVQZ	-1681.28293856	1.7618	1.7378
VDZ-DK	-1693.54197288	1.7586	1.7295
VTZ-DK	-1693.59771041	1.7512	1.7264
VQZ-DK	-1693.61646172	1.7528	1.7278
AVDZ-DK	-1693.56123120	1.7609	1.7340
AVTZ-DK	-1693.60378666	1.7542	1.7294
AVQZ-DK	-1693.61762551	1.7542	1.7285

MRCI

	Energy ($\mathrm{E_h}$)	r_{Ni-F} (Å)	r_{Ni-O} (Å)
VDZ	-1681.77821657	1.7457	1.6559
VTZ	-1681.97729810	1.7387	1.6554
VQZ	-1682.05428609	1.7381	1.6547
AVDZ	-1681.83190576	1.7517	1.6624
AVTZ	-1682.00249430	1.7416	1.6571
AVQZ	-1682.06424149	1.7396	1.6549
VDZ-DK	-1694.11420587	1.7379	1.6469
VTZ-DK	-1694.31353872	1.7302	1.6457
VQZ-DK	-1694.39110912	1.7299	1.6450
AVDZ-DK	-1694.16690986	1.7442	1.6536
AVTZ-DK	-1694.33802092	1.7331	1.6472
AVQZ-DK	-1694.40092898	1.7311	1.6450

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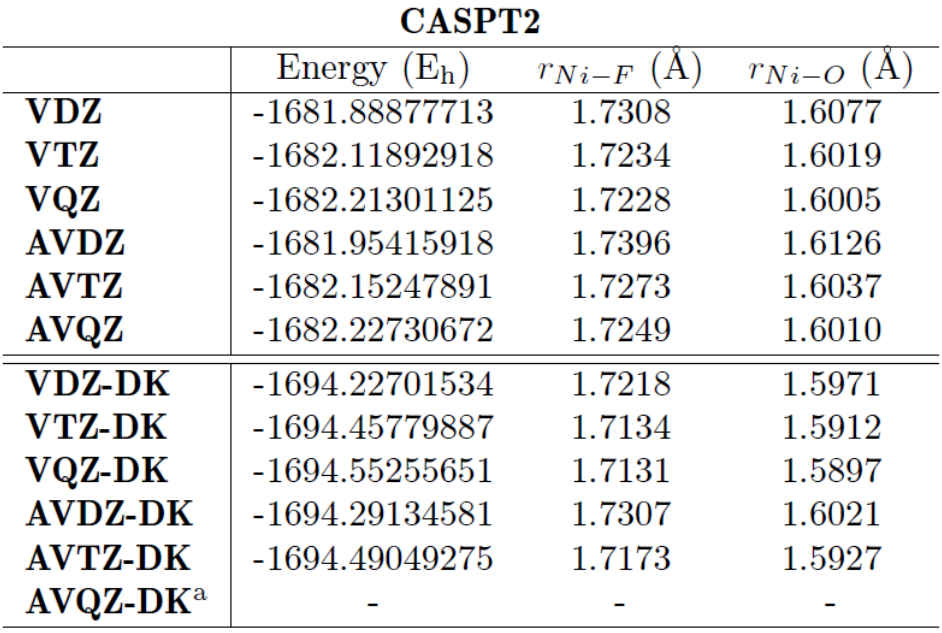

CASPT2

	Energy (E_h)	r_{Ni-F} (Å)	r_{Ni-O} (Å)
VDZ	-1681.88877713	1.7308	1.6077
VTZ	-1682.11892918	1.7234	1.6019
VQZ	-1682.21301125	1.7228	1.6005
AVDZ	-1681.95415918	1.7396	1.6126
AVTZ	-1682.15247891	1.7273	1.6037
AVQZ	-1682.22730672	1.7249	1.6010
VDZ-DK	-1694.22701534	1.7218	1.5971
VTZ-DK	-1694.45779887	1.7134	1.5912
VQZ-DK	-1694.55255651	1.7131	1.5897
AVDZ-DK	-1694.29134581	1.7307	1.6021
AVTZ-DK	-1694.49049275	1.7173	1.5927
AVQZ-DK[a]	-	-	-

[a] No convergence in geometry optimization in CASSCF.

Table S6.4. Harmonic vibrational frequencies for the $^4\Sigma^-$ $^{16}O^{58}NiF$.

		CASSCF				**MRCI**				**CASPT2**			
		$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$
VDZ	ω	163.36	163.36	588.72	742.68	163.01	163.08	642.36	802.09	159.12	159.12	656.09	891.15
	I	69.62	69.62	2.24	137.84	0	0	7.77	140.57	-	-	-	-
	I_r	50.51	50.51	1.63	100	0	0	5.53	100	-	-	-	-
VTZ	ω	166.44	166.44	596.59	748.69	166.37	166.48	645.15	801.67	161.32	161.32	660.33	905.59
	I	68.46	68.46	1.04	154.14	0	0	9.46	151.6	-	-	-	-
	I_r	44.41	44.41	0.67	100	0	0	6.24	100	-	-	-	-
VQZ	ω	167.15	167.15	594.56	746.32	168.5	168.57	646.52	803.39	164.48	164.48	660.91	908.39
	I	68.35	68.35	1.09	158.44	0	0	9.72	155.73	-	-	-	-
	I_r	43.14	43.14	0.69	100	0	0	6.24	100	-	-	-	-
AVDZ	ω	164.71	164.71	587.69	736.67	161.63	161.63	632.63	786.71	156.97	156.97	641.09	875.66
	I	68.4	68.4	1.14	161.32	0	0	10.67	158.2	-	-	-	-
	I_r	42.4	42.4	0.71	100	0	0	6.74	100	-	-	-	-
AVTZ	ω	165.48	165.48	592.25	743.66	166.74	166.89	640.64	797.74	162.70	162.70	652.13	899.72
	I	68.29	68.29	1.04	160.65	0	0	10.35	156.67	-	-	-	-
	I_r	42.51	42.51	0.65	100	0	0	6.6	100	-	-	-	-
AVQZ	ω	165.61	165.62	592.08	742.95	167.02	167.02	643.7	801.19	162.77	162.77	655.69	905.58
	I	67.94	67.94	1.02	160.64	0	0	10.56	156.32	-	-	-	-
	I_r	42.29	42.29	0.63	100	0	0	6.75	100	-	-	-	-

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VDZ-DK	ω	166.64	166.64	591.98	748.69	166.91	166.99	646.45	810.49	164.20	164.20	664.05	907.88
	I	0	0	1.51	133.6	0	0	8.47	133.11	-	-	-	-
	I_r	0	0	1.13	100	0	0	6.36	100	-	-	-	-
VTZ-DK	ω	169.75	169.76	600.71	756.11	170.45	170.52	651.14	812.7	166.88	166.88	671.04	925.67
	I	0	0	0.6	149.07	0	0	10.47	143.21	-	-	-	-
	I_r	0	0	0.4	100	0	0	7.31	100	-	-	-	-
VQZ-DK	ω	170.25	170.26	598.5	753.49	172.15	172.22	652.01	813.75	169.11	169.12	671.07	927.63
	I	0	0	0.62	153.06	0	0	10.75	146.88	-	-	-	-
	I_r	0	0	0.4	100	0	0	7.32	100	-	-	-	-
AVDZ-DK	ω	167.65	167.72	591.41	743.13	164.83	164.9	636.73	794.41	160.88	160.89	649.28	891.79
	I	0	0	0.64	155.64	0	0	11.4	149.04	-	-	-	-
	I_r	0	0	0.41	100	0	0	7.65	100	-	-	-	-
AVTZ-DK	ω	168.49	168.5	596.19	750.81	170.23	170.32	646.2	808.41	167.27	167.28	662.47	919.75
	I	0	0	0.58	155.16	0	0	11.46	147.57	-	-	-	-
	I_r	0	0	0.37	100	0	0	7.76	100	-	-	-	-
AVQZ-DK	ω	168.71	168.72	596.12	750.23	170.78	170.79	649.45	812.05	-	-	-	-
	I	0	0	0.55	155.19	0	0	11.65	147.34	-	-	-	-
	I_r	0	0	0.36	100	0	0	7.9	100	-	-	-	-

Table S6.5. Harmonic vibrational frequencies for the $^4\Sigma^-$ $^{18}\mathrm{O}^{58}\mathrm{NiF}$.

		CASSCF				**MRCI**				**CASPT2**			
		$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$
VDZ	ω	160.2	160.2	565.97	736.06	159.74	159.81	626.2	783.95	155.87	155.87	646.23	862.04
	I	67.19	67.19	4.45	131.38	0	0	2.92	141.27	-	-	-	-
	I_r	51.14	51.14	3.38	100	0	0	2.07	100	-	-	-	-
VTZ	ω	163.23	163.23	573.86	741.6	163.04	163.14	628.34	784.26	158.03	158.03	651.01	875.19
	I	66.06	66.06	2.99	147.86	0	0	3.71	153.28	-	-	-	-
	I_r	44.68	44.68	2.02	100	0	0	2.42	100	-	-	-	-
VQZ	ω	163.92	163.92	571.83	739.36	165.13	165.2	629.59	786.05	161.11	161.11	651.64	877.82
	I	65.96	65.96	3.09	152.02	0	0	3.82	157.49	-	-	-	-
	I_r	43.39	43.39	2.03	100	0	0	2.43	100	-	-	-	-
AVDZ	ω	161.53	161.53	565.25	729.76	158.39	158.39	616.34	769.37	153.76	153.76	631.71	846.72
	I	66.01	66.01	3.21	154.71	0	0	4.37	160.27	-	-	-	-
	I_r	42.67	42.67	2.08	100	0	0	2.73	100	-	-	-	-
AVTZ	ω	162.29	162.29	569.66	736.65	163.4	163.54	624.05	780.29	159.38	159.38	643.05	869.35
	I	65.89	65.89	3.03	154.18	0	0	4.23	158.62	-	-	-	-
	I_r	42.74	42.74	1.96	100	0	0	2.67	100	-	-	-	-
AVQZ	ω	162.41	162.41	569.51	735.93	163.68	163.68	627.12	783.55	159.44	159.44	646.70	874.83
	I	65.55	65.55	3	154.17	0	0	4.35	158.35	-	-	-	-
	I_r	42.52	42.52	1.95	100	0	0	2.75	100	-	-	-	-

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VDZ-DK	ω	163.43	163.43	569.2	741.9	163.57	163.64	630.11	792.27	160.83	160.83	654.29	877.92
	I	0	0	3.38	127.82	0	0	3.53	134.34	-	-	-	-
	I_r	0	0	2.65	100	0	0	2.62	100	-	-	-	-
VTZ-DK	ω	166.45	166.46	577.84	748.91	167.04	167.1	634.11	795.13	163.47	163.47	661.76	894.34
	I	0	0	2.16	143.55	0	0	4.57	145.52	-	-	-	-
	I_r	0	0	1.51	100	0	0	3.14	100	-	-	-	-
VQZ-DK	ω	167.03	167.1	575.73	746.4	168.71	168.78	634.88	796.25	165.65	165.66	661.86	896.14
	I	0	0	2.21	147.42	0	0	4.7	149.27	-	-	-	-
	I_r	0	0	1.5	100	0	0	3.15	100	-	-	-	-
AVDZ-DK	ω	164.39	164.47	568.89	736.07	161.51	161.58	620.2	777.09	157.59	157.59	639.97	862.05
	I	0	0	2.31	149.82	0	0	5.07	151.64	-	-	-	-
	I_r	0	0	1.54	100	0	0	3.34	100	-	-	-	-
AVTZ-DK	ω	165.27	165.27	573.5	743.67	166.83	166.92	629.43	790.77	163.85	163.86	653.45	888.42
	I	0	0	2.17	149.48	0	0	5.19	150.16	-	-	-	-
	I_r	0	0	1.45	100	0	0	3.46	100	-	-	-	-
AVQZ-DK	ω	165.46	165.46	573.47	743.06	167.36	167.36	632.69	794.22	-	-	-	-
	I	0	0	2.13	149.52	0	0	5.3	150	-	-	-	-
	I_r	0	0	1.42	100	0	0	3.54	100	-	-	-	-

Table S6.6. Harmonic vibrational frequencies for the $^{4}\Sigma^{-}$ $^{16}\text{O}^{60}\text{NiF}$.

		CASSCF				**MRCI**				**CASPT2**			
		$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$
VDZ	ω	162.34	162.34	588.65	738.1	162	162.07	642.22	797.23	158.13	158.13	655.48	886.36
	I	68.75	68.75	2.35	135.97	0	0	8.05	138.43	-	-	-	-
	I_r	50.56	50.56	1.73	100	0	0	5.81	100	-	-	-	-
VTZ	ω	165.4	165.4	596.53	744.05	165.33	165.42	645.03	796.77	160.31	160.31	659.66	900.80
	I	67.6	67.6	1.11	152.13	0	0	9.76	149.3	-	-	-	-
	I_r	44.44	44.44	0.73	100	0	0	6.53	100	-	-	-	-
VQZ	ω	166.11	166.11	594.5	741.71	167.44	167.52	646.41	798.48	163.45	163.45	660.24	903.59
	I	67.49	67.49	1.17	156.36	0	0	10.02	153.37	-	-	-	-
	I_r	43.17	43.17	0.75	100	0	0	6.53	100	-	-	-	-
AVDZ	ω	163.68	163.68	587.63	732.11	160.62	160.62	632.51	781.91	155.99	155.99	640.48	870.99
	I	67.54	67.54	1.22	159.21	0	0	11	155.77	-	-	-	-
	I_r	42.42	42.42	0.76	100	0	0	7.06	100	-	-	-	-
AVTZ	ω	164.45	164.45	592.19	739.06	165.7	165.83	640.52	792.87	161.69	161.69	651.47	894.98
	I	67.43	67.43	1.11	158.56	0	0	10.66	154.27	-	-	-	-
	I_r	42.53	42.53	0.7	100	0	0	6.91	100	-	-	-	-
AVQZ	ω	164.58	164.58	592.01	738.35	165.97	165.97	643.57	796.31	161.75	161.75	655.01	900.82
	I	67.09	67.09	1.09	158.54	0	0	10.88	153.91	-	-	-	-
	I_r	42.31	42.31	0.69	100	0	0	7.07	100	-	-	-	-

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VDZ-DK	ω	165.61	165.61	591.9	744.08	165.87	165.94	646.32	805.57	163.17	163.17	663.42	903.03
	I	0	0	1.6	131.82	0	0	8.74	131.07	-	-	-	-
	I_r	0	0	1.21	100	0	0	6.67	100	-	-	-	-
VTZ-DK	ω	168.71	168.71	600.65	751.42	169.4	169.47	651.03	807.73	165.84	165.84	670.35	920.80
	I	0	0	0.65	147.15	0	0	10.76	141.02	-	-	-	-
	I_r	0	0	0.44	100	0	0	7.63	100	-	-	-	-
VQZ-DK	ω	169.19	169.2	598.44	748.83	171.09	171.16	651.9	808.77	168.06	168.07	670.37	922.76
	I	0	0	0.67	151.08	0	0	11.04	144.62	-	-	-	-
	I_r	0	0	0.44	100	0	0	7.63	100	-	-	-	-
AVDZ-DK	ω	166.59	166.67	591.35	738.53	163.8	163.87	636.62	789.57	159.88	159.88	648.65	887.05
	I	0	0	0.7	153.63	0	0	11.72	146.73	-	-	-	-
	I_r	0	0	0.46	100	0	0	7.99	100	-	-	-	-
AVTZ-DK	ω	167.42	167.42	596.12	746.16	169.17	169.27	646.08	803.47	166.23	166.24	661.78	914.93
	I	0	0	0.63	153.16	0	0	11.77	145.29	-	-	-	-
	I_r	0	0	0.41	100	0	0	8.1	100	-	-	-	-
AVQZ-DK	ω	167.67	167.67	596.06	745.58	169.71	169.72	649.34	807.1	-	-	-	-
	I	0	0	0.6	153.19	0	0	11.97	145.05	-	-	-	-
	I_r	0	0	0.39	100	0	0	8.25	100	-	-	-	-

Table S6.7. Harmonic vibrational frequencies for the $^4\Sigma^-$ $^{18}O^{60}NiF$.

		CASSCF				**MRCI**				**CASPT2**			
		$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$	$1B_1$	$2B_2$	$3A_1$	$4A_1$
VDZ	ω	159.16	159.16	565.75	731.55	158.7	158.77	626.19	778.86	154.86	154.86	645.88	856.89
	I	66.32	66.32	4.66	129.41	0	0	2.97	139.36	-	-	-	-
	I_r	51.25	51.25	3.6	100	0	0	2.13	100	-	-	-	-
VTZ	ω	162.16	162.16	573.66	737.03	161.98	162.08	628.33	779.16	157.00	157.00	650.60	870.03
	I	65.2	65.2	3.17	145.73	0	0	3.75	151.24	-	-	-	-
	I_r	44.74	44.74	2.18	100	0	0	2.48	100	-	-	-	-
VQZ	ω	162.86	162.86	571.62	734.81	164.05	164.13	629.59	780.94	160.07	160.07	651.23	872.65
	I	65.1	65.1	3.28	149.83	0	0	3.86	155.4	-	-	-	-
	I_r	43.45	43.45	2.19	100	0	0	2.48	100	-	-	-	-
AVDZ	ω	160.48	160.48	565.05	725.26	157.36	157.36	616.34	764.37	152.76	152.76	631.35	841.69
	I	65.15	65.15	3.41	152.47	0	0	4.43	158.12	-	-	-	-
	I_r	42.73	42.73	2.24	100	0	0	2.8	100	-	-	-	-
AVTZ	ω	161.23	161.23	569.46	732.11	162.34	162.49	624.04	775.22	158.34	158.34	642.64	864.25
	I	65.04	65.04	3.22	151.97	0	0	4.28	156.49	-	-	-	-
	I_r	42.8	42.8	2.12	100	0	0	2.74	100	-	-	-	-
AVQZ	ω	161.36	161.36	569.31	731.39	162.61	162.61	627.12	778.45	158.40	158.40	646.27	869.71
	I	64.7	64.7	3.19	151.96	0	0	4.41	156.22	-	-	-	-
	I_r	42.58	42.58	2.1	100	0	0	2.82	100	-	-	-	-

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VDZ-DK	ω	162.39	162.39	569	737.35	162.5	162.57	630.09	787.12	159.79	159.79	653.92	872.70
	I	0	0	3.56	125.94	0	0	3.58	132.52	-	-	-	-
	I_r	0	0	2.83	100	0	0	2.7	100	-	-	-	-
VTZ-DK	ω	165.38	165.38	577.65	744.29	165.95	166.02	634.11	789.97	162.41	162.41	661.33	889.10
	I	0	0	2.32	141.52	0	0	4.61	143.57	-	-	-	-
	I_r	0	0	1.64	100	0	0	3.21	100	-	-	-	-
VQZ-DK	ω	165.9	165.91	575.48	741.79	167.62	167.7	634.87	791.07	164.57	164.58	661.42	890.89
	I	0	0	2.37	145.35	0	0	4.73	147.27	-	-	-	-
	I_r	0	0	1.63	100	0	0	3.21	100	-	-	-	-
AVDZ-DK	ω	163.33	163.4	568.7	731.53	160.47	160.54	620.19	772.04	156.56	156.56	639.59	856.96
	I	0	0	2.48	147.7	0	0	5.11	149.6	-	-	-	-
	I_r	0	0	1.68	100	0	0	3.42	100	-	-	-	-
AVTZ-DK	ω	164.18	164.18	573.31	739.09	165.75	165.84	629.42	785.63	162.79	162.79	653.02	883.23
	I	0.00	0.00	2.32	147.38	0.00	0.00	5.24	148.14	-	-	-	-
	I_r	0.00	0.00	1.58	100.00	0.00	0.00	3.54	100.00	-	-	-	-
AVQZ-DK	ω	164.52	164.59	573.36	738.51	166.27	166.27	632.68	789.05	-	-	-	-
	I	0	0	2.28	147.42	0	0	5.36	147.98	-	-	-	-
	I_r	0	0	1.55	100.00	0	0	3.62	100.00	-	-	-	-

Table S6.8. ONiF ($C_{2v}/C_{\infty v}$ – $^4A_2/^4\Sigma^-$)

CASSCF(13,8)/MRCI/cc-pVTZ-DK

Optimization and normal mode calculation carried out in C_1 point group symmetry.

Optimized variables
NiO = 1.64817316 ANGSTROM
NiF = 1.73031828 ANGSTROM

```
NATURAL ORBITALS
================

 Orbital  Occupation    Energy     Coefficients
   1.1     2.00000  -308.79061     2 1s    0.99247
   2.1     2.00000   -38.64817     2 1s    0.99244
   3.1     2.00000   -33.12485     2 2pz   0.99996
   4.1     2.00000   -33.10447     2 2py   0.99995
   5.1     2.00000   -33.10447     2 2px   0.99995
   6.1     2.00000   -26.24249     3 1s    0.99920
   7.1     2.00000   -20.59807     1 1s    0.99903
   8.1     2.00000    -5.03053     2 1s    0.99934
   9.1     2.00000    -3.34662     2 2pz  -0.99708
  10.1     2.00000    -3.33295     2 2px   0.99997
  11.1     2.00000    -3.33295     2 2py   0.99997
  12.1     2.00000    -1.49688     3 1s    0.94508
  13.1     2.00000    -1.25760     1 1s    0.93965
  14.1     2.00000    -0.62375     3 2pz   0.88195
  15.1     2.00000    -0.58780     3 2px   0.91774
  16.1     2.00000    -0.58780     3 2py   0.91774
  17.1     1.95997    -0.65356     2 3d2+  1.00267
  18.1     1.95997    -0.65356     2 3d2-  1.00267
  19.1     1.91067    -0.57764     1 2pz   0.82420     2 3d0   0.38813
  20.1     1.79921    -0.53530     1 2py   0.68226     2 3d1- -0.60165
  21.1     1.79921    -0.53530     1 2px   0.68226     2 3d1+ -0.60165
  22.1     1.20619    -0.31090     1 2px   0.60403     2 3d1+  0.79794
  23.1     1.20619    -0.31090     1 2py   0.60403     2 3d1-  0.79794
  24.1     1.15858    -0.29497     1 2pz   0.33559     2 3d0  -0.87352
```

```
CI vector
=========
22222aaa      0.8467492
222aa22a      0.3332225
22a2a2a2     -0.1724011
22aa2a22      0.1724011
22aaa222     -0.1406388
2a2a22a2      0.1315807
2a22aa22     -0.1315807
a22a2a22      0.1315807
a222a2a2      0.1315807
22a22aa2      0.0827662
222a2a2a     -0.0750015
2222a2aa      0.0750015
aaa22222     -0.0570575
```

Harmonic Wavenumbers:

	1 B_1	2 B_2	3 A_1	4 A_1
Wavenumbers [cm-1]	173.93	174.15	653.76	812.43
Intensities [km/mol]	0.00	0.00	9.04	144.46
Intensities [relative]	0.00	0.00	6.26	100.00

	1 B_1	2 B_2	3 A_1	4 A_1
Wavenumbers [cm-1]	170.47	170.59	636.22	795.42
Intensities [km/mol]	0.00	0.00	3.58	146.25
Intensities [relative]	0.00	0.00	2.45	100.00

Spin population: Individual basis function populations:

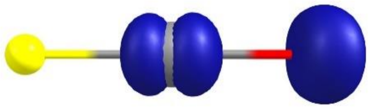
Symmetry no. 1

```
1 1s     1 1s     1 1s     1 1s     1 2px    1 2py    1 2pz    1 2px    1 2py    1 2pz
0.00000  0.00202  0.00003  0.00096  0.40265  0.40265  0.14138  0.00352  0.00352  0.00200

1 2px    1 2py    1 2pz    1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0    1 3d2-
0.01896  0.01896  0.00987  0.00005  0.00000  0.00002  0.00000  0.00002  0.00008  0.00000

1 3d1+   1 3d2+   1 3d1-   1 4f1+   1 4f1-   1 4f0    1 4f3+   1 4f2-   1 4f3-   1 4f2+
-0.00003  0.00000 -0.00003  0.00003  0.00003  0.00009  0.00000  0.00000  0.00000  0.00000


0.00000  0.00015  0.06182  0.01700  0.00076  0.00000  0.00612 -0.00000 -0.00000  0.00000

2 2px    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 2px
0.00003  0.00003  0.00019 -0.00149 -0.00149 -0.00300  0.00851  0.00851  0.00738  0.00053

2 2py    2 2pz    2 2px    2 2py    2 2pz    2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-
0.00053 -0.00058  0.00194  0.00194 -0.00052  0.63791  0.04583  0.51941  0.04583  0.51941

2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-   2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-
0.01995  0.00019  0.03038  0.00019  0.03038 -0.00098  0.00002  0.00333  0.00002  0.00333

2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-   2 4f1+   2 4f1-   2 4f0    2 4f3+   2 4f2-
0.00725 -0.00022 -0.00031 -0.00022 -0.00031  0.00000  0.00000  0.00000  0.00000  0.00000

2 4f3-   2 4f2+   2 4f1+   2 4f1-   2 4f0    2 4f3+   2 4f2-   2 4f3-   2 4f2+   2 5g0
0.00000  0.00000  0.00024  0.00024  0.00009  0.00000  0.00000  0.00000  0.00000 -0.00000

2 5g2-   2 5g1+   2 5g4+   2 5g1-   2 5g2+   2 5g4-   2 5g3+   2 5g3-   3 1s     3 1s
0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 -0.00000  0.00040

3 1s     3 1s     3 2px    3 2py    3 2pz    3 2px    3 2py    3 2pz    3 2px    3 2py
0.00000  0.00021  0.00731  0.00731  0.00585 -0.00001 -0.00001  0.00009  0.00004  0.00004

3 2pz    3 3d0    3 3d2-   3 3d1+   3 3d2+   3 3d1-   3 3d0    3 3d2-   3 3d1+   3 3d2+
0.00127  0.00001  0.00000  0.00000  0.00000  0.00000  0.00017  0.00000  0.00009  0.00000

3 3d1-   3 4f1+   3 4f1-   3 4f0    3 4f3+   3 4f2-   3 4f3-   3 4f2+
0.00009  0.00001  0.00001  0.00002  0.00000  0.00000  0.00000  0.00000
```

Population analysis by basis function type

Unique atom	s	p	d	f	g	Total	Charge
1 O	0.00301	1.00350	0.00013	0.00015	0.00000	1.00679	+ 6.99321
2 Ni	0.08585	0.02252	1.86136	0.00058	-0.00000	1.97030	+26.02970
3 F	0.00060	0.02190	0.00037	0.00004	0.00000	0.02291	+ 8.97709

Spin density plot of ONiF ($^4\Sigma^-$, iso-surface = 0.08 electron a.u.$^{-3}$)

	Spin density ONiF, $^4\Sigma^-$: O: 2*p*(z) = 0.15 Ni: 3*d*(z^2) = 0.66 total σ*-MO: 0.82 O: 2*p*(x) = 0.43; 2*p*(y): 0.43, total: 0.86 Ni: 3*d*(xz) = 0.55: 3*d*(yz) = 0.55, total: 1.11 total xz space: 0.98, total yz space: 0.98.

AIM Charge:

```
Total result:
#Basin       Integral(a.u.)      Vol(Bohr^3)    Vol(rho>0.001)
      1      8.7275249386        1480.095        144.069
      2      26.4642164056        730.919        102.875
      3      9.8081290293        1347.283        128.520
 Sum of above integrals:         44.99987037
 Sum of basin volumes (rho>0.001):     375.465 Bohr^3

Normalization factor of the integral of electron density is    0.999997
The atomic charges after normalization and atomic volumes:
     1 (O )    Charge:   -0.727550     Volume:   144.069 Bohr^3
     2 (Ni)    Charge:    1.535707     Volume:   102.875 Bohr^3
     3 (F )    Charge:   -0.808157     Volume:   128.520 Bohr^3
```

Part 7. CASSCF, CASPT2 calculations of different spin states of ONiF$_2$ ($^3A_1$, $^3B_1$, $^3B_2$, $^3A_2$, $^5A_1$, $^5A_2$; C_{2v})

Table S7.1. Electronic states, structural parameters (Å, deg) and electronic energy differences (kJ mol^{-1}) of selected triplet and quintet states of ONiF$_2$.

Electronic state (C_{2v})	r(Ni–O)	r(Ni–F)	α(F–Ni–F)	$\Delta E_{\mathrm{CASPT2}}$ [d]	ΔE_{MRCI} [e]
$^3A_1$ [a]	1.639	1.714	118.0	126.4	
$^3B_1$ [a]	1.628	1.691	104.9	76.0	
$^3B_2$ [a]	1.622	1.700	107.2	71.7	
$^3A_2$ [a]	1.613	1.697	106.1	0.0	0.0
$^5A_1$ [b]	1.725	1.713	110.7	0.0	11.4
$^5A_2$ [b]	1.732	1.741	113.0	16.6	19.5
$^5A_1$ [c]	1.692	1.722	129.2	--	(6.8) [c]

[a]: CASSCF(12,8)/CASPT2/VTZ-DK level (state-averaging of the four triplet states with equal weights of 0.25). [b]: CASSCF(12,9)/CASPT2/VTZ-DK level (state-averaging of the two quintet states with equal weights of 0.5). [c]: CASSCF(12,9)/CASPT2/AVDZ-DK level. [d]: CASPT2 state energies ($\Delta E_{\mathrm{CASPT2}}$) relative to the lowest state of the same multiplicity. [e]: MRCI single point calculations at CASSCF(12,9)/CASPT2 minimum structures and state-averaging of the three spin states $^3A_2$, $^5A_1$ and $^5A_2$ with equal weights.

Table S7.2. ONiF$_2$ (C_{2v}, $^3A_1$)

SA-CASSCF(12,8)/CASPT2/VTZ-DK
One state of each irrep was included in the state average formalism with equal weights of 0.25: $^3A_1$, $^3B_1$, $^3B_2$, $^3A_2$

```
NiO=         1.63905401 ANGSTROM
NiF=         1.71416023 ANGSTROM
A1=        118.00635602 DEGREE

   OPTG(RS2C)    -1794.39728019
```

```
 CI vector for state symmetry 1
 ==============================

 2aa 22 20 2       0.8215916
 2aa 22 02 2      -0.3929021
 2ab 22 aa 2      -0.2051485
 2aa 22 ba 2       0.1736848
 2aa 22 ab 2       0.1584947
 2ba 22 aa 2      -0.1270311
 a2a 22 ba 2      -0.1128319
 22a 2a 2b a       0.1017100
 a2a 22 ab 2       0.0781010
 22a 2a b2 a       0.0683184
 2aa 20 22 2      -0.0529065
```

NATURAL ORBITALS FOR STATE 1.1 (ms2=2)

```
  Orbital  Occupation    Energy     Coefficients
   10.1     2.00000    -0.70918     3 2pz   0.50365     3 2py   0.66143
   11.1     2.00000    -0.65028     3 2pz  -0.71366     3 2py   0.55061
   12.1     1.97325    -0.69723     1 2pz   0.80236     2 2pz   0.35893     2 2pz  -0.32141     2 3d0   0.40901
   13.1     1.04532    -0.40172     1 2pz   0.36453     2 2pz   0.25400     2 2pz  -0.26310     2 3d0  -0.74279     2 3d2+ -0.45396
                                    3 2pz   0.26757
   14.1     1.00597    -0.42566     2 3d0   0.46580     2 3d2+ -0.83963
   15.1    -0.00000     0.04716     2 1s    0.49386     2 1s    1.57952     2 1s   -0.39118     2 1s   -2.66670
   16.1    -0.00000     0.11462     2 1s    0.40845     2 1s   -0.30979     2 2pz  -2.85072     2 2pz   1.42828     2 2pz   2.49318
   17.1    -0.00000     0.21208     1 1s   -0.28333     2 1s    1.19197     2 1s    5.42406     2 1s   -1.10275     2 1s    0.32508
                                    2 1s   -4.98882     2 2pz   0.40044     2 2pz  -0.29169     2 3d2+  0.25646     3 1s   -0.28716
                                    3 2py   0.29990
   18.1    -0.00000     0.36796     1 1s    0.34679     2 1s   -0.36214     2 1s   -1.65610     2 1s    1.01603     2 2pz  -4.21482
                                    2 2pz   2.06659     2 2pz  -0.28682     2 2pz   2.06871     2 3d0  -0.90672     2 3d2+  0.90129
                                    3 1s    0.68038     3 2py  -0.27494
    4.2     1.99550    -0.68440     1 2px   0.82616     2 3d1+ -0.39051
    5.2     1.96783    -0.79574     1 2px   0.41369     2 3d1+  0.90170
    6.2    -0.00000     0.07363     2 2px  -1.00740     2 2px   0.73189     2 2px   1.45514
    7.2    -0.00000     0.23001     2 2px   6.33962     2 2px  -2.93682     2 2px   0.41183     2 2px  -3.39531
    8.2    -0.00000     0.37970     1 2px   0.26190     1 2px   0.40564     2 2px  -0.63446     2 2px   0.30706     2 2px   0.25834
                                    2 3d1+ -0.29554     2 3d1+  1.60077
    9.2    -0.00000     0.86844     1 2px  -0.49443     1 2px  -0.46307     1 2px   1.64139     2 2px   6.44802     2 2px  -4.75574
                                    2 2px   0.73116     2 2px  -2.71260     2 3d1+  0.36822
    5.3     2.00000    -0.68698     2 2py  -0.41401     2 2py   0.39699     3 2py  -0.84164
    6.3     2.00000    -0.63122     3 2py  -0.27116     3 2pz   0.89084
    7.3     1.54320    -0.52865     1 2py   0.60309     2 3d1- -0.68983
    8.3     0.49434    -0.19569     1 2py   0.70955     2 3d1-  0.63841
    9.3    -0.00000     0.12185     2 2py  -2.83979     2 2py   1.45143     2 2py   2.49399
   10.3    -0.00000     0.39464     1 2py  -0.26593     1 2py  -0.29926     2 2py   0.41581     2 2py   9.31728     2 2py  -4.47118
                                    2 2py   0.60884     2 2py  -4.34605     2 3d1- -0.36962     3 1s   -0.69421     3 2pz   0.27164
                                    3 2py   0.26531     3 2pz   0.28992
   11.3    -0.00000     0.50835     1 2py   0.34928     2 2py   0.31770     2 2py   4.85550     2 2py  -2.10310     2 2py   0.25121
                                    2 2py  -2.08047     2 3d1-  2.16938     3 1s   -1.68923     3 2py   0.60121
   12.3    -0.00000     0.89270     1 2py   0.39561     1 2py   0.43841     1 2py  -1.56075     2 2py  -8.10632     2 2py   5.85445
                                    2 2py  -0.87934     2 2py   3.24532     2 3d1- -0.36303     2 3d1- -0.38506     3 1s    0.42882
    1.4     2.00000    -0.65577     3 2px   0.92094
    2.4     1.97459    -0.88394     2 3d2- -0.97675
    3.4    -0.00000     0.37600     2 3d2- -0.30326     2 3d2-  1.53872     3 2px  -0.28766     3 2px  -0.36083
    4.4    -0.00000     1.09612     2 3d2-  0.49262     3 2px   0.59781     3 2px   0.47335     3 2px  -1.73417
    5.4    -0.00000     1.34811     2 3d2-  1.07234     2 3d2-  2.86959     2 3d2-  0.92906     2 3d2- -3.16151     3 2px   0.39607
    6.4    -0.00000     1.70711     1 3d2-  1.00139     2 3d2- -0.29394     3 2px   0.36486
```

Table S7.3. ONiF$_2$ (C_{2v}, $^3B_1$)

SA-CASSCF(12,8)/CASPT2/VTZ-DK
One state of each irrep was included in the state average formalism with equal weights of 0.25: $^3A_1$, $^3B_1$, $^3B_2$, $^3A_2$

```
 NiO=               1.62846725 ANGSTROM
 NiF=               1.69084681 ANGSTROM
 A1=             104.91145451 DEGREE

     OPTG(RS2C)     -1794.41644445
```

```
 CI vector for state symmetry 2
 ==============================

 220 22 2a a      0.8955373
 202 22 2a a     -0.2598133
 a20 2a 22 2     -0.1773850
 2ba 22 a2 a      0.1473950
 2aa 22 2a b     -0.1454093
 2ab 22 a2 a     -0.1205321
 2aa 22 2b a      0.1096303
 222 20 2a a     -0.0524042
 22a 2b aa 2      0.0505131
```

NATURAL ORBITALS FOR STATE 1.2 (ms2=2)

```
==========================================
Orbital  Occupation    Energy     Coefficients
 10.1     2.00000    -0.69269     3 2pz   0.26431     3 2py   0.79291
 11.1     2.00000    -0.62277     3 2pz  -0.86120     3 2py   0.30435
 12.1     1.95825    -0.72025     2 3d0   0.37890     2 3d2+ -0.89543
 13.1     1.78012    -0.60450     1 2pz   0.66841     2 2pz   0.25337     2 3d0   0.60315     2 3d2+  0.25141
 14.1     0.24449    -0.05040     1 2pz   0.72015     2 3d0  -0.69287
 15.1    -0.00000     0.05170     2 1s   -0.55489     2 1s   -1.85102     2 1s    0.42845     2 1s    2.86727
 16.1    -0.00000     0.10415     2 1s    0.91578     2 1s   -0.91259     2 2pz  -2.72478     2 2pz   1.39984     2 2pz   2.39073
 17.1    -0.00000     0.22751     2 1s   -1.15827     2 1s   -5.35188     2 1s    1.16577     2 1s   -0.33562     2 1s    4.94181
                                  2 2pz  -1.36100     2 2pz   0.66532     2 2pz   0.82471     2 3d2+  0.28123     2 3d2+ -0.28379
                                  3 1s    0.29855     3 2py  -0.33645
 18.1    -0.00000     0.34299     2 1s    0.32031     2 2pz   5.05690     2 2pz  -2.53390     2 2pz   0.35691     2 2pz  -2.53149
                                  2 3d0  -0.25919     2 3d0   0.91507     2 3d2+ -0.57790
  4.2     1.99177    -0.77934     1 2px   0.58673     2 3d1+ -0.74872
  5.2     1.95052    -0.62223     1 2px  -0.76339     2 3d1+ -0.66304
  6.2    -0.00000     0.08215     2 2px  -1.33977     2 2px   0.87148     2 2px   1.63621
  7.2    -0.00000     0.25731     2 2px   6.75407     2 2px  -3.22926     2 2px   0.45294     2 2px  -3.49528
  8.2    -0.00000     0.38014     1 2px   0.26317     1 2px   0.36199     2 2px  -1.19651     2 2px   0.57419     2 2px   0.50601
                                  2 3d1+ -0.33621     2 3d1+ -0.27913     2 3d1+  1.57746
  9.2    -0.00000     0.83746     1 2px  -0.55614     1 2px  -0.48867     1 2px   1.85931     2 2px   1.33129     2 2px  -1.31471
                                  2 2px  -0.69376     2 3d1+  0.33638     2 3d1+  0.26222
  5.3     2.00000    -0.65022     2 2py  -0.28255     2 2py   0.28985     3 2py  -0.85935     3 2pz   0.27668
  6.3     2.00000    -0.61764     3 2py   0.25894     3 2pz   0.88036
  7.3     1.94824    -0.72737     1 2py  -0.30694     2 3d1-  0.91313
  8.3     1.07744    -0.36467     1 2py   0.94302     2 3d1-  0.37597
  9.3    -0.00000     0.13235     2 2py   3.03961     2 2py  -1.50679     2 2py  -2.61945
 10.3    -0.00000     0.45475     1 2py  -0.28489     2 2py   0.53758     2 2py  11.60866     2 2py  -5.70143     2 2py   0.77132
                                  2 2py  -5.23324     3 1s   -1.11931     3 2py   0.43963
 11.3    -0.00000     0.50676     1 2py  -0.25685     1 2py  -0.32131     2 2py  -1.84188     2 2py   0.78371     2 2py   0.78936
                                  2 3d1-  0.30487     2 3d1-  0.33615     2 3d1- -2.11295     3 1s    0.82495     3 2pz   0.34876
                                  3 2py  -0.32769     3 2pz   0.34019
 12.3    -0.00000     0.85771     1 2py  -0.45172     1 2py  -0.48043     1 2py   1.88652     2 2py   2.32063     2 2py  -2.44515
                                  2 2py   0.41057     2 2py  -0.90080     2 3d1-  0.69605     3 2py  -0.45156
  1.4     2.00000    -0.63069     3 2px   0.91739
  2.4     1.04917    -0.32777     2 3d2- -0.99073
  3.4    -0.00000     0.42251     2 3d2- -0.33868     2 3d2- -0.32116     2 3d2-  1.69160     3 2px  -0.33352     3 2px  -0.40783
  4.4    -0.00000     1.17010     2 3d2- -0.61141     3 2px  -0.56646     3 2px  -0.48368     3 2px   1.85333
  5.4    -0.00000     1.44049     2 3d2-  1.02870     2 3d2-  2.82057     2 3d2-  0.93098     2 3d2- -3.17885     3 2px  -0.29904
                                  3 2px   0.54343
  6.4    -0.00000     1.67333     1 3d2-  0.99908     2 3d2- -0.33566     3 2px   0.46714
```

Table S7.4. $ONiF_2$ (C_{2v}, $^3B_2$)

SA-CASSCF(12,8)/CASPT2/VTZ-DK
One state of each irrep was included in the state average formalism with equal weights of 0.25: $^3A_1$, $^3B_1$, $^3B_2$, $^3A_2$

```
Optimized variables
NiO=              1.62227942 ANGSTROM
NiF=              1.70008875 ANGSTROM
A1=             107.16317080 DEGREE

    OPTG(RS2C)    -1794.41811465

CI vector for state symmetry 3
==============================

 2a0 22 2a 2      0.9207864
 0a2 22 2a 2     -0.2405264
 baa 22 a2 2      0.1765311
 aab 22 a2 2     -0.1380549
 aba 22 2a 2      0.1230884
 aaa 22 2b 2     -0.0810875
 2a2 20 2a 2     -0.0508304
```

NATURAL ORBITALS FOR STATE 1.3 (ms2=2)

```
=========================================
Orbital  Occupation    Energy     Coefficients
 10.1     2.00000    -0.67989     3 2pz   0.28308     3 2py   0.78730
 11.1     2.00000    -0.61782     3 2pz  -0.85110     3 2py   0.32731
 12.1     1.80066    -0.61183     1 2pz   0.66626     2 2pz   0.26224     2 3d0   0.64814
 13.1     1.00660    -0.31524     2 3d0   0.30226     2 3d2+ -0.91756
 14.1     0.21611    -0.04361     1 2pz   0.70606     2 3d0  -0.68471     2 3d2+ -0.25809
 15.1    -0.00000     0.05247     2 1s   -0.55886     2 1s   -1.87154     2 1s    0.43495     2 1s    2.89734
 16.1    -0.00000     0.10545     2 1s    0.83479     2 1s   -0.80932     2 2pz  -2.72695     2 2pz   1.39518     2 2pz   2.39887
 17.1    -0.00000     0.22944     1 1s    0.25509     2 1s   -1.16578     2 1s   -5.38217     2 1s    1.16386     2 1s   -0.33575
                                  2 1s    4.94934     2 2pz  -1.27583     2 2pz   0.62059     2 2pz   0.77586     2 3d2+  0.27589
                                  2 3d2+ -0.28949     3 1s    0.30333     3 2py  -0.33689
 18.1    -0.00000     0.34457     2 1s    0.27140     2 2pz   5.15752     2 2pz  -2.56896     2 2pz   0.36053     2 2pz  -2.57143
                                  2 3d0  -0.25723     2 3d0   0.90870     2 3d2+ -0.60259     3 1s   -0.26848
  4.2     1.99712    -0.75959     1 2px   0.74325     2 3d1+ -0.57673
  5.2     1.98477    -0.67341     1 2px   0.60652     2 3d1+  0.81544
  6.2    -0.00000     0.07953     2 2px  -1.24408     2 2px   0.82567     2 2px   1.58784
  7.2    -0.00000     0.25100     2 2px   6.70003     2 2px  -3.18925     2 2px   0.44614     2 2px  -3.48833
  8.2    -0.00000     0.37684     1 2px   0.26069     1 2px   0.37514     2 2px  -1.13808     2 2px   0.54547     2 2px   0.48176
                                  2 3d1+ -0.32846     2 3d1+ -0.26946     2 3d1+  1.57868
  9.2    -0.00000     0.84176     1 2px  -0.55061     1 2px  -0.48945     1 2px   1.84844     2 2px   1.79346     2 2px  -1.62887
                                  2 2px   0.26754     2 2px  -0.87465     2 3d1+  0.35220
  5.3     2.00000    -0.64596     2 2py  -0.29541     2 2py   0.30198     3 2py  -0.87537
  6.3     2.00000    -0.60917     3 2pz   0.89923
  7.3     1.94189    -0.71142     1 2py   0.38247     2 3d1- -0.87501
  8.3     1.05983    -0.35447     1 2py   0.90715     2 3d1-  0.44980
  9.3    -0.00000     0.13190     2 2py  -3.02815     2 2py   1.50790     2 2py   2.61039
 10.3    -0.00000     0.44870     1 2py   0.29620     2 2py  -0.51819     2 2py -11.28098     2 2py   5.53072     2 2py  -0.74877
                                  2 2py   5.10459     3 1s    1.04513     3 2py  -0.41490
 11.3    -0.00000     0.50941     1 2py   0.30560     2 2py   2.75627     2 2py  -1.20695     2 2py  -1.18033     2 3d1- -0.28333
                                  2 3d1- -0.31638     2 3d1-  2.11557     3 1s   -1.01739     3 2pz  -0.32338     3 2py   0.40269
                                  3 2pz  -0.28109
 12.3    -0.00000     0.86687     1 2py   0.44618     1 2py   0.47762     1 2py  -1.85550     2 2py  -2.93341     2 2py   2.78450
                                  2 2py  -0.45672     2 2py   1.14854     2 3d1- -0.67290     3 2py   0.42367
  1.4     2.00000    -0.63202     3 2px   0.91885
  2.4     1.99300    -0.76749     2 3d2- -0.98952
  3.4    -0.00000     0.41174     2 3d2- -0.32776     2 3d2- -0.28742     2 3d2-  1.64810     3 2px  -0.32550     3 2px  -0.40316
  4.4    -0.00000     1.15855     2 3d2-  0.62579     3 2px   0.56883     3 2px   0.48168     3 2px  -1.81970
  5.4    -0.00000     1.40675     2 3d2-  1.03333     2 3d2-  2.82148     2 3d2-  0.92023     2 3d2- -3.17973     3 2px  -0.28988
                                  3 2px   0.54019
  6.4    -0.00000     1.68110     1 3d2-  0.99917     2 3d2- -0.33775     3 2px   0.45799
```

Table S7.5. ONiF$_2$ (C_{2v}, $^3A_2$)

SA-CASSCF(12,8)/CASPT2/VTZ-DK
One state of each irrep was included in the state average formalism with equal weights of 0.25: $^3A_1$, $^3B_1$, $^3B_2$, $^3A_2$

Optimized variables
NiO= 1.61334849 ANGSTROM
NiF= 1.69730988 ANGSTROM
A1= 106.14936968 DEGREE

```
    OPTG(RS2C)
 -1794.44540863
```

```
 CI vector for state symmetry 4
 ==============================
 220 2a 2a 2      0.8846321
 220 a2 a2 2     -0.2089927
 202 2a 2a 2     -0.1747528
 2ba 2a a2 2      0.1494223
 2ab 2a a2 2     -0.1321089
 2ba a2 2a 2      0.1306030
 202 a2 a2 2      0.1297548
 2ab a2 2a 2     -0.1073386
 2aa b2 2a 2     -0.0632194
 022 2a 2a 2     -0.0627763
 22b aa 22 a     -0.0583334
 202 a2 2a 2      0.0574001
 22a 20 22 a     -0.0562372
 2aa 2b 2a 2      0.0556615
 2aa 2a b2 2     -0.0546472
 222 2a 2a 0     -0.0543905
```

```
NATURAL ORBITALS FOR STATE 1.4 (ms2=2)
==============================================
  Orbital  Occupation    Energy     Coefficients
   10.1     2.00000    -0.68025     3 2pz   0.27370     3 2py   0.78957
   11.1     2.00000    -0.61603     3 2pz  -0.85631     3 2py   0.31582
   12.1     1.97836    -0.73346     2 3d0   0.61357     2 3d2+ -0.75862

15.1    -0.00000     0.05263     2 1s   -0.56483     2 1s   -1.89512     2 1s    0.43518     2 1s    2.91423
   16.1    -0.00000     0.10340     2 1s    0.82638     2 1s   -0.78125     2 2pz  -2.68984     2 2pz   1.37822     2 2pz   2.37925
   17.1    -0.00000     0.23123     1 1s    0.27261     2 1s   -1.17174     2 1s   -5.41100     2 1s    1.18393     2 1s   -0.34044
                                    2 1s    4.98085     2 2pz  -1.26251     2 2pz   0.60917     2 2pz   0.78393     2 3d2+  0.27615
                                    2 3d2+ -0.28952     3 1s    0.29620     3 2py  -0.33671
   18.1    -0.00000     0.34126     2 1s    0.39043     2 2pz   5.12354     2 2pz  -2.56783     2 2pz   0.36115     2 2pz  -2.55230
                                    2 3d0  -0.25105     2 3d0   0.89093     2 3d2+ -0.58756
    4.2     1.88583    -0.65664     1 2px   0.73485     2 3d1+ -0.58651
    5.2     1.11121    -0.38858     1 2px   0.61538     2 3d1+  0.80847
    6.2    -0.00000     0.08320     2 2px  -1.39722     2 2px   0.89285     2 2px   1.66988
    7.2    -0.00000     0.26131     2 2px   6.82390     2 2px  -3.27915     2 2px   0.45971     2 2px  -3.50721
    8.2    -0.00000     0.38298     1 2px   0.26401     1 2px   0.37239     2 2px  -1.34562     2 2px   0.66128     2 2px   0.57578
                                    2 3d1+ -0.33730     2 3d1+ -0.29805     2 3d1+  1.60236
    9.2    -0.00000     0.83282     1 2px  -0.55021     1 2px  -0.49201     1 2px   1.86828     2 2px   1.41577     2 2px  -1.38168
                                    2 2px  -0.72629     2 3d1+  0.34181     2 3d1+  0.26718
    5.3     2.00000    -0.64213     2 2py  -0.29168     2 2py   0.29822     3 2py  -0.86664
    6.3     2.00000    -0.60787     3 2pz   0.89022
    7.3     1.88732    -0.67962     1 2py   0.55659     2 3d1- -0.76725
    8.3     1.12247    -0.39710     1 2py   0.81192     2 3d1-  0.61682
    9.3    -0.00000     0.13270     2 2py  -3.06052     2 2py   1.51948     2 2py   2.62615
   10.3    -0.00000     0.45577     1 2py  -0.28911     2 2py   0.52569     2 2py  11.47138     2 2py  -5.64645     2 2py   0.76554
                                    2 2py  -5.17679     3 1s   -1.06456     3 2py   0.42138
   11.3    -0.00000     0.50822     1 2py   0.25703     1 2py   0.29426     2 2py   2.50818     2 2py  -1.09394     2 2py  -1.07339
                                    2 3d1- -0.29089     2 3d1- -0.32936     2 3d1-  2.10998     3 1s   -0.94640     3 2pz  -0.33044
                                    3 2py   0.37580     3 2pz  -0.30535
   12.3    -0.00000     0.85606     1 2py   0.45652     1 2py   0.47597     1 2py  -1.90640     2 2py  -2.25603     2 2py   2.36190
                                    2 2py  -0.39613     2 2py   0.88996     2 3d1- -0.72168     3 2py   0.40867
    1.4     2.00000    -0.62815     3 2px   0.91832
    2.4     1.97156    -0.71737     2 3d2- -0.98936
    3.4    -0.00000     0.41964     2 3d2- -0.33281     2 3d2- -0.30347     2 3d2-  1.66901     3 2px  -0.32856     3 2px  -0.40626
    4.4    -0.00000     1.16613     2 3d2- -0.61512     3 2px  -0.56738     3 2px  -0.48176     3 2px   1.82851
    5.4    -0.00000     1.42658     2 3d2-  1.02908     2 3d2-  2.81353     2 3d2-  0.91982     2 3d2- -3.17538     3 2px  -0.29429
                                    3 2px   0.54665
    6.4    -0.00000     1.66250     1 3d2-  0.99719     2 3d2- -0.30747     3 2px   0.47539
```

Table S7.6. ONiF$_2$ (C_{2v}, $^3A_2$)

CASSCF(12,8)/CASPT2/VTZ-DK (State specific reference wavefunction)
Optimization and normal mode calculation carried out in C_1 point group symmetry.
NiO= 1.60065022 ANGSTROM
NiF= 1.69444611 ANGSTROM
A1= 107.85986869 DEGREE

```
 PSEUDO CANONICAL ORBITALS
 =======================


   Orbital  Occupation    Energy     Coefficients
     1.1     2.00000  -308.87462     2 1s    0.99248
     2.1     2.00000   -38.74149     2 1s    0.99241
     3.1     2.00000   -33.21709     2 2pz   0.99995
     4.1     2.00000   -33.20500     2 2py   0.99996
     5.1     2.00000   -33.18995     2 2px   0.99995
     6.1     2.00000   -26.27000     3 1s    0.70657     4 1s   -0.70656
     7.1     2.00000   -26.26999     3 1s    0.70654     4 1s    0.70655
     8.1     2.00000   -20.77408     1 1s    0.99912
     9.1     2.00000    -5.06522     2 1s    0.99065
    10.1     2.00000    -3.42727     2 2pz   0.99636
    11.1     2.00000    -3.41480     2 2py   0.99735
    12.1     2.00000    -3.40206     2 2px   0.99957
    13.1     2.00000    -1.53148     3 1s    0.66532     4 1s    0.66532
    14.1     2.00000    -1.52171     3 1s    0.67110     4 1s   -0.67110
    15.1     2.00000    -1.38502     1 1s    0.98287
    16.1     2.00000    -0.68427     3 2py   0.54300     4 2py  -0.54300
    17.1     2.00000    -0.64205     2 2py  -0.29144     2 2py   0.29802     3 2py  -0.62588
                                     4 2py  -0.62588
    18.1     2.00000    -0.62496     3 2px   0.65461     4 2px  -0.65461
    19.1     2.00000    -0.61649     3 2py   0.25937     3 2pz  -0.58844     4 2py  -0.25937
                                     4 2pz  -0.58844
    20.1     2.00000    -0.61582     3 2px   0.65169     4 2px   0.65169
    21.1     2.00000    -0.60517     3 2pz   0.64126     4 2pz  -0.64126
    22.1     1.97105    -0.78225     1 2pz   0.26043     2 3d0   0.66211     2 3d2+ -0.64394
    23.1     1.98090    -0.72439     2 3d2- -0.99709
    24.1     1.88561    -0.68633     1 2py   0.51591     2 3d1- -0.79930
    25.1     1.88427    -0.66110     1 2px   0.66247     2 3d1+ -0.66911
    26.1     1.81922    -0.61965     1 2pz  -0.76619     2 3d2+ -0.53021
    27.1     1.12004    -0.39123     1 2py   0.84344     2 3d1-  0.57562
    28.1     1.11111    -0.38485     1 2px   0.71454     2 3d1+  0.73900
    29.1     0.22780     0.00657     1 2pz  -0.64716     2 3d0   0.70291     2 3d2+  0.42539
    30.1    -0.00000     0.05447     2 1s   -0.58431     2 1s   -1.98008     2 1s    0.44597
                                     2 1s    2.99393
    31.1    -0.00000     0.08392     2 2px  -1.43258     2 2px   0.91086     2 2px   1.68801
    32.1    -0.00000     0.10477     2 1s    0.63754     2 1s   -0.52807     2 2pz  -2.72599
                                     2 2pz   1.39148
                                     2 2pz   2.40275
    33.1    -0.00000     0.13167     2 2py  -3.06290     2 2py   1.51928     2 2py   2.62372
```

```
CI vector
=========
22222aa0       0.8837864
22aa2220      -0.2073761
22220aa2      -0.1516064
22a2b2aa       0.1441517
22a2a2ab      -0.1332465
222aba2a      -0.1286885
22aa0222       0.1199331
222aaa2b       0.1080996
```

```
2222aaab      -0.0917411
2222baaa       0.0877084
a22a2a2b       0.0679282
b22a2a2a      -0.0666418
02222aa2      -0.0631732
222baa2a       0.0582711
```

```
Gradient norm at reference geometry: 0.29822D-04
Atomic masses
Center    Mass
O       15.99491
Ni      57.93530
F       18.99840
F       18.99840
```

$^{16}O^{58}NiF_2$

```
                        1 B2     2 A1     3 B1     4 A1     5 B2     6 A1
 Wavenumbers [cm-1]     161.14   193.73   212.20   687.21   782.62   908.89
 Intensities [km/mol]    0.00     0.00     0.00     0.00     0.00     0.00
 Intensities [relative]  0.00     0.00     0.00     0.00     0.00     0.00
```

$^{16}O^{60}NiF_2$

```
                        1 B2     2 A1     3 B1     4 A1     5 B2     6 A1
 Wavenumbers [cm-1]     160.03   192.88   209.94   686.55   777.59   905.32
 Intensities [km/mol]    0.00     0.00     0.00     0.00     0.00     0.00
 Intensities [relative]  0.00     0.00     0.00     0.00     0.00     0.00
```

$^{16}O^{62}NiF_2$

```
                        1 B2     2 A1     3 B1     4 A1     5 B2     6 A1
 Wavenumbers [cm-1]     160.04   192.02   208.43   686.20   772.99   902.02
 Intensities [km/mol]    0.00     0.00     0.00     0.00     0.00     0.00
 Intensities [relative]  0.00     0.00     0.00     0.00     0.00     0.00
```

$^{18}O^{58}NiF_2$

```
                        1 B2     2 A1     3 B1     4 A1     5 B2     6 A1
 Wavenumbers [cm-1]     153.98   192.48   210.52   685.91   782.44   869.13
 Intensities [km/mol]    0.00     0.00     0.00     0.00     0.00     0.00
 Intensities [relative]  0.00     0.00     0.00     0.00     0.00     0.00
```

$^{18}O^{60}NiF_2$

```
                        1 B2     2 A1     3 B1     4 A1     5 B2     6 A1
 Wavenumbers [cm-1]     154.27   192.25   208.97   685.80   777.58   865.55
 Intensities [km/mol]    0.00     0.00     0.00     0.00     0.00     0.00
 Intensities [relative]  0.00     0.00     0.00     0.00     0.00     0.00
```

$^{18}O^{62}NiF_2$

```
                        1 B2     2 A1     3 B1     4 A1     5 B2     6 A1
 Wavenumbers [cm-1]     154.89   191.43   207.41   685.44   772.94   862.02
 Intensities [km/mol]    0.00     0.00     0.00     0.00     0.00     0.00
 Intensities [relative]  0.00     0.00     0.00     0.00     0.00     0.00
```

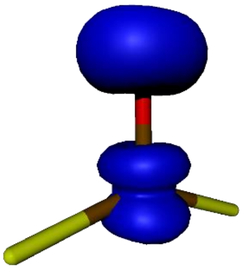
Spin population: Individual basis function populations:

```
Symmetry no. 1
    1 1s     1 1s     1 1s     1 1s     1 2px    1 2py    1 2pz    1 2px    1 2py    1 2pz
   0.00000  0.00012 -0.00000  0.00005  0.44611  0.57322  0.00960  0.00356  0.00568  0.00004

    1 2px    1 2py    1 2pz    1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0    1 3d2-
   0.00063 -0.00514 -0.00060  0.00000  0.00000  0.00002  0.00000  0.00001  0.00002  0.00000

    1 3d1+   1 3d2+   1 3d1-   1 4f1+   1 4f1-   1 4f0    1 4f3+   1 4f2-   1 4f3-   1 4f2+
  -0.00033  0.00000 -0.00038  0.00002  0.00001  0.00000  0.00000  0.00000  0.00000 -0.00000

    2 1s     2 1s     2 1s     2 1s     2 1s     2 1s     2 1s     2 2px    2 2py    2 2pz
   0.00000  0.00010 -0.00027 -0.00005  0.00000  0.00000 -0.00000 -0.00000  0.00000  0.00000

    2 2px    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 2px
   0.00005  0.00007  0.00006 -0.00852 -0.00491 -0.00037  0.00768  0.00216  0.00042  0.00040

    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-
   0.00020 -0.00004  0.00243  0.00302 -0.00001  0.01693  0.00737  0.49617 -0.00316  0.34271

    2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-   2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-
   0.00148  0.00014  0.03145  0.00003  0.04499 -0.00005  0.00001  0.00310 -0.00001  0.00363

    2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-   2 4f1+   2 4f1-   2 4f0    2 4f3+   2 4f2-
   0.00015 -0.00002 -0.00312 -0.00011 -0.00795  0.00000  0.00000  0.00000  0.00000  0.00000

    2 4f3-   2 4f2+   2 4f1+   2 4f1-   2 4f0    2 4f3+   2 4f2-   2 4f3-   2 4f2+   2 5g0
   0.00000  0.00000  0.00031  0.00046  0.00001  0.00001  0.00000  0.00004 -0.00000 -0.00000

    2 5g2-   2 5g1+   2 5g4+   2 5g1-   2 5g2+   2 5g4-   2 5g3+   2 5g3-   3 1s     3 1s
   0.00000 -0.00000  0.00000 -0.00000 -0.00000  0.00000  0.00000 -0.00000  0.00000  0.00028

    3 1s     3 1s     3 2px    3 2py    3 2pz    3 2px    3 2py    3 2pz    3 2px    3 2py
  -0.00000 -0.00008  0.00233  0.01121  0.00047 -0.00002  0.00024 -0.00001  0.00006  0.00070

    3 2pz    3 3d0    3 3d2-   3 3d1+   3 3d2+   3 3d1-   3 3d0    3 3d2-   3 3d1+   3 3d2+
  -0.00003  0.00000  0.00000  0.00000  0.00000  0.00000  0.00002  0.00000  0.00000 -0.00002

    3 3d1-   3 4f1+   3 4f1-   3 4f0    3 4f3+   3 4f2-   3 4f3-   3 4f2+   4 1s     4 1s
   0.00002  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00028

    4 1s     4 1s     4 2px    4 2py    4 2pz    4 2px    4 2py    4 2pz    4 2px    4 2py
  -0.00000 -0.00008  0.00233  0.01121  0.00047 -0.00002  0.00024 -0.00001  0.00006  0.00070

    4 2pz    4 3d0    4 3d2-   4 3d1+   4 3d2+   4 3d1-   4 3d0    4 3d2-   4 3d1+   4 3d2+
  -0.00003  0.00000  0.00000  0.00000  0.00000  0.00000  0.00002  0.00000  0.00000 -0.00002

    4 3d1-   4 4f1+   4 4f1-   4 4f0    4 4f3+   4 4f2-   4 4f3-   4 4f2+
   0.00002  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
```

Population analysis by basis function type

```
  Unique atom      s        p          d          f        g      Total      Charge
    1   O       0.00017  1.03309 -0.00065  0.00003 0.00000  1.03263   +6.96737
    2   Ni     -0.00023  0.00263  0.93375  0.00083 -0.00000  0.93698  +27.06302
    3   F       0.00020  0.01496  0.00003  0.00001  0.00000  0.01519  +8.98481
    4   F       0.00020  0.01496  0.00003  0.00001  0.00000  0.01519  +8.98481
```

Spin density plots of ONiF$_2$ ($^3A_2$; iso-surface = 0.05 electron a.u.$^{-3}$)

	Spin density ONiF$_2$, $^3A_2$: O: 2*p*(x) = 0.45; 2*p*(y): 0.57, total: 1.03 Ni: 3*d*(xz) = 0.53: 3*d*(yz) = 0.39, total: 0.92 total xz space: 0.98, total yz space: 0.97.

AIM Charge:

```
Total result:
  #Basin      Integral(a.u.)      Vol(Bohr^3) Vol(rho > 0.001)
      1         8.2788193535        1208.853 116.755
      2        26.1908143122         309.992 78.373
      3         9.7649091561        1115.337 123.987
      4         9.7649092619        1115.347 123.987
Sum of above integrals:        53.99945208
Sum of basin volumes (rho > 0.001):     443.103 Bohr^3


Normalization factor of the integral of electron density is    0.999990
The atomic charges after normalization and atomic volumes:
      1 (O )    Charge:   -0.278903     Volume:   116.755 Bohr^3
      2 (Ni)    Charge:    1.808920     Volume:    78.373 Bohr^3
      3 (F )    Charge:   -0.765008     Volume:   123.987 Bohr^3
      4 (F )    Charge:   -0.765008     Volume:   123.987 Bohr^3
```

Summary of Natural Population Analysis:

```
                                      Natural Population
           Natural  -----------------------------------------------
Atom No    Charge        Core      Valence    Rydberg      Total
  --------------------------------------------------------------------
    O  1    -0.22559      2.00000      6.21413  0.01146      8.22559
   Ni  2     1.81370     17.99892      8.13876  0.04862     26.18630
    F  3    -0.79406      2.00000      7.78546  0.00860      9.79406
    F  4    -0.79406      2.00000      7.78546  0.00860      9.79406
  ====================================================================
    Total    0.00000     23.99891     29.92381  0.07728     54.00000
```

Table S7.7. ONiF$_2$ (C_{2v}, $^5A_1$)

SA-CASSCF(12,9)/CASPT2/VTZ-DK
With equal weights of 0.5: $^5A_1$, $^5A_2$

Optimized variables
NiO= 1.72522963 ANGSTROM
NiF= 1.71334104 ANGSTROM
A1= 110.67700622 DEGREE

OPTG(RS2C) -1794.59535611

CI vector for state symmetry 1
===============================

```
22a0 2a 2a a      0.8971782
2a20 2a a2 a     -0.2071621
22a0 a2 a2 a      0.1928959
22a0 a2 2a a     -0.1543252
22a0 2a a2 a      0.1542808
2a20 a2 2a a      0.1239580
a2a0 aa 22 2     -0.1188943
2a20 2a 2a a      0.1006073
a220 a2 2a a      0.0576828
2aa0 22 aa 2     -0.0524862
```

NATURAL ORBITALS FOR STATE 1.1 (ms2=4)

```
   10.1     2.00000    -0.68549     3 2pz   0.41982     3 2py   0.73395
   11.1     2.00000    -0.61730     3 2pz  -0.79337     3 2py   0.44818
   12.1     1.98144    -0.76956     2 3d0  -0.30020     2 3d2+  0.92351
   13.1     1.90996    -0.71005     1 2pz  -0.76664     2 2pz  -0.31356     2 2pz   0.27523     2 3d0  -0.51188
   14.1     1.07305    -0.33662     1 2pz   0.54933     2 3d0  -0.79138     2 3d2+ -0.25414
   15.1     0.01927     0.77403     1 1s    0.29617     1 2pz   1.08964     1 2pz  -0.65922     2 1s   -0.32643     2 1s   -0.40141
                                    2 1s   -0.28343     2 2pz  -1.52019     2 2pz   1.52889     2 2pz   0.47932     2 3d0  -0.51900
                                    2 3d2+ -0.35197     2 3d0   0.39947
   16.1    -0.00000     0.06904     2 1s   -0.76024     2 1s   -2.89060     2 1s    0.57830     2 1s    3.71199     2 2pz   0.90948
                                    2 2pz  -0.38100     2 2pz  -0.73650
   17.1    -0.00000     0.11213     2 1s   -0.66133     2 1s    0.82795     2 2pz  -2.46120     2 2pz   1.33853     2 2pz   2.24666
   18.1    -0.00000     0.31798     2 1s    0.73361     2 1s    3.47543     2 1s   -0.93310     2 1s    0.25882     2 1s   -3.28523
                                    2 2pz   5.60612     2 2pz  -2.60004     2 2pz   0.36065     2 2pz  -2.75701     2 3d0   0.30465
                                    3 1s   -0.31938     3 2py   0.32359     3 2py   0.25223
   19.1    -0.00000     0.37987     1 1s    0.93684     1 2pz   0.26766     2 1s   -0.25298     2 1s   -1.00952     2 2pz   1.57684
                                    2 2pz  -0.59123     2 2pz  -0.59611     2 3d0  -1.07625     2 3d2+  1.15945     3 1s    0.41851
    4.2     1.90802    -0.71214     1 2px   0.38108     2 3d1+ -0.88734
    5.2     1.07920    -0.38838     1 2px   0.90221     2 3d1+  0.44912
    6.2    -0.00000     0.07790     2 2px  -1.19482     2 2px   0.80362     2 2px   1.56073
    7.2    -0.00000     0.24572     2 2px  -6.65568     2 2px   3.16527     2 2px  -0.44431     2 2px   3.48339
    8.2    -0.00000     0.38098     1 2px   0.30836     2 2px  -0.54047     2 2px   0.28965     2 3d1+ -0.35425     2 3d1+ -0.28574
                                    2 3d1+  1.57775
    9.2    -0.00000     0.82628     1 2px  -0.54569     1 2px  -0.50225     1 2px   1.80748     2 2px   0.75384     2 2px  -0.82580
                                    2 2px  -0.47369     2 3d1+  0.27890     2 3d1+  0.28616
    5.3     2.00000    -0.64572     2 2py  -0.33638     2 2py   0.34490     3 2py  -0.88972
    6.3     2.00000    -0.60909     3 2pz   0.92304
    7.3     1.89097    -0.65632     1 2py  -0.57289     2 3d1-  0.75395
    8.3     1.11840    -0.40054     1 2py   0.78518     2 3d1-  0.62597
    9.3    -0.00000     0.12927     2 2py  -2.97662     2 2py   1.49406     2 2py   2.57616
   10.3    -0.00000     0.42289     1 2py  -0.26703     2 2py   0.43138     2 2py   9.83681     2 2py  -4.82202     2 2py   0.65717
                                    2 2py  -4.53041     2 3d1- -0.52199     3 1s   -0.74346     3 2py   0.30673     3 2pz   0.28682
   11.3    -0.00000     0.51576     2 2py   0.31643     2 2py   5.35474     2 2py  -2.44686     2 2py   0.30699     2 2py  -2.30988
                                    2 3d1- -0.26263     2 3d1-  2.01259     3 1s   -1.37843     3 2py   0.54418
   12.3    -0.00000     0.85829     1 2py  -0.49018     1 2py  -0.47711     1 2py   1.79747     2 2py   2.86562     2 2py  -2.42527
                                    2 2py   0.38861     2 2py  -1.19713     2 3d1-  0.70044     3 2py  -0.26824
    2.4     1.01970    -0.34299     2 3d2- -0.98378
    3.4    -0.00000     0.40719     2 3d2-  0.33240     2 3d2-  0.30781     2 3d2- -1.65051     3 2px   0.31542     3 2px   0.39686
    4.4    -0.00000     1.14559     2 3d2-  0.50577     3 2px   0.58650     3 2px   0.48260     3 2px  -1.79801
    5.4    -0.00000     1.42690     2 3d2-  1.05907     2 3d2-  2.86748     2 3d2-  0.94627     2 3d2- -3.16503     3 2px  -0.26125
                                    3 2px   0.42478
    6.4    -0.00000     1.66328     1 3d2-  1.00332     2 3d2- -0.41851     3 2px   0.43579
```

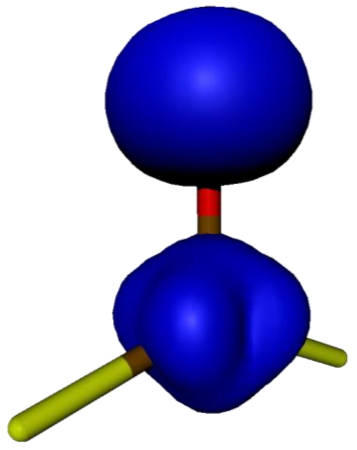
Spin population: Individual basis function populations:

```
Symmetry no. 1
1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0
0.00000  0.00144 -0.00001 -0.00004  0.29911  0.00377 -0.00167  0.00003 -0.00000  0.00003

1 3d2+   1 4f0    1 4f2+   2 1s     2 1s     2 1s     2 1s     2 1s     2 1s     2 1s
-0.00002  0.00009 -0.00000 -0.00000 -0.00002 -0.00853 -0.00030  0.00012 -0.00000  0.00043

2 2pz    2 2pz    2 2pz    2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+
0.00000  0.00033 -0.02179  0.03714 -0.00153 -0.00076  0.53871  0.06347  0.03521  0.01612

2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0    2 4f2+   2 4f0    2 4f2+   2 5g0    2 5g4+
-0.00030  0.00004  0.00225  0.00320  0.00000 -0.00000  0.00016  0.00001  0.00000  0.00000

2 5g2+   3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py    3 2pz    3 2py    3 2pz
-0.00000  0.00000  0.00077 -0.00000 -0.00011  0.02903  0.00913  0.00003  0.00018  0.00098

3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-
0.00073  0.00000 -0.00000  0.00001 -0.00001 -0.00001  0.00007  0.00001  0.00001  0.00000

3 4f3-
-0.00000

 Symmetry no. 2
1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 4f1+   1 4f3+   2 2px    2 2px    2 2px
0.79256  0.00854 -0.01135  0.00001 -0.00018  0.00001  0.00000  0.00000  0.00003 -0.01024

2 2px    2 2px    2 2px    2 3d1+   2 3d1+   2 3d1+   2 3d1+   2 4f1+   2 4f3+   2 4f1+
0.00885  0.00066  0.00294  0.18710  0.02576  0.00310 -0.00630  0.00000  0.00000  0.00028

2 4f3+   2 5g1+   2 5g3+   3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
0.00000  0.00000  0.00000  0.00352 -0.00003  0.00014  0.00000  0.00000  0.00000 -0.00000

3 4f1+   3 4f3+   3 4f2-
0.00000  0.00000 -0.00000

 Symmetry no. 3
1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 4f1-   1 4f3-   2 2py    2 2py    2 2py
0.65533  0.00636 -0.00847  0.00001 -0.00024  0.00002  0.00000  0.00000  0.00006 -0.00233

2 2py    2 2py    2 2py    2 3d1-   2 3d1-   2 3d1-   2 3d1-   2 4f1-   2 4f3-   2 4f1-
0.00127  0.00002  0.00201  0.29059  0.03747  0.00371 -0.00746  0.00000  0.00000  0.00024

2 4f3-   2 5g1-   2 5g3-   3 1s     3 1s     3 1s     3 1s     3 2py    3 2pz    3 2py
0.00003  0.00000  0.00000  0.00000  0.00046  0.00000 -0.00007  0.01926  0.00042  0.00031

3 2pz    3 2py    3 2pz    3 3d1-   3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 4f1-
-0.00001  0.00119 -0.00007 -0.00000  0.00000  0.00000  0.00000  0.00004 -0.00001  0.00001

3 4f3-   3 4f0    3 4f2+
0.00000  0.00000 -0.00000

 Symmetry no. 4
1 3d2-   1 3d2-   1 4f2-   2 3d2-   2 3d2-   2 3d2-   2 3d2-   2 4f2-   2 4f2-   2 5g2-
0.00000  0.00005  0.00000  0.92390  0.03413  0.00282  0.00246  0.00000  0.00003  0.00000

2 5g4-   3 2px    3 2px    3 2px    3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 4f2-   3 4f1+
0.00000  0.02300 -0.00010  0.00058  0.00001  0.00000  0.00001  0.00003  0.00001 -0.00000

3 4f3+
0.00001
```

Population analysis by basis function type

```
Unique atom    s          p          d          f          g         Total       Charge
  1  O       0.00139  1.74419   -0.00030   0.00013   0.00000   1.74540     +6.25460
  2  Ni     -0.00831  0.01666    2.15596   0.00075   0.00001   2.16507     +25.83493
  3  F       0.00052   0.04415    0.00007   0.00002   0.00000   0.04476    + 8.95524
  4  F       0.00052   0.04415    0.00007   0.00002   0.00000   0.04476    + 8.95524
```

Spin densities of ONiF$_2$ ($^5A_1$; iso-surface = 0.05 electron a.u.$^{-3}$)



Spin density ONiF$_2$, $^5A_1$:
O: 2*p*(x) = 0.79; 2*p*(y): 0.65, total: 1.44
Ni: 3*d*(xz) = 0.21: 3*d*(yz) = 0.33, total: 0.54
total xz space: 1.00, total yz space: 0.98
Conclusion: 2 unpaired electrons distributed over the π*-MOs and strongly polarized towards oxygen (inversion!).

O: 2*p*(z) = 0.30
Ni: 3*d*(x^2)/3*d*(y^2-z^2): 0.65
total σ*-MO: 0.95, well polarized towards Ni (ionic bond)

Ni: 3*d*(xy) = 0.96
one unpaired electron in a Ni 3*d*(xy)-based orbital (ligand on nodal surfaces).

NPA Charge (aus NBO Programm):

```
                                 Natural Population
              Natural  ---------------------------------
  Atom No     Charge          Core      Valence    Rydberg       Total
 -------------------------------------------------------------------
    O  1    -0.12737      2.00000     6.11925     0.00812      8.12737
   Ni  2     1.79734     17.99955     8.14235     0.06075     26.20266
    F   3    -0.83499      2.00000      7.82479     0.01020      9.83499
    F   4    -0.83499      2.00000      7.82479     0.01020      9.83499
 ===================================================================
 * Total *   0.00000     23.99955    29.91119     0.08926     54.00000
```

AIM Ladungen:

```
 Total result:
  #Basin      Integral(a.u.)     Vol(Bohr^3)    Vol(rho > 0.001)
     1         8.1523581247       1256.891        119.256
     2        26.2675125866        352.368         84.731
     3         9.7900107256       1116.780        126.445
     4         9.7900100472       1109.084        126.445
 Sum of above integrals:         53.99989148
 Sum of basin volumes (rho > 0.001):     456.877 Bohr^3

Normalization factor of the integral of electron density is    0.999998
 The atomic charges after normalization and atomic volumes:
      1 (O )    Charge:   -0.152375     Volume:   119.256 Bohr^3
      2 (Ni)    Charge:    1.732435     Volume:    84.731 Bohr^3
      3 (F )   Charge:   -0.790030     Volume:   126.445 Bohr^3
      4 (F )   Charge:   -0.790030     Volume:   126.445 Bohr^3
```

ONiF_2 (C_{2v}, $^5A_1$)

SS-CASSCF (12,9) (SS: State-Specific)

CI vector for state symmetry 1

```
==============================
22a0 2a 2a a      0.9214245
2A20 2a a2 a     -0.2541023
2A20 a2 2a a      0.1659817
22a0 a2 a2 a      0.1496710
2A20 a2 a2 a     -0.0747341
a2a0 aa 22 2     -0.0642670
2BA0 22 aa 2     -0.0550659
02a2 2a 2a a     -0.0538621
2220 aa aa 2     -0.0528501
```

Table S7.8. ONiF$_2$ (C_{2v}, $^5A_2$)

SA-CASSCF(12,9)/CASPT2/VTZ-DK
- With equal weights of 0.5: $^5A_1$, $^5A_2$

```
 Optimized variables
 NiO=               1.73212203 ANGSTROM
 NiF=               1.74061303 ANGSTROM
 A1=              113.00320763 DEGREE

     OPTG(RS2C)     -1794.58902559

 CI vector for state symmetry 2
 ==============================

  2aa0 2a 2a 2      0.9257083
  a2a0 2a a2 2     -0.2135060
  2aa0 a2 a2 2      0.1973532
  a2a0 a2 2a 2      0.1391540
  2a20 22 aa a      0.0935902
  2a20 aa 22 a     -0.0571379
```

NATURAL ORBITALS FOR STATE 1.4 (ms2=4)

```
================================================
 Orbital  Occupation    Energy     Coefficients
  10.1     2.00000    -0.66519     3 2pz   0.43674     3 2py   0.72413
  11.1     2.00000    -0.60756     3 2pz  -0.78142     3 2py   0.46853
  12.1     1.91164    -0.70997     1 2pz  -0.75778     2 2pz  -0.32660     2 2pz   0.28835     2 3d0  -0.53226
  13.1     1.07247    -0.35477     1 2pz   0.54726     2 3d0  -0.83001
  14.1     1.01457    -0.33775     2 3d2+  0.96557
  15.1     0.01921     0.76519     1 1s    0.29214     1 2pz   1.10379     1 2pz  -0.66716     2 1s   -0.29309     2 1s   -0.41781
                                   2 1s   -0.31364     2 2pz  -1.51839     2 2pz   1.52825     2 2pz   0.47998     2 3d0  -0.50540
                                   2 3d2+ -0.31467     2 3d0   0.39083
  16.1    -0.00000     0.06710     2 1s   -0.73821     2 1s   -2.80310     2 1s    0.56343     2 1s    3.63490     2 2pz   0.94728
                                   2 2pz  -0.40469     2 2pz  -0.79036
  17.1    -0.00000     0.11427     2 1s   -0.76787     2 1s    0.96768     2 2pz  -2.42860     2 2pz   1.32375     2 2pz   2.22819
  18.1    -0.00000     0.32039     2 1s    0.74216     2 1s    3.53610     2 1s   -0.95589     2 1s    0.26529     2 1s   -3.36606
                                   2 2pz   5.63320     2 2pz  -2.59515     2 2pz   0.35859     2 2pz  -2.75373     2 3d2+  0.28617
                                   3 1s   -0.32228     3 2py   0.33800     3 2py   0.26452
  19.1    -0.00000     0.37729     1 1s    0.83385     2 1s   -0.26903     2 1s   -1.13203     2 1s    0.35564     2 2pz   0.72236
                                   2 3d0  -1.04754     2 3d2+  1.19355     3 1s    0.48043
   1.2     2.00000   -33.23794     2 2px   0.99995
   4.2     1.92754    -0.74921     1 2px   0.31570     2 3d1+ -0.91762
   5.2     1.07794    -0.38394     1 2px   0.92988     2 3d1+  0.38330
   6.2    -0.00000     0.07442     2 2px   1.06955     2 2px  -0.74311     2 2px  -1.49524
   7.2    -0.00000     0.23859     2 2px   6.60185     2 2px  -3.13275     2 2px   0.43879     2 2px  -3.48312
   8.2    -0.00000     0.37868     1 2px   0.30406     2 2px  -0.45408     2 2px   0.25667     2 3d1+ -0.35161     2 3d1+ -0.27875
                                   2 3d1+  1.57644
   9.2    -0.00000     0.82367     1 2px  -0.54329     1 2px  -0.50429     1 2px   1.80477     2 2px   0.74621     2 2px  -0.81217
                                   2 2px  -0.47099     2 3d1+  0.27746     2 3d1+  0.28934
   5.3     2.00000    -0.63384     2 2py  -0.33325     2 2py   0.34643     3 2py  -0.88007
   6.3     2.00000    -0.59625     3 2pz   0.91531
   7.3     1.89076    -0.64152     1 2py  -0.64910     2 3d1-  0.68709
   8.3     1.10319    -0.39609     1 2py   0.72467     2 3d1-  0.69770
   9.3    -0.00000     0.12825     2 2py  -2.95818     2 2py   1.50179     2 2py   2.55860
  10.3    -0.00000     0.41018     1 2py  -0.26432     2 2py   0.40181     2 2py   9.42042     2 2py  -4.60978     2 2py   0.62950
                                   2 2py  -4.37706     2 3d1- -0.52078     3 1s   -0.65215     3 2pz   0.25786     3 2py   0.28474
                                   3 2pz   0.28913
  11.3    -0.00000     0.51794     2 2py   0.32896     2 2py   5.69361     2 2py  -2.60823     2 2py   0.32639     2 2py  -2.44092
                                   2 3d1-  2.02477     3 1s   -1.47287     3 2py   0.58721
  12.3    -0.00000     0.85863     1 2py   0.49545     1 2py   0.47636     1 2py  -1.78916     2 2py  -3.08217     2 2py   2.44118
                                   2 2py  -0.38431     2 2py   1.31743     2 3d1- -0.68572     3 1s    0.25939
   1.4     2.00000    -0.61206     3 2px   0.91769
   2.4     1.98268    -0.79165     2 3d2- -0.98426
```

```
    3.4    -0.00000      0.39549      2 3d2- -0.32618      2 3d2- -0.27653      2 3d2-  1.60095      3 2px  -0.30488      3 2px  -0.38175
    5.4    -0.00000      1.39660      2 3d2-  1.07139      2 3d2-  2.88783      2 3d2-  0.94286      2 3d2- -3.18230      3 2px   0.40031
```

Table S7.9. ONiF$_2$ (C_{2v}, $^5A_2$)

SS-CASSCF (12,9) (SS: State-Specific)

CI vector for state symmetry 2

```
==============================
2aa0 2a 2a 2       0.9281837
2ba0 a2 a2 2       0.2069617
a2a0 2a a2 2      -0.1996394
a2a0 a2 2a 2       0.1370911
2a20 22 aa a      -0.0891214
2a20 aa 22 a       0.0575935
22a0 aa 22 a      -0.0519345
```

Spin population: Individual basis function populations

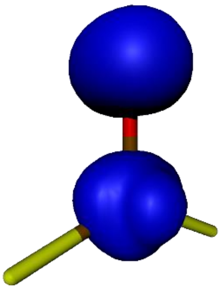
```
Symmetry no. 1

1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0
-0.00000  0.00198 -0.00006  0.00042  0.33100 -0.00517 -0.02233 -0.00004  0.00000 -0.00117

1 3d2+   1 4f0    1 4f2+   2 1s     2 1s     2 1s     2 1s     2 1s     2 1s     2 1s
0.00003  0.00004  0.00000  0.00000  0.00017  0.01114  0.00375  0.00026  0.00000  0.00399

2 2pz    2 2pz    2 2pz    2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+
-0.00000  0.00061 -0.02002  0.03156 -0.00043  0.00138  0.60636  0.89317  0.04956  0.03292

2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0    2 4f2+   2 4f0    2 4f2+   2 5g0    2 5g4+
0.00026  0.00094  0.00631  0.00589 -0.00000  0.00000  0.00005  0.00004 -0.00000  0.00000

2 5g2+   3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py    3 2pz    3 2py    3 2pz
0.00000 -0.00000  0.00118 -0.00000  0.00021  0.03364  0.01256  0.00011  0.00031  0.00125

3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-
0.00166  0.00000  0.00001  0.00001 -0.00000  0.00001  0.00004  0.00000  0.00001  0.00000

3 4f3-
0.00001


 Symmetry no. 2

1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 4f1+   1 4f3+   2 2px    2 2px    2 2px
0.78946  0.00880 -0.00321  0.00002 -0.00001  0.00000  0.00000  0.00000  0.00001 -0.01088

2 2px    2 2px    2 2px    2 3d1+   2 3d1+   2 3d1+   2 3d1+   2 4f1+   2 4f3+   2 4f1+
0.01161  0.00082  0.00322  0.16646  0.02928  0.00358 -0.00729  0.00000 -0.00000  0.00033

2 4f3+   2 5g1+   2 5g3+   3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
0.00000  0.00000  0.00000  0.00325 -0.00003  0.00012  0.00000  0.00000 -0.00000 -0.00000

3 4f1+   3 4f3+   3 4f2-
0.00000  0.00000 -0.00000


 Symmetry no. 3

1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 4f1-   1 4f3-   2 2py    2 2py    2 2py
0.44964  0.00333  0.00037  0.00001 -0.00029  0.00001  0.00000  0.00000  0.00006  0.00014

2 2py    2 2py    2 2py    2 3d1-   2 3d1-   2 3d1-   2 3d1-   2 4f1-   2 4f3-   2 4f1-
0.00216 -0.00039  0.00086  0.46154  0.05174  0.00460 -0.00634 -0.00000 -0.00000  0.00016
```

```
2 4f3-    2 5g1-    2 5g3-    3 1s      3 1s      3 1s      3 1s      3 2py     3 2pz     3 2py
0.00004  -0.00000  -0.00000   0.00000   0.00071  -0.00000  -0.00005   0.03304   0.00026   0.00055

3 2pz     3 2py     3 2pz     3 3d1-    3 3d0     3 3d2+    3 3d1-    3 3d0     3 3d2+    3 4f1-
-0.00002  0.00199  -0.00006   0.00000   0.00000   0.00000  -0.00001   0.00003  -0.00003   0.00001

3 4f3-    3 4f0     3 4f2+
0.00000   0.00000   0.00000


 Symmetry no. 4

1 3d2-    1 3d2-    1 4f2-    2 3d2-    2 3d2-    2 3d2-    2 3d2-    2 4f2-    2 4f2-    2 5g2-
0.00000   0.00000   0.00000   0.01598   0.00040   0.00004  -0.00000   0.00000   0.00000   0.00000

2 5g4-    3 2px     3 2px     3 2px     3 3d2-    3 3d1+    3 3d2-    3 3d1+    3 4f2-    3 4f1+
0.00000   0.00036  -0.00000   0.00001   0.00000   0.00000   0.00000   0.00000   0.00000   0.00000

3 4f3+
0.00000
```

Population analysis by function type base

```
Unique atom       s          p          d          f          g          Total       Charge
1 O            0.00233    1.55188   -0.00144    0.00006    0.00000    1.55284     + 6.44716
2 Ni           0.01930    0.02070    2.31539    0.00063    0.00000    2.35602     +25.64398
3 F            0.00102    0.04450    0.00003    0.00002    0.00000    0.04557     + 8.95443
4 F            0.00102    0.04450    0.00003    0.00002    0.00000    0.04557     + 8.95443
```

Spin densities of $ONiF_2$ ($^5A_2$; iso-surface = 0.05 electron a.u.$^{-3}$)

	Spin density $ONiF_2$, $^5A_2$: 2 unpaired electrons in the π*-MOs (less symmetrically than in $^5A_1$ due to different contributions by *p*(x) and *p*(y) and polarized towards oxygen due to inversion) 1 unpaired electron in the σ*-MO (polarized to Ni) 1 unpaired electron in a Ni[3*d*(x^2)] MO.

NPA batch (NBO) ($^5A_2$)

```
                                Natural Population
          Natural    -----------------------------------------
Atom No   Charge     Core       Valence       Rydberg       Total
-------------------------------------------------- ------------------
1 O        -0.30430   2.00000     6.29018    0.01412      8.30430
2 Ni        1.98952   17.99956    7.94849    0.06243      26.01048
3 F        -0.84261   2.00000     7.83390    0.00871      9.84261
4 F        -0.84261   2.00000     7.83390    0.00871      9.84261
================================================== ==================
* Total * 0.00000 23.99956 29.90648 0.09396 54.00000
```

AIM Charges ($^5A_2$)

```
Total result:
#Basin    integral (au)         Vol (Bohr ^ 3) volume (rho> 0001)
1 O         8.2969247159       1387,852         125,614
2 Ni        26.1187140877      263,022          78,374
3 F         9.7921372486       1114,735         126,863
4 F         9.7921365794       1107,393         126,863
Sum of above integrals: 53.99991263
Sum of basin volumes (rho> 0001): 457,713 Bohr ^ 3

Normalization factor of the integral of electron density is 0.999998
The atomic charges after normalization and atomic volumes:
1 (O) Charge: -0.296938 Volume: 125 614 Bohr ^ 3
2 (Ni) Charge: 1.881244 Volume: 78374 Bohr ^ 3
3 (F) Charge: -0.792152 Volume: 126,863 Bohr ^ 3
4 (F) Charge: -0.792153 Volume: 126 863 Bohr ^ 3
```

Part 8. CASSCF calculations of $OPdF_2$ ($^3A_2$; C_{2v}), $OPtF_2$ ($^3A_2$; C_{2v}) and $OPtF_3$ ($^4A_1$, C_{2v})

Table S8.1. $OPdF_2$ (C_{2v}; $^3A_2$)

CASSCF(12,8)/AVTZ(-PP)

PdO = 1.72161707
PdF = 1.87659933
A1 = 101.60981416

TOTAL ENERGIES -400.39680758

CI vector

```
 =========

 220 2a 2a 2      0.9355843
 220 a2 a2 2      0.1755761
 2ba 2a a2 2     -0.1266081
 2ab 2a a2 2      0.1240501
 202 2a 2a 2     -0.1207369
 2ba a2 2a 2      0.1176422
 2ab a2 2a 2     -0.1043761
 202 a2 a2 2     -0.0938946
```

NATURAL ORBITALS STATE 1.4 (ms = 2)

```
================
  Orbital  Occupation    Energy     Coefficients

   8.1      2.00000    -0.59571    1 1s   -0.12212     1 1s    0.04534     1 2pz  -0.04142     1 2pz   0.05748     1 3d0   0.06892
                                   1 3d2+ -0.15426     1 3d2+  0.01018     1 4f2+ -0.01168     2 1s   -0.01599     2 1s   -0.01584
                                   2 1s   -0.01294     2 2pz  -0.03063     2 2pz   0.01243     3 1s    0.01405     3 1s    0.03352
                                   3 2pz   0.84546     3 2py   0.33287     3 2pz   0.04941     3 2py   0.01619     3 2pz   0.04423
                                   3 3d1- -0.02025
   9.1      1.99622    -0.80436    1 1s   -0.17501     1 1s    0.37511     1 1s    0.05213     1 1s   -0.01074     1 1s   -0.04988
                                   1 2pz  -0.17921     1 2pz   0.04398     1 2pz   0.02424     1 3d0  -0.48530     1 3d2+  0.52769
                                   1 3d0   0.03358     1 3d2+ -0.04030     1 4f0   0.01489     2 1s    0.33754     2 1s   -0.01333
                                   2 1s   -0.07142     2 2pz   0.01381     3 1s   -0.04461     3 2pz   0.26315     3 2py  -0.35686
                                   3 2pz   0.01725     3 2py  -0.01134
  10.1      1.88707    -0.66553    1 1s    0.02474     1 1s   -0.32734     1 1s   -0.05288     1 1s    0.02711     1 2pz   0.08866
                                   1 2pz  -0.04426     1 2pz  -0.07601     1 2pz   0.01016     1 3d0  -0.43383     1 3d2+ -0.27574
                                   1 3d2+  0.02144     1 3d0   0.01089     1 4f0  -0.01782     1 4f0  -0.02631     2 1s    0.05178
                                   2 1s    0.12860     2 1s    0.11330     2 2pz   0.78664     2 2pz  -0.08481     2 2pz  -0.02208
                                   2 3d0  -0.01756     3 1s   -0.02151     3 1s    0.03241     3 2pz  -0.01642     3 2py   0.02062
  11.1      0.12280     0.04137    1 1s    0.01807     1 1s    0.18797     1 1s    0.13477     1 1s   -0.02038     1 1s    0.07844
                                   1 2pz   0.11503     1 2pz  -0.03437     1 2pz   0.06165     1 2pz   0.01774     1 3d0   0.73841
                                   1 3d2+  0.35335     1 3d0  -0.11150     1 3d2+ -0.06925     1 3d0  -0.01732     1 3d0   0.01068
                                   1 3d2+  0.01685     2 1s   -0.15468     2 1s   -0.09464     2 1s   -0.04769     2 2pz   0.79665
                                   2 2pz  -0.01394     2 2pz  -0.15843     2 2pz  -0.02091     3 1s    0.03980     3 2pz   0.16031
                                   3 2py  -0.21423     3 2pz   0.01722     3 2py  -0.01611     3 2pz   0.01169     3 2py  -0.01256

   2.2      2.00000    -0.60074    1 2px  -0.04429     1 2px   0.03200     1 3d1+ -0.03976     1 4f3+ -0.01331     2 2px   0.01298
                                   3 2px   0.92882     3 2px   0.05218     3 2px   0.04451     3 3d2- -0.01070     3 3d2- -0.02308
   3.2      1.92886    -0.65769    1 2px  -0.04197     1 2px  -0.01081     1 2px   0.02220     1 3d1+  0.77395     1 3d1+ -0.03849
                                   1 3d1+ -0.01201     1 3d1+ -0.01232     1 4f1+  0.01039     2 2px   0.52655     2 3d1+ -0.02159
                                   2 3d1+ -0.01172     3 2px   0.02832
   4.2      1.06864    -0.35820    1 2px   0.04119     1 2px   0.01130     1 2px  -0.01696     1 2px  -0.01072     1 3d1+  0.64099
                                   1 3d1+ -0.03913     1 4f1+ -0.01425     2 2px  -0.84881     2 3d1+  0.01015     3 2px   0.06031

   5.3      2.00000    -0.58236    1 2py   0.08957     1 2py  -0.10804     1 2py  -0.09692     1 2py   0.01308     1 2py   0.03834
                                   1 3d1-  0.05016     1 4f1-  0.01593     1 4f3-  0.01880     1 4f1-  0.02289     1 4f3-  0.02252
                                   2 2py  -0.01662     3 1s    0.06860     3 1s    0.03097     3 1s    0.10053     3 2py   0.58952
                                   3 2pz  -0.69415     3 2pz  -0.03182     3 2pz  -0.02839     3 3d1-  0.01038     3 3d1-  0.01180
   6.3      1.92344    -0.64748    1 2py  -0.06017     1 2py   0.06197     1 3d1-  0.72064     1 3d1- -0.05243     1 3d1- -0.01321
                                   1 3d1- -0.02227     1 4f1-  0.01149     2 2py   0.59234     2 3d1- -0.02105     2 3d1- -0.01070
                                   3 1s    0.02100     3 1s   -0.03131     3 2py  -0.11292     3 2pz  -0.14806     3 2pz  -0.02372
                                   3 2pz  -0.01075
```

```
7.3     1.07722    -0.35331     1 2py  -0.01604     1 2py  -0.08982     1 2py   0.03556     1 3d1- -0.68268     1 3d1-  0.06631
                                1 4f1-  0.01442     2 2py   0.80877     2 2py  -0.01015     2 2py   0.01092     3 1s   -0.03390
                                3 1s    0.01884     3 2py   0.17528     3 2pz   0.09655     3 2py   0.01725     3 2pz   0.01780
                                3 2pz   0.01973

1.4     2.00000    -0.61506     1 3d2-  0.10580     3 2px   0.92411     3 2px   0.04708     3 2px   0.04629     3 3d2- -0.01041
                                3 3d2- -0.01880
2.4     1.99575    -0.60441     1 3d2-  1.00681     1 3d2- -0.06111     1 3d2- -0.01006     1 3d2- -0.01262     3 2px  -0.20502
                                3 2px  -0.03372     3 2px  -0.02621
```

Spin population: Individual basis function populations

```
 Symmetry no. 1

1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz    1 2pz
0.00010 -0.00673 -0.00200 -0.00010 -0.00056  0.00004  0.00076  0.00068  0.00006  0.00001

1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+
-0.00002 -0.00000 -0.00354 -0.01500  0.00063 -0.00043 -0.00013  0.00002  0.00006 -0.00010

1 3d0    1 3d2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 5g0    1 5g4+
0.00002 -0.00000  0.00001  0.00000  0.00016  0.00000  0.00022  0.00001 -0.00000  0.00000

1 5g2+   1 5g0    1 5g4+   1 5g2+   2 1s     2 1s     2 1s     2 1s     2 1s     2 2pz
-0.00000  0.00001 -0.00001 -0.00001  0.00000  0.00163 -0.00004  0.00082  0.00078  0.04247

2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0
-0.00039 -0.00440 -0.00027 -0.00001 -0.00000 -0.00008  0.00000  0.00003  0.00000 -0.00000

2 4f2+   2 4f0    2 4f2+   3 1s     3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py
-0.00000  0.00001  0.00000 -0.00000 -0.00004  0.00000 -0.00000  0.00015 -0.00218 -0.00408

3 2pz    3 2py    3 2pz    3 2py    3 2pz    3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0
-0.00000 -0.00005 -0.00014 -0.00017 -0.00008 -0.00018 -0.00000 -0.00000  0.00000 -0.00000

3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-   3 4f3-   3 4f0
-0.00000  0.00000 -0.00000  0.00000  0.00005 -0.00000 -0.00000 -0.00000 -0.00000  0.00000

3 4f2+   3 4f1-   3 4f3-
0.00000 -0.00000  0.00000


 Symmetry no. 2

1 2px    1 2px    1 2px    1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 3d1+   1 3d1+
0.00022 -0.00186  0.00271 -0.00009  0.00110 -0.00009  0.34810  0.01047  0.00043 -0.00012

1 3d1+   1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 5g1+   1 5g3+   1 5g1+
0.00030  0.00007  0.00000  0.00175  0.00001  0.00152  0.00008 -0.00003  0.00000  0.00023

1 5g3+   2 2px    2 2px    2 2px    2 2px    2 3d1+   2 3d1+   2 3d1+   2 4f1+   2 4f3+
0.00000  0.62915  0.00395 -0.00400  0.00099  0.00001 -0.00022 -0.00130  0.00004  0.00000

2 4f1+   2 4f3+   3 2px    3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
-0.00013  0.00000  0.00256  0.00000  0.00004 -0.00051  0.00000  0.00000  0.00001  0.00002

3 3d1+   3 3d2-   3 4f1+   3 4f3+   3 4f2-   3 4f1+   3 4f3+   3 4f2-
-0.00001 -0.00005  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000


 Symmetry no. 3

1 2py    1 2py    1 2py    1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 3d1-   1 3d1-
0.00011 -0.00768  0.00114 -0.00017  0.00306 -0.00015  0.37331  0.02223  0.00114 -0.00166

1 3d1-   1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 5g1-   1 5g3-   1 5g1-
-0.00007  0.00009  0.00001  0.00179  0.00011  0.00259  0.00025 -0.00001 -0.00000  0.00007

1 5g3-   2 2py    2 2py    2 2py    2 2py    2 3d1-   2 3d1-   2 3d1-   2 4f1-   2 4f3-
0.00004  0.56593  0.00268 -0.00446  0.00212  0.00001 -0.00005 -0.00124  0.00004  0.00000

2 4f1-   2 4f3-   3 1s     3 1s     3 1s     3 1s     3 1s     3 2py    3 2pz    3 2py
-0.00012  0.00000 -0.00000  0.00037 -0.00000 -0.00004  0.00092  0.02328  0.00719  0.00009

3 2pz    3 2py    3 2pz    3 2py    3 2pz    3 3d1-   3 3d0    3 3d2+   3 3d1-   3 3d0
-0.00004  0.00087  0.00025  0.00006  0.00150  0.00001  0.00000  0.00000  0.00012  0.00003

3 3d2+   3 3d1-   3 3d0    3 3d2+   3 4f1-   3 4f3-   3 4f0    3 4f2+   3 4f1-   3 4f3-
```

```
0.00004 -0.00034 -0.00004 -0.00028  0.00000  0.00000  0.00000  0.00000  0.00006 -0.00002

3 4f0    3 4f2+
-0.00001  0.00002


 Symmetry no. 4

1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 4f2-   1 4f2-   1 4f2-   1 5g2-   1 5g4-
0.00153  0.00002  0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 -0.00000

1 5g2-   1 5g4-   2 3d2-   2 3d2-   2 3d2-   2 4f2-   2 4f2-   3 2px    3 2px    3 2px
0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00004 -0.00000 -0.00000

3 2px    3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 4f2-   3 4f1+   3 4f3+
-0.00000  0.00000  0.00000  0.00000  0.00000 -0.00000 -0.00000  0.00000  0.00000  0.00000

3 4f2-   3 4f1+   3 4f3+
0.00000  0.00000  0.00000
```

```
 Population analysis by basis function type

 Unique atom     s        p        d        f        g       Total    Charge
   1  Pd     -0.00926 -0.00022  0.73721  0.00867  0.00027  0.73666  +17.26334
   2  O       0.00319  1.23376 -0.00284 -0.00017  0.00000  1.23394  + 6.76606
   3  F      0.00068  0.01422 -0.00023  0.00003  0.00000  0.01470  + 8.98530
   4  F      0.00068  0.01422 -0.00023  0.00003  0.00000  0.01470  + 8.98530
```

NPA batch (NBO) ($^3A_2$)

```
Summary of Natural Population Analysis:
                                     Natural Population                 Natural
            Natural    -------------------------------------------        Spin
  Atom No    Charge         Core      Valence    Rydberg      Total      Density
 -------------------------------------------------------------------------------
   Pd  1    1.61170     35.99840     8.36056    0.02934    44.38830     0.70272
    O  2   -0.06701      2.00000     6.05073    0.01628     8.06701     1.26278
    F  3   -0.77235      2.00000     7.75721    0.01514     9.77235     0.01725
    F  4   -0.77235      2.00000     7.75721    0.01514     9.77235     0.01725
 ======================================================================
 * Total *  0.00000     41.99839    29.92570    0.07590    72.00000     2.00000
```

AIM Charges ($^3A_2$)

```
Total result:
   #Basin      Integral(a.u.)     Vol(Bohr^3)   Vol(rho>0.001)
       1        9.7494738997       1407.843         125.509
       2       44.3433968383        545.942         127.373
       3        9.7494723896       1393.966         125.509
       4        8.1574005460       1026.609         111.966
 Sum of above integrals:        71.99974367
 Sum of basin volumes (rho>0.001):     490.357 Bohr^3

 Normalization factor of the integral of electron density is    0.999996
 The atomic charges after normalization and atomic volumes:
      1 (Pd)    Charge:    1.656446     Volume:   127.373 Bohr^3
      2 (O )    Charge:   -0.157429     Volume:   111.966 Bohr^3
      3 (F )    Charge:   -0.749507     Volume:   125.509 Bohr^3
      4 (F )    Charge:   -0.749508     Volume:   125.509 Bohr^3
```

Table S8.2. $OPtF_2$ (C_{2v}; $^3A_2$)

CASSCF(12,8)/AVTZ(-PP)

PtO = 1.72278697
PtF = 1.89176963
Ang = 101.91519688

TOTAL ENERGIES -392.35680127

CI vector

```
=========

220 2a 2a 2      0.9519959
220 a2 a2 2     -0.1698289
2ba a2 2a 2      0.1093964
202 2a 2a 2     -0.1093116
2ba 2a a2 2      0.1085684
2ab 2a a2 2     -0.1012533
2ab a2 2a 2     -0.0935376
202 a2 a2 2      0.0663323
```

NATURAL ORBITALS STATE 1.4 (ms = 2)

```
================
   8.1     2.00000    -0.53032    1 1s    0.45168    1 3d0  -0.48472    1 3d2+  0.73698
   9.1     1.99865    -1.48946    1 2pz   0.37227    2 1s   -0.93007
  10.1     1.92118    -0.68606    1 1s   -0.35433    1 3d0  -0.49270    2 2pz   0.76867
  11.1     0.08354     0.12917    1 1s   -0.33931    1 3d0  -0.74762    1 3d2+ -0.25192
                                  2 2pz  -0.88713
   2.2     2.00000    -0.62344    3 2px   0.93384
   3.2     1.94321    -0.64159    1 3d1+ -0.72600    2 2px  -0.56783
   4.2     1.05521    -0.31204    1 3d1+  0.70281    2 2px  -0.81029
   5.3     2.00000    -0.60233    1 2py  -0.26998    3 2py   0.61442    3 2pz  -0.66986
   6.3     1.94259    -0.63741    1 3d1- -0.62715    2 2py  -0.66189
   7.3     1.05760    -0.29529    1 3d1-  0.78244    2 2py  -0.73776
   1.4     2.00000    -0.63597    3 2px   0.93208
   2.4     1.99802    -0.54776    1 3d2-  1.01525
```

Spin population: Individual basis function populations

```
 Symmetry no. 1

1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz    1 2pz
0.00004 -0.00444 -0.00030 -0.00005  0.00024 -0.00001  0.00077  0.00174 -0.00052 -0.00001

1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+
-0.00017 -0.00001 -0.01058 -0.00106  0.00087  0.00000 -0.00005 -0.00000  0.00001 -0.00002

1 3d0    1 3d2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 5g0    1 5g4+
-0.00001  0.00000  0.00003  0.00000  0.00021  0.00000  0.00011  0.00000 -0.00001  0.00000

1 5g2+   1 5g0    1 5g4+   1 5g2+   2 1s     2 1s     2 1s     2 1s     2 1s     2 2pz
0.00000 -0.00000 -0.00000 -0.00000  0.00001  0.00416 -0.00008  0.00124 -0.00014  0.01383

2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0
-0.00017 -0.00159 -0.00002 -0.00001 -0.00000 -0.00007 -0.00000  0.00005  0.00000 -0.00001

2 4f2+   2 4f0    2 4f2+   3 1s     3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py
-0.00000  0.00000  0.00000 -0.00000  0.00000 -0.00000 -0.00000 -0.00004 -0.00014 -0.00012

3 2pz    3 2py    3 2pz    3 2py    3 2pz    3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0
0.00000  0.00000 -0.00001 -0.00002 -0.00003 -0.00010 -0.00000 -0.00000 -0.00000 -0.00000
```

```
3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-   3 4f3-   3 4f0
-0.00000 -0.00000 -0.00000  0.00000  0.00001 -0.00000 -0.00000 -0.00000 -0.00000 -0.00000

3 4f2+   3 4f1-   3 4f3-
-0.00000 -0.00000 -0.00000


 Symmetry no. 2

1 2px    1 2px    1 2px    1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 3d1+   1 3d1+
0.00028 -0.00009  0.00394 -0.00007  0.00039 -0.00005  0.39521  0.01042  0.00027 -0.00001

1 3d1+   1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 5g1+   1 5g3+   1 5g1+
0.00015  0.00033  0.00000  0.00508  0.00005 -0.00024  0.00002 -0.00006  0.00000  0.00039

1 5g3+   2 2px    2 2px    2 2px    2 2px    2 3d1+   2 3d1+   2 3d1+   2 4f1+   2 4f3+
-0.00000  0.57266  0.00350  0.00246  0.00245  0.00001 -0.00019 -0.00147  0.00004  0.00000

2 4f1+   2 4f3+   3 2px    3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
0.00004  0.00000  0.00295 -0.00002  0.00001 -0.00079  0.00000  0.00000  0.00002  0.00004

3 3d1+   3 3d2-   3 4f1+   3 4f3+   3 4f2-   3 4f1+   3 4f3+   3 4f2-
0.00000 -0.00019  0.00000  0.00000  0.00000  0.00000  0.00001  0.00001


 Symmetry no. 3

1 2py    1 2py    1 2py    1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 3d1-   1 3d1-
0.00011 -0.00339  0.00023 -0.00031  0.00148 -0.00012  0.45347  0.02121  0.00063 -0.00063

1 3d1-   1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 5g1-   1 5g3-   1 5g1-
-0.00023  0.00034  0.00003  0.00459  0.00038 -0.00136  0.00004 -0.00003 -0.00001  0.00002

1 5g3-   2 2py    2 2py    2 2py    2 2py    2 3d1-   2 3d1-   2 3d1-   2 4f1-   2 4f3-
0.00006  0.46856  0.00163  0.00610  0.00387  0.00002  0.00014 -0.00273  0.00005  0.00000

2 4f1-   2 4f3-   3 1s     3 1s     3 1s     3 1s     3 1s     3 2py    3 2pz    3 2py
-0.00017  0.00000  0.00000  0.00050  0.00001 -0.00021 -0.00020  0.02853  0.01247  0.00012

3 2pz    3 2py    3 2pz    3 2py    3 2pz    3 3d1-   3 3d0    3 3d2+   3 3d1-   3 3d0
-0.00008  0.00134  0.00014  0.00023  0.00146  0.00001  0.00000  0.00000  0.00020  0.00009

3 3d2+   3 3d1-   3 3d0    3 3d2+   3 4f1-   3 4f3-   3 4f0    3 4f2+   3 4f1-   3 4f3-
0.00008 -0.00048 -0.00022 -0.00031  0.00000  0.00000  0.00000  0.00000  0.00005 -0.00002

3 4f0    3 4f2+
-0.00003  0.00000


 Symmetry no. 4

1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 4f2-   1 4f2-   1 4f2-   1 5g2-   1 5g4-
0.00116  0.00001  0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 -0.00000

1 5g2-   1 5g4-   2 3d2-   2 3d2-   2 3d2-   2 4f2-   2 4f2-   3 2px    3 2px    3 2px
0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00003 -0.00000 -0.00000

3 2px    3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 4f2-   3 4f1+   3 4f3+
-0.00000  0.00000  0.00000  0.00000  0.00000 -0.00000 -0.00000  0.00000  0.00000  0.00000

3 4f2-   3 4f1+   3 4f3+
0.00000  0.00000  0.00000
```

Population analysis by basis function type

```
 Unique atom        s      p        d        f        g     Total    Charge
   1  Pt     -0.00453  0.00422  0.87083  0.00962  0.00037  0.88051  +17.11949
   2  O       0.00519  1.07329 -0.00425 -0.00004  0.00000  1.07419  + 6.92581
   3  F       0.00003  0.02298 -0.00037  0.00002  0.00000  0.02265  + 8.97735
   4  F       0.00003  0.02298 -0.00037  0.00002  0.00000  0.02265  + 8.97735
```

NPA batch (NBO) ($^3A_2$)

```
                                  Natural Population                 Natural
            Natural    - - - - - - - - - - - - - - - - - - - - - - -   Spin
 Atom No    Charge         Core      Valence    Rydberg      Total      Density
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
  Pt  1    1.62718     67.99822     8.33382    0.04079    76.37282     0.84265
   O  2   -0.17559      2.00000     6.15374    0.02185     8.17559     1.10038
   F  3   -0.72580      2.00000     7.70908    0.01671     9.72580     0.02849
   F  4   -0.72580      2.00000     7.70908    0.01671     9.72580     0.02849
=========================================================================
* Total *  0.00000     73.99821    29.90572    0.09606   104.00000     2.00000
```

AIM Charges ($^3A_2$)

```
Total result:
  #Basin       Integral(a.u.)     Vol(Bohr^3)   Vol(rho>0.001)
      1         9.7229946528       1321.462       120.975
      2        76.2755283325        791.221       152.833
      3         9.7229929347       1306.951       120.975
      4         8.2782042345       1208.529       112.868
 Sum of above integrals:        103.99972015
 Sum of basin volumes (rho>0.001):     507.650 Bohr^3

 Normalization factor of the integral of electron density is    0.999997
 The atomic charges after normalization and atomic volumes:
     1 (Pt)    Charge:    1.724266     Volume:   152.833 Bohr^3
     2 (O )    Charge:   -0.278227     Volume:   112.868 Bohr^3
     3 (F )    Charge:   -0.723019     Volume:   120.975 Bohr^3
     4 (F )    Charge:   -0.723021     Volume:   120.975 Bohr^3
```

Table S8.3. $OPtF_3$ (C_{2v}; $^4A_1$)

CASSCF(11,8)/CASPT2/AVTZ(-PP)

Optimization and normal mode calculation carried out in C_1 point group symmetry (y-axis in the C_2 axis and x-axis perpendicular to the molecular plane). In the main text (Table 3) and in Table S3.7 the z-axis was placed along the C_2 axis.

```
OPT2=       1.78490998 ANGSTROM
FPT3=       1.82576796 ANGSTROM
FPTO3=      92.44618513 DEGREE
FPT4=       1.82577139 ANGSTROM
FPTO4=      92.44610803 DEGREE
FPT5=       1.87447191 ANGSTROM
FPTO5=      179.99999565 DEGREE
```

TOTAL ENERGIES -491.78467492

CI vector

```
=========

 2222aaa0      0.9604760
 2aa222a0      0.1653963
 22ab2aaa      0.0962865
 2a2ba2aa     -0.0929145
 22aa2aab     -0.0916928
 2a2aa2ab      0.0856573
 2220aaa2     -0.0773071
```

NATURAL ORBITALS FOR STATE 1.1 (ms2=3)

```
================

 Orbital  Occupation    Energy     Coefficients
   1.1     2.00000   -26.31039     3 1s   -0.81546     4 1s    0.57655
   2.1     2.00000   -26.31038     3 1s   -0.57662     4 1s   -0.81551
   3.1     2.00000   -26.26063     5 1s    0.99873
   4.1     2.00000   -20.76459     2 1s    0.99885
   5.1     2.00000    -4.70122     1 1s    0.99941
   6.1     2.00000    -2.84921     1 2pz   0.99147
   7.1     2.00000    -2.83446     1 2px  -0.99841
   8.1     2.00000    -2.83429     1 2py  -0.97913
   9.1     2.00000    -1.59750     3 1s   -0.65658     4 1s   -0.65654
  10.1     2.00000    -1.57003     3 1s    0.68179     4 1s   -0.68183
  11.1     2.00000    -1.51710     5 1s    0.91866
  12.1     2.00000    -1.30623     2 1s    0.90437
  13.1     2.00000    -0.79149     1 1s   -0.25042     1 3d0  -0.44649     1 3d2+  0.31547
                                   3 2pz   0.48473     4 2pz  -0.48472
  14.1     2.00000    -0.72685     3 2py   0.54155     4 2py  -0.54153     5 2pz   0.40940
  15.1     2.00000    -0.70561     1 3d1+  0.28880     3 2px   0.61124     4 2px  -0.61122
  16.1     2.00000    -0.67598     3 2py  -0.66754     4 2py  -0.66755
  17.1     2.00000    -0.66329     3 2px   0.57822     4 2px   0.57824     5 2px   0.39818
  18.1     2.00000    -0.65501     1 2pz   0.38465     3 2pz  -0.59668     4 2pz  -0.59668
  19.1     2.00000    -0.63760     3 2px   0.30928     4 2px   0.30929     5 2px  -0.81351
  20.1     2.00000    -0.60884     3 2py  -0.30528     4 2py   0.30528     5 2pz   0.82173
  21.1     2.00000    -0.58831     1 1s    0.53808     1 3d0  -0.41234     1 3d2+  0.64243
                                   5 2py  -0.29582
  22.1     1.99593    -0.77427     1 2py  -0.27378     1 3d2+  0.37351     2 1s    0.31607
                                   5 2py   0.71580
  23.1     1.95066    -0.66127     1 3d2- -0.78507     2 2px   0.48793
  24.1     1.94903    -0.64384     1 3d1- -0.80076     2 2pz   0.49251
  25.1     1.94478    -0.74254     1 2py   0.35595     1 3d0   0.25242     1 3d2+  0.27509
                                   2 2py  -0.83143
```

```
26.1     1.04993    -0.35902     1 3d1-  0.59836     2 2pz   0.87335
27.1     1.04816    -0.35488     1 3d2-  0.61398     2 2px   0.86789
28.1     1.00099    -0.35139     1 3d1+ -0.96808     3 2px   0.27951     4 2px  -0.27951
29.1     0.06053     0.22247     1 1s   -0.38958     1 3d0   0.62891     1 3d2+  0.58148
                                 2 1s    0.27874     2 2py   0.86651     5 2py  -0.35933
30.1    -0.00000     0.01681     1 1s    2.62171     1 1s   -1.94698     1 2py  -0.37795
                                 1 2py   0.85257     1 3d0  -0.38828     1 3d2+ -0.49619
                                 2 1s   -1.26036     2 2py  -0.49319     5 1s   -0.82879
                                 5 2py   0.30328
```

Spin population: Individual basis function populations

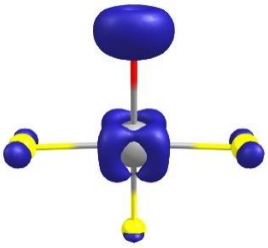
```
1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2px    1 2py    1 2pz    1 2px
0.00001 -0.00296 -0.00022 -0.00002 -0.00012 -0.00000  0.00014  0.00031  0.00004 -0.00304

1 2py    1 2pz    1 2px    1 2py    1 2pz    1 2px    1 2py    1 2pz    1 2px    1 2py
-0.00066  0.00134  0.00121 -0.00520 -0.00051 -0.00015  0.00005 -0.00020  0.00106 -0.00007

1 2pz    1 2px    1 2py    1 2pz    1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0
0.00005 -0.00008 -0.00000 -0.00008  0.00088  0.28979  0.84280  0.00623  0.26573  0.00008

1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0
0.01864  0.03275  0.00042  0.02874 -0.00002  0.00055  0.00180  0.00000  0.00113 -0.00022

1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 4f1+
-0.00038 -0.00030 -0.00000 -0.00451  0.00003  0.00020 -0.00003 -0.00000 -0.00021  0.00002

1 4f1-   1 4f0    1 4f3+   1 4f2-   1 4f3-   1 4f2+   1 4f1+   1 4f1-   1 4f0    1 4f3+
-0.00001  0.00010  0.00011  0.00000 -0.00000  0.00008  0.00022 -0.00021  0.00160  0.00203

1 4f2-   1 4f3-   1 4f2+   1 4f1+   1 4f1-   1 4f0    1 4f3+   1 4f2-   1 4f3-   1 4f2+
0.00005 -0.00022  0.00146 -0.00050  0.00000 -0.00355 -0.00368  0.00004  0.00006 -0.00364

1 5g0    1 5g2-   1 5g1+   1 5g4+   1 5g1-   1 5g2+   1 5g4-   1 5g3+   1 5g3-   1 5g0
-0.00000  0.00006 -0.00003 -0.00000  0.00006  0.00000  0.00004  0.00000  0.00004 -0.00000

1 5g2-   1 5g1+   1 5g4+   1 5g1-   1 5g2+   1 5g4-   1 5g3+   1 5g3-   2 1s     2 1s
0.00025  0.00049 -0.00003  0.00040 -0.00002  0.00144  0.00000  0.00072  0.00000  0.00387

2 1s     2 1s     2 1s     2 2px    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 2px
0.00002  0.00151  0.00195  0.66596  0.02523  0.67684  0.00362 -0.00076  0.00282  0.00192

2 2py    2 2pz    2 2px    2 2py    2 2pz    2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-
-0.00315  0.00244  0.00231  0.00030  0.00391 -0.00000  0.00000  0.00000 -0.00001  0.00000

2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-   2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-
-0.00002 -0.00032  0.00010 -0.00004 -0.00028  0.00001 -0.00251  0.00011  0.00004 -0.00276

2 4f1+   2 4f1-   2 4f0    2 4f3+   2 4f2-   2 4f3-   2 4f2+   2 4f1+   2 4f1-   2 4f0
0.0    -0.00000  0.00002  0.00005  0.00001 -0.00000  0.00003 -0.00002  0.00001 -0.00007

2 4f3+   2 4f2-   2 4f3-   2 4f2+   3 1s     3 1s     3 1s     3 1s     3 1s     3 2px
0.00001  0.00012  0.00001 -0.00001  0.00000  0.00003  0.00000 -0.00012 -0.00122  0.05975

3 2py    3 2pz    3 2px    3 2py    3 2pz    3 2px    3 2py    3 2pz    3 2px    3 2py
0.00488 -0.00010  0.00009  0.00005 -0.00001  0.00185  0.00018 -0.00019 -0.00011  0.00130

3 2pz    3 3d0    3 3d2-   3 3d1+   3 3d2+   3 3d1-   3 3d0    3 3d2-   3 3d1+   3 3d2+
-0.00037  0.00000  0.00000  0.00001  0.00000  0.00001  0.00001  0.00001  0.00033  0.00000

3 3d1-   3 3d0    3 3d2-   3 3d1+   3 3d2+   3 3d1-   3 4f1+   3 4f1-   3 4f0    3 4f3+
0.00014 -0.00000 -0.00000 -0.00150  0.00002  0.00021  0.00002  0.00001  0.00000  0.00000

3 4f2-   3 4f3-   3 4f2+   3 4f1+   3 4f1-   3 4f0    3 4f3+   3 4f2-   3 4f3-   3 4f2+
0.00000  0.00000  0.00000  0.00002  0.00009  0.00000  0.00000  0.00001 -0.00000 -0.00000

4 1s     4 1s     4 1s     4 1s     4 1s     4 2px    4 2py    4 2pz    4 2px    4 2py
0.00000  0.00003  0.00000 -0.00012 -0.00122  0.05975  0.00488 -0.00010  0.00009  0.00005

4 2pz    4 2px    4 2py    4 2pz    4 2px    4 2py    4 2pz    4 3d0    4 3d2-   4 3d1+
-0.00001  0.00185  0.00018 -0.00019 -0.00011  0.00130 -0.00037  0.00000  0.00000  0.00001

4 3d2+   4 3d1-   4 3d0    4 3d2-   4 3d1+   4 3d2+   4 3d1-   4 3d0    4 3d2-   4 3d1+
0.00000  0.00001  0.00001  0.00001  0.00033  0.00000  0.00014 -0.00000 -0.00000 -0.00150

4 3d2+   4 3d1-   4 4f1+   4 4f1-   4 4f0    4 4f3+   4 4f2-   4 4f3-   4 4f2+   4 4f1+
0.00002  0.00021  0.00002  0.00001  0.00000  0.00000  0.00000  0.00000  0.00000  0.00002
```

```
4 4f1-   4 4f0    4 4f3+   4 4f2-   4 4f3-   4 4f2+   5 1s     5 1s     5 1s     5 1s
0.00009  0.00000  0.00000  0.00001 -0.00000 -0.00000  0.00000 -0.00040  0.00001 -0.00017

5 1s     5 2px    5 2py    5 2pz    5 2px    5 2py    5 2pz    5 2px    5 2py    5 2pz
-0.00047  0.01811 -0.01643  0.01204  0.00008 -0.00013  0.00011  0.00036 -0.00022  0.00016

5 2px    5 2py    5 2pz    5 3d0    5 3d2-   5 3d1+   5 3d2+   5 3d1-   5 3d0    5 3d2-
-0.00023 -0.00014  0.00010  0.00000  0.00000  0.00000  0.00000  0.00000  0.00001  0.00013

5 3d1+   5 3d2+   5 3d1-   5 3d0    5 3d2-   5 3d1+   5 3d2+   5 3d1-   5 4f1+   5 4f1-
0.00001  0.00004  0.00010  0.00001 -0.00005  0.00001  0.00005  0.00036  0.00000  0.00000

5 4f0    5 4f3+   5 4f2-   5 4f3-   5 4f2+   5 4f1+   5 4f1-   5 4f0    5 4f3+   5 4f2-
0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00001  0.00002  0.00005  0.00001

5 4f3-   5 4f2+
0.00001  0.00004
```

Population analysis by basis function type

```
 Unique atom        s         p         d         f         g     Total     Charge
   1  PT     -0.00331 -0.00580  1.48408 -0.00602  0.00343  1.47237  +16.52763
   2  O       0.00736  1.38143 -0.00568  0.00017  0.00000  1.38328  + 6.61672
   3  F      -0.00131  0.06731 -0.00078  0.00015  0.00000  0.06537  + 8.93463
   4  F      -0.00131  0.06731 -0.00078  0.00015  0.00000  0.06537  + 8.93463
   5  F      -0.00104  0.01382  0.00068  0.00015  0.00000  0.01361  + 8.98639
```

Spin density (BP86/AVTZ(-PP), iso-surface = 0.08 electron a.u.$^{-3}$)



NPA batch (NBO) ($^4A_1$)

Summary of Natural Population Analysis:

```
                                    Natural Population
               Natural    -----------------------------------------------
  Atom No      Charge         Core      Valence    Rydberg      Total
 -----------------------------------------------------------------------
   Pt  1     2.07220     67.99889      7.86537    0.06354    75.92780
    O  2    -0.12526      2.00000      6.10609    0.01918     8.12526
    F  3    -0.62988      2.00000      7.61152    0.01836     9.62988
    F  4    -0.62988      2.00000      7.61152    0.01836     9.62988
    F  5    -0.68717      2.00000      7.66809    0.01908     9.68717
 =======================================================================
 * Total *   0.00000     75.99889     36.86259    0.13852   113.00000
```

AIM Charges ($^4A_1$)

Total result:

```
  #Basin      Integral(a.u.)     Vol(Bohr^3)   Vol(rho>0.001)
     1        9.6682883151        1113.161       112.576
     2       75.7400296961         441.330       121.373
     3        9.6988587638        1202.439       115.252
     4        8.2242414397        1012.075       110.163
     5        9.6683210564        1128.976       112.573
 Sum of above integrals:        112.99973927
 Sum of basin volumes (rho>0.001):     571.938 Bohr^3
```

```
Normalization factor of the integral of electron density is    0.999998
The atomic charges after normalization and atomic volumes:
     1 (Pt)    Charge:    2.259796     Volume:   121.373 Bohr^3
     2 (O )    Charge:   -0.224260     Volume:   110.163 Bohr^3
     3 (F )    Charge:   -0.668343     Volume:   112.573 Bohr^3
     4 (F )    Charge:   -0.668311     Volume:   112.576 Bohr^3
     5 (F )    Charge:   -0.698881     Volume:   115.252 Bohr^3
```

Part 9. CASSCF calculations on different spin states of OCuF ($^3\Sigma^-$; $C_{\infty v}$) and OCuF$_2$ ($^2B_2$, $^4A_2$; C_{2v})

Table S9.1. OCuF (C_{2v}/ $C_{\infty v}$; $^3A_2$/ $^3\Sigma^-$)

CASSCF(14,9)/CASPT2/VTZ-DK

Optimization and normal mode calculation carried out in C_1 point group symmetry.
CuF= 1.68706376 ANG
CuO= 1.63489075 ANG
A1 = 180.000000 DEGREE

TOTAL ENERGIES -1827.66479990

CI vector

```
=========

 222222aa0       0.8850348
 2222aa220       0.4404442
 222022aa2      -0.0696963
 2220aa222      -0.0519433
```

NATURAL ORBITALS FOR STATE 1.4 (ms2=2)

```
================

     Orbital  Occupation    Energy     Coefficients
      1.1     2.00000  -332.73456    1 1s     0.97828
      2.1     2.00000   -41.96310    1 1s     0.97824
      3.1     2.00000   -36.10835    1 2pz    0.99997
      4.1     2.00000   -36.10370    1 2px    0.99973
      5.1     2.00000   -36.10370    1 2py    0.99973
      6.1     2.00000   -26.25004    2 1s     0.99916
      7.1     2.00000   -20.63786    3 1s     0.99914
      8.1     2.00000    -5.44392    1 1s     0.99788
      9.1     2.00000    -3.64203    1 2pz    0.99580
     10.1     2.00000    -3.63761    1 2px    0.99986
     11.1     2.00000    -3.63761    1 2py    0.99986
     12.1     2.00000    -1.50725    2 1s     0.94529
     13.1     2.00000    -1.18327    3 1s     0.94264     3 2pz  -0.25925
     14.1     2.00000    -0.62768    2 2pz    0.87729
     15.1     2.00000    -0.59791    2 2py    0.91798
     16.1     2.00000    -0.59791    2 2px    0.91798
     17.1     1.99923    -0.75727    1 3d2+  1.00494
     18.1     1.99923    -0.75727    1 3d2- -1.00494
     19.1     1.98859    -0.61823    1 1s     0.32645     1 3d0  -0.69610
                                     3 2pz    0.50090
     20.1     1.97549    -0.77134    1 3d0    0.66322     3 2pz   0.65818
     21.1     1.83175    -0.59636    1 3d1-   0.73716     3 2py  -0.57480
     22.1     1.83175    -0.59636    1 3d1+   0.73716     3 2px  -0.57480
     23.1     1.16833    -0.33998    1 3d1+ -0.68745     3 2px  -0.73276
     24.1     1.16833    -0.33998    1 3d1-   0.68745     3 2py   0.73276
     25.1     0.03729     0.35433    1 1s    -0.83973     1 2pz   0.40061
                                     1 3d0  -0.28422     1 3d0    0.27189
                                     3 1s     0.35654      3 2pz   0.77469
                                     3 2pz  -0.36542
```

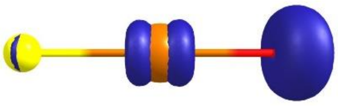
Spin population: Individual basis function populations

```
1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2px    1 2py    1 2pz
0.00000  0.00000 -0.00000 -0.01956 -0.00194 -0.00006  0.00049  0.00000  0.00000 -0.00000

1 2px    1 2py    1 2pz    1 2px    1 2py    1 2pz    1 2px    1 2py    1 2pz    1 2px
0.00006  0.00006 -0.00000 -0.00379 -0.00379  0.00121  0.00927  0.00927 -0.00580  0.00044

1 2py    1 2pz    1 2px    1 2py    1 2pz    1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-
0.00044  0.00012  0.00229  0.00229 -0.00001  0.00577  0.00039  0.43644  0.00039  0.43644

1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-
0.00206  0.00000  0.01147  0.00000  0.01147  0.00009  0.00000  0.00276  0.00000  0.00276

1 3d0    1 3d2-   1 3d1+   1 3d2+   1 3d1-   1 4f1+   1 4f1-   1 4f0    1 4f3+   1 4f2-
-0.00032 -0.00000  0.00196 -0.00000  0.00196  0.00000  0.00000  0.00000  0.00000 -0.00000

1 4f3-   1 4f2+   1 4f1+   1 4f1-   1 4f0    1 4f3+   1 4f2-   1 4f3-   1 4f2+   1 5g0
0.00000 -0.00000  0.00018  0.00018  0.00003  0.00000  0.00000  0.00000  0.00000 -0.00000

1 5g2-   1 5g1+   1 5g4+   1 5g1-   1 5g2+   1 5g4-   1 5g3+   1 5g3-   2 1s     2 1s
0.00000 -0.00000  0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000 -0.00001

2 1s     2 1s     2 2px    2 2py    2 2pz    2 2px    2 2py    2 2pz    2 2px    2 2py
0.00000 -0.00001  0.00835  0.00835 -0.00070 -0.00010 -0.00010 -0.00003  0.00021  0.00021

2 2pz    2 3d0    2 3d2-   2 3d1+   2 3d2+   2 3d1-   2 3d0    2 3d2-   2 3d1+   2 3d2+
-0.00001 -0.00000  0.00000  0.00000  0.00000  0.00000 -0.00000  0.00000  0.00010  0.00000

2 3d1-   2 4f1+   2 4f1-   2 4f0    2 4f3+   2 4f2-   2 4f3-   2 4f2+   3 1s     3 1s
0.00010  0.00001  0.00001 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00332

3 1s     3 1s     3 2px    3 2py    3 2pz    3 2px    3 2py    3 2pz    3 2px    3 2py
0.00006 -0.00000  0.50879  0.50879  0.02646  0.00383  0.00383 -0.00088  0.01667  0.01667

3 2pz    3 3d0    3 3d2-   3 3d1+   3 3d2+   3 3d1-   3 3d0    3 3d2-   3 3d1+   3 3d2+
-0.00863  0.00001  0.00000  0.00002  0.00000  0.00002 -0.00006  0.00000 -0.00015  0.00000

3 3d1-   3 4f1+   3 4f1-   3 4f0    3 4f3+   3 4f2-   3 4f3-   3 4f2+
-0.00015  0.00002  0.00002 -0.00000  0.00000  0.00000  0.00000  0.00000
```

Population analysis by basis function type

```
 Unique atom        s         p         d         f         g     Total     Charge
   1   CU      -0.02107   0.01205   0.91364   0.00039  -0.00000   0.90500  +28.09500
   2   F       -0.00002   0.01617   0.00020   0.00001   0.00000   0.01637  + 8.98363
   3   O        0.00338   1.07553  -0.00031   0.00003   0.00000   1.07863  + 6.92137
```

Spin density (BP86/AVTZ(-PP), iso-surface = 0.08 electron a.u.$^{-3}$)



NPA batch (NBO) ($^3\Sigma^-$)
Summary of Natural Population Analysis:

```
                                 Natural Population                 Natural
             Natural    - - - - - - - - - - - - - - - - - - - - - -   Spin
  Atom No    Charge         Core      Valence    Rydberg      Total      Density
 - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
    Cu  1    1.47630     17.99973     9.47996    0.04402    27.52370     0.85150
     F  2   -0.83510      2.00000     7.82569    0.00941     9.83510     0.01999
     O  3   -0.64120      2.00000     6.62491    0.01629     8.64120     1.12851
 ====================================================================
 * Total *   0.00000     21.99972    23.93055    0.06972    46.00000     2.00000
```

AIM Charges ($^3\Sigma^-$)

```
Total result:
  #Basin      Integral(a.u.)     Vol(Bohr^3)   Vol(rho > 0.001)
      1         8.5884401254       1373.669        137.113
      2        27.6325391379        859.778        114.458
      3         9.7790901595       1270.583        125.766
 Sum of above integrals:         46.00006942
 Sum of basin volumes (rho>0.001):     377.337 Bohr^3
```

```
 Normalization factor of the integral of electron density is    1.000002
The atomic charges after normalization and atomic volumes:
      1 (Cu)    Charge:    1.367503     Volume:   114.458 Bohr^3
      2 (F )    Charge:   -0.779075     Volume:   125.766 Bohr^3
      3 (O )    Charge:   -0.588427     Volume:   137.113 Bohr^3
```

Vibrational Frequencies:

OCuF ($C_{\infty v}$, $^3\Sigma^-$)

		CASPT2[a] /VTZ-DK	CASPT2[a] /AVTZ-DK
$d_{Cu\text{-}F}$ [Å]		1.687	1.692
$d_{Cu\text{-}O}$ [Å]		1.635	1.636
ν_1 (π) [cm^{-1}]		78.62	85.56
ν_2 (σ^+) [cm^{-1}]	$^{16}O^{63}CuF$	672.73	664.03
ν_3 (σ^-) [cm^{-1}]		925.55	918.15
ν_1 (π) [cm^{-1}]		78.13	85.01
ν_2 (σ^+) [cm^{-1}]	$^{16}O^{65}CuF$	672.70	663.99
ν_3 (σ^-) [cm^{-1}]		920.49	913.14
ν_1 (π) [cm^{-1}]		80.57	87.38
ν_2 (σ^+) [cm^{-1}]	$^{18}O^{63}CuF$	653.30	645.14
ν_3 (σ^-) [cm^{-1}]		907.60	899.93
ν_1 (π) [cm^{-1}]		80.09	86.85
ν_2 (σ^+) [cm^{-1}]	$^{18}O^{65}CuF$	653.30	645.14
ν_3 (σ^-) [cm^{-1}]		902.41	894.79

[a] CASSCF(14,9) reference function.

Table S9.2. Structural parameters (Å, deg) and relative energies (kJ mol^{-1}) of the energetically lowest doublet and quartet states of $OCuF_2$.

Electronic state (C_{2v})	r(Cu–O)	r(Cu–F)	α(O–Cu–F)	$\Delta E_{CCSD(T)}$ [a]	$\Delta E_{\mathrm{CASPT2}}$ [b]	$\Delta E_{\mathrm{CASSCF}}$ [c]
$^2B_2$	1.748	1.687	95.5	0	6.6	47.7
$^4A_2$-2	1.945	1.727	96.9	20.4	32.1	0
$^4A_2$-1	1.596	1.703	120.6	45.1	0	134.4

Structures were optimized on CASSCF(13,8)/CASPT2/VTZ-DK level. Values were calculated on the [a] CCSD(T)/VTZ-DK, [b] CASSCF(13,8)/CASPT2/VTZ-DK, and [c] CASSCF(13,9)/VTZ-DK level.

Table S9.3. Structural parameters (Å, deg) and vibrational frequencies (cm^{-1}) of the energetically lowest doublet and quartet states of $OCuF_2$.

Electronic States	**$^2B_2$**	**$^4A_2$-1**					**$^4A_2$-2**
	CASPT2/VTZ-DK [a]	**NEVPT2/VTZ-DK** [b]	**NEVPT2/cc-pwCVTZ** [b]	**NEVPT2/cc-pwCVTZ-DK** [b]	**CASPT2/cc-pwCVTZ-DK** [b]	**CASPT2/VTZ-DK** [a]	**CASPT2/VTZ-DK** [a]
r(CuO)	1.75	1.65	1.67	1.65	1.63	1.60	1.95
r(CuF)	1.69	1.71	1.72	1.71	1.70	1.70	1.73
a(OCuF)	95.5	112.8	111.0	113.8	117.3	120.6	96.9
Cu-O str. (a_1)	-	788	705	890	1075	1031	-
F-Cu-F (b_2)	-	746	745	765	750	713	-
F-Cu-F (a_1)	-	636	584	652	684	500	-
C_0^2 [c]	0.749	0.886	0.899	0.876	0.867	0.852	0.991

[a] CASSCF(13,8); [b] CASSCF(9,7); [c] Square of the CI coefficient for the leading electron configuration.

Table S9.4. $OCuF_2$ (C_{2v}, $^2B_2$)

CASSCF(13,8)/CASPT2/VTZ-DK

```
 CuO=              1.74797088 ANG
 CuF=              1.68745055 ANG
 A1=            95.54567128 DEGREE
```

```
TOTAL ENERGIES                    -1928.331559163
```

```
CI vector
 =========

  220 22 2a 2      0.8657032
  202 22 2a 2     -0.4188549
  2aa 22 2b 2      0.2115417
  2ba 22 2a 2     -0.1097699
  2ab 22 2a 2     -0.1017718
```

```
NATURAL ORBITALS FOR STATE 1.3 (ms2=1)
=======================================
   11.1     2.00000    -0.60144     3 2pz  -0.87760     3 2py  -0.25726
   12.1     1.99734    -0.75196     1 3d0  -0.54498     1 3d2+  0.44511     3 2py  -0.50811
   13.1     1.57702    -0.52248     1 3d0  -0.49035     1 3d2+ -0.45030     2 2pz   0.66409
   14.1     0.42967    -0.11871     1 3d0   0.59768     1 3d2+  0.40772     2 2pz   0.75596
    3.2     2.00000    -0.59928     3 2px   0.92361
    4.2     1.99968    -0.75593     1 3d1+  0.69816     2 2px   0.67191
    5.2     1.99715    -0.67176     1 3d1+ -0.73004     2 2px   0.71564
    6.3     2.00000    -0.59311     3 2py   0.31920     3 2pz  -0.86836
    7.3     1.99522    -0.79562     1 3d1-  1.00100
    8.3     1.00446    -0.34978     2 2py   1.02622
    1.4     2.00000    -0.62462     3 2px   0.91004
    2.4     1.99947    -0.73594     1 3d2-  0.99929
```

Table S9.5. $OCuF_2$ (C_{2v}, $^2B_2$)

CASSCF(13,9)/VTZ-DK

```
CuO=              1.74797088 ANG
CuF=              1.68745055 ANG
A1=              95.54567128 DEGREE
```

```
TOTAL ENERGIES                    -1927.19072291
```

CI vector
=========

```
2200 22 2a 2      0.8912460
2020 22 2a 2     -0.3787268
2aa0 22 2b 2     -0.1764282
2ba0 22 2a 2      0.0917583
2ab0 22 2a 2      0.0846699
2ba0 22 a2 2      0.0533127
```

NATURAL ORBITALS FOR STATE 1.3 (ms2=1)

```
==========================================

Orbital    Occupation   Energy      Coefficients
   11.1     2.00000    -0.60673     1 1s   -0.01270     1 1s   -0.02088     1 1s    0.02271     1 2pz   0.02996    1 2pz  -0.08370
                                    1 2pz   0.01178     1 2pz  -0.02135     1 3d0   0.02453     1 3d2+  0.01474     2 1s    0.05027
                                    2 1s    0.02812     2 2pz   0.05295     3 1s   -0.01149     3 1s    0.02009     3 2pz  -0.90964
                                    3 2py  -0.13227     3 2pz  -0.05817     3 2py  -0.01695     3 3d1-  0.02146
   12.1     1.98958    -0.77125     1 1s    0.07489     1 1s    0.10759     1 1s    0.03016     1 2pz   0.04989     1 2pz  -0.02748
                                    1 2pz  -0.02007     1 3d0  -0.58167     1 3d2+  0.80659     1 3d0   0.01696     1 3d2+ -0.01077
                                    2 1s    0.02013     2 1s    0.01085     2 2pz   0.04689     2 2pz  -0.01113     3 1s    0.01788
                                    3 2py   0.02596     3 2py  -0.01317
   13.1     1.65477    -0.55010     1 1s    0.01132     1 1s    0.06820     1 1s   -0.05655     1 1s   -0.09118     1 1s    0.01247
                                    1 1s   -0.08363     1 2pz   0.05000     1 2pz   0.23547     1 2pz  -0.18530     1 2pz   0.01506
                                    1 2pz  -0.08342     1 3d0  -0.52201     1 3d2+ -0.40514     1 3d0  -0.02101     1 3d0   0.04721
                                    1 3d2+  0.01114     2 1s    0.10758     2 1s    0.01772     2 2pz   0.66361     2 2pz   0.01681
                                    2 2pz  -0.01731     2 3d0  -0.02115     3 1s   -0.01720     3 2pz   0.03618     3 2py  -0.02499
   14.1     0.35085    -0.09222     1 1s   -0.02186     1 1s   -0.14832     1 1s   -0.06253     1 2pz  -0.05930     1 2pz  -0.17170
                                    1 2pz   0.11300     1 2pz  -0.01429     1 2pz   0.07103     1 3d0  -0.62213     1 3d2+ -0.37865
                                    1 3d0   0.07993     1 3d2+  0.06287     1 3d0   0.02289     1 3d2+  0.01744     1 3d0  -0.01663
                                    2 1s    0.03193     2 1s    0.07517     2 2pz  -0.75899     2 2pz  -0.01534     2 2pz   0.07654
                                    3 1s   -0.04406     3 1s   -0.01077     3 2pz  -0.12100     3 2py   0.21689     3 2pz  -0.01659
                                    3 2py   0.02470
   15.1     0.00996     1.38601     1 1s    0.01638     1 1s    0.46127     1 1s    0.13895     1 1s    0.04298     1 1s   -0.06955
                                    1 2pz   0.01266     1 2pz   0.23510     1 2pz  -0.09972     1 2pz  -0.10371     1 3d0  -0.09549
                                    1 3d2+  0.03507     1 3d0  -0.54256     1 3d2+  0.97142     1 3d0  -0.04686     1 3d2+  0.09375
                                    1 3d0   0.19461     1 3d2+ -0.26273     1 4f0  -0.01762     1 4f2+  0.01745     2 1s   -0.01989
                                    2 1s   -0.03414     2 2pz   0.06644     2 2pz  -0.02601     2 3d0  -0.01623     3 1s   -0.05490
                                    3 1s    0.08274     3 2pz  -0.01834     3 2py   0.14798     3 2py  -0.04135
   16.1    -0.00000     0.08444     1 1s   -0.05141     1 1s   -0.13877     1 1s   -0.71434     1 1s   -2.91523     1 1s    0.64523
                                    1 1s   -0.16389     1 1s    3.56518     1 2pz   0.05781     1 2pz   0.77396     1 2pz  -0.44316
                                    1 2pz   0.04926     1 2pz  -0.95020     1 3d0  -0.04816     1 3d2+ -0.02830     1 3d0   0.01203
                                    1 3d2+ -0.03903     1 3d0   0.20876     1 3d2+  0.10854     2 1s   -0.01284     2 2pz  -0.01972
                                    2 2pz   0.03203     3 1s   -0.01447     3 1s   -0.12992     3 1s    0.15396     3 2pz   0.12071
                                    3 2pz  -0.01421     3 2py   0.02034     3 2pz   0.08906     3 2py  -0.18521

    3.2     2.00000    -0.60574     1 2px  -0.03043     1 2px   0.07495     1 2px   0.02018     1 3d1+ -0.01809     3 2px   0.92364
                                    3 2px   0.06076     3 3d2- -0.02215
    4.2     1.99964    -0.76130     1 2px  -0.04990     1 2px   0.05403     1 2px   0.02259     1 3d1+  0.67467     1 3d1+ -0.02133
                                    2 2px   0.69226     2 3d1+ -0.01809     3 2px  -0.01170
    5.2     1.99654    -0.67869     1 2px  -0.02829     1 2px  -0.03646     1 2px   0.04524     1 2px   0.01876     1 3d1+ -0.75148
                                    1 3d1+  0.02454     1 3d1+  0.01261     2 2px   0.69388     2 2px   0.01962     3 2px  -0.04810
```

```
6.2    -0.00000     0.08683     1 2px  -0.07876     1 2px  -1.14925     1 2px   0.74976     1 2px  -0.08987     1 2px   1.56665
                                1 3d1+  0.02199     1 3d1+ -0.01590     2 2px  -0.14752     2 2px   0.01069     2 2px  -0.06103
                                3 2px  -0.20666     3 2px   0.01836     3 2px  -0.10277

6.3     2.00000    -0.59898     1 2py   0.05741     1 2py   0.19658     1 2py  -0.18511     1 2py   0.01692     1 2py  -0.06293
                                1 3d1-  0.04679     1 3d1- -0.01395     1 3d1- -0.03101     2 2py  -0.03438     3 1s    0.05670
                                3 1s   -0.01258     3 2py   0.34010     3 2pz  -0.86011     3 2py   0.02377     3 2pz  -0.05273
                                3 3d1-  0.01772
7.3     1.99303    -0.80829     1 2py  -0.02230     1 2py  -0.03776     1 2py   0.05880     1 3d1-  0.99816     1 3d1- -0.03256
                                1 3d1- -0.02644     2 2py   0.08956     2 2py  -0.01009     3 1s    0.01360     3 2py  -0.10772
                                3 2pz  -0.08195     3 2py  -0.01155     3 2pz  -0.02593
8.3     1.00656    -0.34626     1 2py  -0.06739     1 2py   0.05509     1 2py   0.02687     1 3d1- -0.13601     1 3d1-  0.02344
                                1 3d1- -0.01081     2 2py   1.02212     2 2py   0.01185     2 2py  -0.05037     2 3d1- -0.01427
                                3 1s   -0.02131     3 1s   -0.01879     3 2py   0.06550     3 2pz  -0.06664     3 2py   0.01409
9.3    -0.00000     0.14402     1 2py  -0.01140     1 2py  -0.19269     1 2py  -2.98615     1 2py   1.45209     1 2py  -0.15336
                                1 2py   2.65476     2 2py  -0.10228     2 2py  -0.02106     3 1s   -0.15114     3 1s   -0.10389
                                3 2py  -0.08244     3 2py   0.05328     3 2py  -0.25152     3 2pz   0.01562

1.4     2.00000    -0.61900     1 3d2-  0.10543     1 3d2-  0.01251     1 3d2-  0.02424     3 2px   0.92438     3 2px   0.05246
                                3 3d2- -0.01824
2.4     1.99909    -0.75877     1 3d2-  1.00839     1 3d2- -0.02939     1 3d2- -0.02997     3 2px  -0.17869     3 2px  -0.03222
3.4    -0.00000     0.64242     1 3d2- -0.48447     1 3d2- -0.32098     1 3d2- -0.14951     1 3d2-  1.64588     2 3d2-  0.04790
                                3 2px  -0.38359     3 2px  -0.05874     3 2px  -0.20934     3 3d2- -0.01156     3 3d2-  0.01773
```

Spin population: Individual basis function populations

```
Symmetry no. 1

1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz
-0.00000 -0.00000  0.00002 -0.00724 -0.00242  0.00013 -0.00060 -0.00000  0.00010 -0.00908

1 2pz    1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0
0.01301 -0.00056 -0.00145 -0.11468 -0.06098  0.00314 -0.00033 -0.00008 -0.00008 -0.00140

1 3d2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 5g0    1 5g4+   1 5g2+   2 1s     2 1s
-0.00043  0.00000  0.00000  0.00012  0.00000  0.00000 -0.00000 -0.00000  0.00000 -0.00011

2 1s     2 1s     2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0
0.00004 -0.00037  0.24788  0.00534 -0.01223 -0.00001  0.00000 -0.00022  0.00001  0.00002

2 4f2+   3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py    3 2pz    3 2py    3 2pz
0.00000  0.00000 -0.00018  0.00000 -0.00006  0.00208  0.00392  0.00001  0.00009  0.00004

3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-
-0.00033 -0.00000 -0.00000 -0.00000 -0.00001 -0.00001 -0.00002 -0.00000 -0.00000 -0.00000

3 4f3-
-0.00000


 Symmetry no. 2

1 2px    1 2px    1 2px    1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 3d1+   1 3d1+
0.00000  0.00000 -0.00000  0.00000  0.00000  0.00000 -0.00017  0.00000  0.00000  0.00000

1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 5g1+   1 5g3+   2 2px    2 2px    2 2px    2 3d1+
-0.00000  0.00000  0.00000  0.00000 -0.00000 -0.00000  0.00028  0.00000  0.00000 -0.00000

2 3d1+   2 4f1+   2 4f3+   3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
-0.00000 -0.00000  0.00000  0.00000 -0.00000 -0.00000 -0.00000  0.00000 -0.00000 -0.00000

3 4f1+   3 4f3+   3 4f2-
-0.00000 -0.00000 -0.00000


 Symmetry no. 3

1 2py    1 2py    1 2py    1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 3d1-   1 3d1-
0.00000 -0.00000 -0.00953  0.00604  0.00082  0.00354  0.01620  0.00434  0.00143 -0.00253

1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 5g1-   1 5g3-   2 2py    2 2py    2 2py    2 3d1-
0.00000  0.00000  0.00023  0.00001  0.00000  0.00000  0.93255  0.01027 -0.03172  0.00000

2 3d1-   2 4f1-   2 4f3-   3 1s     3 1s     3 1s     3 1s     3 2py    3 2pz    3 2py
-0.00001 -0.00000  0.00004  0.00000  0.00012  0.00000 -0.00032  0.00295  0.00246  0.00017

3 2pz    3 2py    3 2pz    3 3d1-   3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 4f1-
0.00001 -0.00005 -0.00025 -0.00000  0.00000 -0.00000 -0.00000  0.00002 -0.00002  0.00000

3 4f3-   3 4f0    3 4f2+
-0.00000  0.00000  0.00000


 Symmetry no. 4

1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 4f2-   1 4f2-   1 5g2-   1 5g4-   2 3d2-   2 3d2-
0.00003  0.00000  0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000

2 4f2-   3 2px    3 2px    3 2px    3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 4f2-   3 4f1+
0.00000  0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
```

```
3 4f3+
0.00000
```

Population analysis by basis function type

```
 Unique atom        s         p         d         f         g     Total    Charge
   1  CU     -0.01010  0.00290 -0.15553  0.00036  0.00000 -0.16238  +29.16238
   2  O      -0.00044  1.15237 -0.00023  0.00005  0.00000  1.15175  + 6.84825
   3  F1     -0.00022  0.00556 -0.00002 -0.00000  0.00000  0.00531  + 8.99469
```

NPA batch (NBO) ($^2B_2$)

```
                                      Natural Population
            Natural    ---------------------------------------------
  Atom No    Charge        Core      Valence    Rydberg      Total
 --------------------------------------------------------------------
   Cu  1    1.68216     17.99962      9.27094    0.04728    27.31784
    O  2   -0.05801      2.00000      6.04989    0.00813     8.05801
    F  3   -0.81207      2.00000      7.80391    0.00816     9.81207
    F  4   -0.81207      2.00000      7.80391    0.00816     9.81207
 ====================================================================
 * Total *  0.00000     23.99962     30.92864    0.07173    55.00000
```

AIM Charges ($^2B_2$)

```
Total result:
  #Basin      Integral(a.u.)      Vol(Bohr^3)    Vol(rho>0.001)
      1        9.7629373919        1107.963         121.716
      2       27.4065135687         433.902          82.499
      3        9.7629375290        1107.973         121.716
      4        8.0672110811        1154.297         115.161
 Sum of above integrals:         54.99959957
 Sum of basin volumes (rho>0.001):     441.092 Bohr^3

 Normalization factor of the integral of electron density is    0.999993
 The atomic charges after normalization and atomic volumes:
     1 (Cu)    Charge:    1.593287     Volume:    82.499 Bohr^3
     2 (O )    Charge:   -0.067270     Volume:   115.161 Bohr^3
     3 (F )    Charge:   -0.763008     Volume:   121.716 Bohr^3
     4 (F )    Charge:   -0.763008     Volume:   121.716 Bohr^3
```

Table S9.6. OCuF$_2$ (C_{2v}, $^4A_2$-1)

CASSCF(13,8)/CASPT2/VTZ-DK

CuO=   1.59555342 ANG
CuF=   1.70290557 ANG
A1=   120.63916148 DEGREE

TOTAL ENERGIES   -1928.334057309137

CI vector

```
=========

22222aaa      0.9232968
222aa22a     -0.2893757
22a2a2a2      0.1841784
22aa2a22      0.1343200
22aaa222     -0.0843995
```

NATURAL ORBITALS FOR STATE 1.4 (ms2=3)

```
========================================
Orbital  Occupation  Energy  Coefficients

   11.1     2.00000    -0.61317     3 2py   0.85301
   12.1     1.99968    -1.09545     1 3d2+ -0.28058     2 1s   -0.73211     3 2pz   0.54787
   13.1     1.87430    -0.75844     1 3d0   0.51756     1 3d2+  0.26986     2 2pz  -0.75235
   14.1     1.12710    -0.37571     1 3d0   0.75411     1 3d2+  0.32451     2 2pz   0.59882
    3.2     2.00000    -0.59245     3 2px   0.91174
    4.2     1.93837    -0.76286     1 3d1+  0.91835     2 2px   0.32587
    5.2     1.06106    -0.42199     1 3d1+ -0.41499     2 2px   0.94519
    6.3     2.00000    -0.57638     3 2py   0.37873     3 2pz   0.85131
    7.3     1.88959    -0.71646     1 3d1-  0.81030     2 2py   0.50298
    8.3     1.11107    -0.41733     1 3d1- -0.57610     2 2py   0.85480
    1.4     2.00000    -0.60312     3 2px   0.91517
    2.4     1.99882    -0.76589     1 3d2-  0.99887
```

Table S9.7. OCuF$_2$ (C_{2v}, $^4A_2$-1)

CASSCF(13,9)/VTZ-DK

CuO= 1.59555342 ANG
CuF= 1.70290557 ANG
A1= 120.63916148 DEGREE

CI vector

```
=========
 22a0 2a 2a 2       0.9280886
 2a20 2a a2 2      -0.2580225
 2a20 a2 2a 2      -0.1657932
 22a0 a2 a2 2      -0.1514666
 2a20 a2 a2 2      -0.0689251
 02a2 2a 2a 2      -0.0521667
```

TOTAL ENERGIES -1927.15768893

NATURAL ORBITALS FOR STATE 1.4 (ms2=3)

```
================================================
Orbital  Occupation  Energy  Coefficients

   11.1     2.00000    -0.60831     1 1s    0.02369     1 1s   -0.01051     1 1s   -0.01706     1 2pz  -0.04621     1 2pz  -0.09717
                                    1 2pz   0.10587     1 2pz   0.06428     1 3d0  -0.07931     1 3d2+ -0.02170     1 3d0  -0.01369
                                    1 3d0  -0.03065     1 3d2+ -0.02597     2 1s   -0.01952     2 1s    0.01760     2 2pz  -0.10070
                                    2 2pz  -0.02139     3 1s   -0.01427     3 2pz   0.73292     3 2py   0.52596     3 2pz   0.03219
                                    3 2py   0.03494     3 3d0   0.01527
   12.1     1.98480    -0.82453     1 1s    0.07575     1 1s    0.12960     1 1s    0.04551     1 2pz   0.04240     1 2pz   0.07594
                                    1 2pz  -0.02478     1 2pz  -0.03421     1 3d0  -0.42690     1 3d2+  0.89033     1 3d2+ -0.01766
                                    1 3d0   0.01860     2 1s   -0.04596     2 1s   -0.01448     2 2pz   0.03471     3 1s    0.01753
                                    3 1s    0.03115     3 2pz  -0.01527     3 2py   0.01091     3 2pz   0.01222     3 2py  -0.01509
   13.1     1.89554    -0.76720     1 1s    0.01469     1 1s    0.08230     1 1s    0.02928     1 1s   -0.06117     1 1s   -0.08635
                                    1 2pz   0.07526     1 2pz   0.22800     1 2pz  -0.19319     1 2pz   0.01435     1 2pz  -0.08152
                                    1 3d0  -0.52140     1 3d2+ -0.26290     1 3d0   0.03427     2 1s    0.11585     2 1s    0.03023
                                    2 2pz   0.74642     2 2pz   0.01340     2 2pz  -0.02794     2 3d0  -0.02416     3 1s   -0.01312
                                    3 2pz   0.05395     3 2py  -0.04548
   14.1     1.10558    -0.38572     1 1s    0.01027     1 1s    0.05784     1 1s    0.04431     1 1s   -0.02432     1 1s   -0.05236
                                    1 2pz   0.07705     1 2pz   0.17244     1 2pz  -0.18329     1 2pz   0.01441     1 2pz  -0.04674
                                    1 3d0   0.74078     1 3d2+  0.34617     1 3d0  -0.07509     1 3d2+ -0.03583     1 3d0  -0.02138
                                    2 1s   -0.04653     2 1s   -0.02693     2 2pz   0.59117     2 2pz   0.01020     3 1s    0.02973
                                    3 2pz   0.25454     3 2py  -0.04282     3 2pz   0.02698
   15.1     0.01595     0.96704     1 1s    0.02283     1 1s    0.53582     1 1s    0.23241     1 1s    0.01446     1 1s    0.02592
                                    1 2pz   0.04507     1 2pz   0.19655     1 2pz   0.13791     1 2pz  -0.11459     1 3d0   0.01808
                                    1 3d2+  0.03052     1 3d0  -0.37825     1 3d2+  0.88016     1 3d0  -0.04845     1 3d2+  0.12946
                                    1 3d0   0.17026     1 3d2+ -0.19626     1 4f0  -0.01805     1 4f2+  0.02617     2 1s   -0.11200
                                    2 1s   -0.15755     2 2pz   0.30748     2 2pz  -0.09884     2 3d0  -0.01258     2 3d2+  0.01682
                                    3 1s   -0.07834     3 1s    0.12587     3 2pz  -0.09436     3 2py   0.13589     3 2pz   0.04182
                                    3 2py  -0.03890
   16.1    -0.00000     0.08051     1 1s   -0.05934     1 1s   -0.16008     1 1s   -0.81514     1 1s   -3.29350     1 1s    0.68310
                                    1 1s   -0.18196     1 1s    3.91344     1 2pz  -0.13626     1 2pz  -1.96548     1 2pz   0.89696
                                    1 2pz  -0.09219     1 2pz   1.56948     1 3d2+ -0.02185     1 3d0  -0.08720     1 3d2+ -0.07562
                                    2 1s   -0.01707     2 1s   -0.17209     2 1s    0.17809     2 2pz  -0.10009     2 2pz   0.02293
                                    2 2pz  -0.25276     3 1s   -0.02833     3 1s   -0.04846     3 2pz  -0.04935     3 2py  -0.06606
                                    3 2py   0.01365     3 2pz  -0.02561     3 2py  -0.05251
    3.2     2.00000    -0.59929     1 2px  -0.02866     1 2px   0.01964     1 2px   0.07317     1 2px   0.01565     1 3d1+ -0.06362
                                    2 2px   0.02941     3 2px   0.91267     3 2px   0.05730     3 3d1+  0.01195     3 3d2- -0.01791
    4.2     1.93733    -0.77739     1 2px  -0.01977     1 2px  -0.06065     1 2px   0.08292     1 2px   0.02516     1 3d1+  0.89860
                                    1 3d1+ -0.01172     1 3d1+ -0.02708     2 2px   0.36525     2 2px   0.01074     2 3d1+ -0.02407
                                    3 2px   0.05591     3 2px   0.01111
    5.2     1.06159    -0.42172     1 2px  -0.02714     1 2px  -0.06731     1 2px   0.05853     1 2px   0.02442     1 3d1+ -0.45403
```

```
                                1 3d1+  0.04971     1 3d1+  0.01382     2 2px   0.92098     2 2px   0.01332     2 2px  -0.02352
                                2 3d1+ -0.01926     3 2px  -0.08516
6.2    -0.00000     0.08589     1 2px  -0.07670     1 2px  -1.18471     1 2px   0.76899     1 2px  -0.09189     1 2px   1.58758
                                1 3d1+ -0.02571     1 3d1+ -0.01402     1 3d1+  0.04615     2 2px  -0.15087     2 2px  -0.06558
                                3 2px  -0.21164     3 2px   0.01883     3 2px  -0.09873
6.3     2.00000    -0.58297     1 2py  -0.02758     1 2py  -0.03428     1 2py   0.06644     1 2py   0.02946     1 3d1-  0.02246
                                1 3d1-  0.03723     2 2py  -0.01980     3 1s   -0.03063     3 1s    0.01646     3 2py   0.38566
                                3 2pz   0.84944     3 2py   0.01488     3 2pz   0.06455     3 3d1- -0.01254     3 3d0   0.01650
7.3     1.89929    -0.73067     1 2py  -0.04910     1 2py  -0.09213     1 2py   0.13082     1 2py  -0.01092     1 2py   0.02786
                                1 3d1-  0.78970     1 3d1- -0.01563     1 3d1- -0.01638     2 2py   0.53067     2 2py   0.01303
                                2 3d1- -0.02741     3 1s    0.03797     3 1s    0.03247     3 2py  -0.10641     3 2pz  -0.03394
                                3 2py  -0.03211
8.3     1.10216    -0.41867     1 2py  -0.02167     1 2py  -0.03422     1 2py   0.02410     1 3d1- -0.60258     1 3d1-  0.07026
                                1 3d1-  0.02029     2 2py   0.82800     2 2py   0.01027     2 2py  -0.01919     2 3d1- -0.01210
                                3 1s   -0.04227     3 1s   -0.01394     3 2py   0.20152     3 2pz  -0.07666     3 2py   0.02278
9.3    -0.00000     0.12782     1 2py  -0.01107     1 2py  -0.18949     1 2py  -2.94468     1 2py   1.42723     1 2py  -0.14724
                                1 2py   2.59191     1 3d1- -0.03290     1 3d1-  0.22392     2 2py  -0.13736     2 2py  -0.05842
                                3 1s   -0.15016     3 1s    0.05684     3 2py  -0.08751     3 2pz  -0.06118     3 2py   0.04063
                                3 2pz  -0.01637     3 2py  -0.26692     3 2pz   0.09393
1.4     2.00000    -0.60267     1 3d2-  0.11353     1 3d2-  0.01099     1 3d2-  0.01954     3 2px   0.92433     3 2px   0.06164
                                3 3d2- -0.01681     3 3d1+  0.01072
2.4     1.99776    -0.80351     1 3d2-  1.00369     1 3d2- -0.03720     1 3d2- -0.02428     3 2px  -0.17245     3 2px  -0.03093
3.4    -0.00000     0.57570     1 3d2- -0.48179     1 3d2- -0.31268     1 3d2- -0.14659     1 3d2-  1.60110     2 3d2-  0.05554
                                3 2px  -0.28074     3 2px  -0.01513     3 2px  -0.27210     3 3d2-  0.02724
```

Spin population: Individual basis function populations

```
Symmetry no. 1

1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz
-0.00000 -0.00000  0.00001 -0.00565  0.00255  0.00010  0.00151  0.00000  0.00046 -0.01921

1 2pz    1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0
0.04031 -0.00186 -0.00218  0.45859  0.10502  0.01559  0.00604  0.00131  0.00068 -0.00103

1 3d2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 5g0    1 5g4+   1 5g2+   2 1s     2 1s
0.00116  0.00000 -0.00000  0.00009  0.00003 -0.00000 -0.00000 -0.00000  0.00000  0.00126

2 1s     2 1s     2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0
-0.00001  0.00015  0.34208  0.00540 -0.00486  0.00003 -0.00000 -0.00011 -0.00001  0.00009

2 4f2+   3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py    3 2pz    3 2py    3 2pz
-0.00000  0.00000  0.00041 -0.00001 -0.00009  0.04694  0.00177  0.00011  0.00008  0.00175

3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-
0.00008  0.00000 -0.00000  0.00000  0.00002  0.00001 -0.00002  0.00000  0.00000  0.00000

3 4f3-
0.00000


 Symmetry no. 2

1 2px    1 2px    1 2px    1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 3d1+   1 3d1+
-0.00000  0.00004 -0.01266  0.01082  0.00047  0.00337  0.20435  0.01346  0.00330 -0.00135

1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 5g1+   1 5g3+   2 2px    2 2px    2 2px    2 3d1+
-0.00000  0.00000  0.00025  0.00000 -0.00000  0.00000  0.77622  0.01079 -0.01370  0.00001

2 3d1+   2 4f1+   2 4f3+   3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
-0.00036  0.00001  0.00000  0.00570 -0.00004  0.00023  0.00000  0.00000 -0.00001  0.00001

3 4f1+   3 4f3+   3 4f2-
0.00000  0.00000 -0.00000


 Symmetry no. 3

1 2py    1 2py    1 2py    1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 3d1-   1 3d1-
0.00000  0.00009 -0.00385  0.00180 -0.00008  0.00291  0.32970  0.02098  0.00455 -0.00168

1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 5g1-   1 5g3-   2 2py    2 2py    2 2py    2 3d1-
0.00000 -0.00000  0.00013  0.00002 -0.00000 -0.00000  0.60619  0.00755 -0.00902  0.00001

2 3d1-   2 4f1-   2 4f3-   3 1s     3 1s     3 1s     3 1s     3 2py    3 2pz    3 2py
-0.00035  0.00002  0.00000 -0.00000  0.00077 -0.00001 -0.00001  0.03117  0.00483  0.00045

3 2pz    3 2py    3 2pz    3 3d1-   3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 4f1-
0.00010  0.00188  0.00029  0.00000  0.00000  0.00000 -0.00007  0.00003 -0.00004  0.00000

3 4f3-   3 4f0    3 4f2+
0.00000  0.00000 -0.00000

 Symmetry no. 4

1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 4f2-   1 4f2-   1 5g2-   1 5g4-   2 3d2-   2 3d2-
0.00212  0.00001  0.00000 -0.00001  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000

2 4f2-   3 2px    3 2px    3 2px    3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 4f2-   3 4f1+
0.00000  0.00005 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000

3 4f3+
0.00000
```

Population analysis by basis function type

```
Unique atom        s         p         d         f         g     Total     Charge
  1  CU     -0.00148  0.02042  1.16278  0.00053 -0.00000  1.18224  +27.81776
  2  O       0.00140  1.72064 -0.00078  0.00011  0.00000  1.72136  + 6.27864
  3  F1      0.00053  0.04769 -0.00002  0.00000  0.00000  0.04820  + 8.95180
```

AIM Charges ($^4A_2$)

```
Total result:
  #Basin      Integral(a.u.)     Vol(Bohr^3)   Vol(rho > 0.001)
     1         9.7752299840       1010.878        124.430
     2        27.3091889995        302.024         78.889
     3         9.7752300670       1010.885        124.430
     4         8.1401691375       1307.501        115.896
 Sum of above integrals:        54.99981819
 Sum of basin volumes (rho > 0.001):     443.646 Bohr^3
```

```
Normalization factor of the integral of electron density is    0.999997
 The atomic charges after normalization and atomic volumes:
     1 (Cu)    Charge:    1.690721     Volume:    78.889 Bohr^3
     2 (O )    Charge:   -0.140196     Volume:   115.896 Bohr^3
     3 (F )    Charge:   -0.775262     Volume:   124.430 Bohr^3
     4 (F )    Charge:   -0.775262     Volume:   124.430 Bohr^3
```

Summary of Natural Population Analysis:

```
                                    Natural Population
             Natural    ---------------------------------------------
 Atom No     Charge         Core      Valence    Rydberg      Total
-------------------------------------------------------------------
   Cu  1    1.79330     17.99960      9.14439    0.06271    27.20670
    O  2   -0.12877      2.00000      6.11736    0.01141     8.12877
    F  3   -0.83227      2.00000      7.82242    0.00985     9.83227
    F  4   -0.83227      2.00000      7.82242    0.00985     9.83227
===================================================================
 * Total *  0.00000     23.99960     30.90659    0.09380    55.00000
```

Table S9.8. $OCuF_2$ (C_{2v}, $^4A_2$-2)

CASSCF(13,8)/CASPT2/VTZ-DK

CuO= 1.94526412 ANG
CuF= 1.72682449 ANG
A1= 96.94402658 DEGREE

TOTAL ENERGIES -1928.321850634891

CI vector
=========

```
22a 2a 2a 2      0.9955934
2a2 a2 2a 2     -0.0692200
2a2 2a a2 2      0.0630527
```

NATURAL ORBITALS FOR STATE 1.4 (ms2=3)
=====================================

```
   12.1     2.00000    -1.31234     2 1s    0.98181
   13.1     1.99122    -0.68513     2 2pz   0.93512
   14.1     1.00879    -0.24787     1 3d0   0.66456     1 3d2+  0.71366
    3.2     2.00000    -0.57684     3 2px   0.91813
    4.2     1.99518    -0.72565     1 3d1+  1.00261
    5.2     1.00481    -0.36815     2 2px   1.02595
    6.3     2.00000    -0.58042     3 2py  -0.28433     3 2pz   0.87961
    7.3     1.99601    -0.75314     1 3d1- -1.00468
    8.3     1.00400    -0.36230     2 2py   1.03321
    1.4     2.00000    -0.59380     3 2px   0.91437
    2.4     1.99999    -0.72667     1 3d2-  1.00471
```

Vibrational frequency:

$OCuF_2$ ($^4A_2$, C_{2v}),
CASSCF(13,8)/CASPT2/VTZ-DK

	16O/63Cu	**16O/65Cu**	**18O/63Cu**	**18O/65Cu**	**Sym.**
	1031.44	1027.28	990.57	986.21	A_1
	712.66	709.41	712.64	709.39	B_2
	500.18	499.99	497.18	497.04	A_1
	237.47	236.82	230.23	229.56	B_2
	220.52	218.97	217.74	216.17	B_1
	159.57	159.09	158.87	158.41	A_1

Table S9.9 OCuF$_2$ (C_{2v}, $^4A_2$-2)

CASSCF(13,9)/VTZ-DK

CuO= 1.94526412 ANG
CuF= 1.72682449 ANG
A1= 96.94402658 DEGREE

CI vector
=========

```
22a0 2a 2a 2      0.9908901
2a20 a2 2a 2      0.0868568
2a20 2a a2 2     -0.0809841
02a2 2a 2a 2     -0.0534279
```

TOTAL ENERGIES -1927.20887665

NATURAL ORBITALS FOR STATE 1.4 (ms2=3)

```
=====================================
Orbital  Occupation  Energy  Coefficients

   10.1     2.00000     -0.65599    1 1s   -0.01850     1 1s   -0.10561     1 1s    0.09487     1 1s    0.11253     1 1s   -0.02246
                                    1 1s    0.08766     1 2pz   0.01555     1 3d0  -0.14012     1 3d2+ -0.09118     1 3d0  -0.01842
                                    1 3d2+ -0.04711     1 3d2+ -0.01591     1 3d0   0.02564     1 3d2+  0.05695     2 1s   -0.06194
                                    2 2pz  -0.28250     3 1s   -0.14909     3 1s   -0.01256     3 2pz   0.22688     3 2py  -0.76265
                                    3 2pz   0.01306     3 2py  -0.04002     3 3d2+ -0.01638
   11.1     2.00000     -0.58177    1 1s    0.02801     1 1s    0.02573     1 1s   -0.03011     1 1s   -0.04653     1 2pz  -0.02899
                                    1 2pz   0.03011     1 2pz   0.05403     1 2pz   0.01638     1 3d0  -0.01184     1 3d2+ -0.02929
                                    2 1s   -0.02946     2 1s   -0.02306     2 2pz  -0.04321     3 1s    0.02804     3 1s   -0.02186
                                    3 2pz   0.87854     3 2py   0.25960     3 2pz   0.06087     3 2py   0.02785     3 3d1- -0.01817
   12.1     1.99328     -0.78963    1 1s    0.12360     1 1s    0.07845     1 1s    0.02443     1 2pz   0.04374     1 2pz  -0.01843
                                    1 2pz  -0.01813     1 3d0  -0.67312     1 3d2+  0.73142     1 3d0   0.01796     1 3d2+ -0.01029
                                    2 1s    0.02142     2 2pz   0.02911     3 1s    0.01388     3 2pz  -0.01307     3 2py   0.03240
   13.1     1.98535     -0.69789    1 1s    0.03907     1 1s    0.06092     1 1s   -0.02866     1 1s   -0.06582     1 2pz   0.05752
                                    1 2pz   0.21628     1 2pz  -0.18418     1 2pz   0.02014     1 2pz  -0.07178     1 3d0  -0.11458
                                    1 3d2+ -0.14752     1 3d0  -0.03736     1 3d2+ -0.01596     1 3d0  -0.01299     1 3d0   0.03648
                                    2 1s   -0.02402     2 2pz   0.90111     2 2pz   0.01094     2 2pz   0.01234     2 3d0  -0.01986
                                    3 1s   -0.01114     3 2pz   0.14842     3 2py  -0.25844     3 2pz   0.01476     3 2py  -0.01286
   14.1     1.01451     -0.25004    1 1s   -0.01942     1 1s    0.14507     1 1s    0.06701     1 1s    0.01506     1 2pz   0.01797
                                    1 2pz   0.05093     1 2pz  -0.05816     1 2pz  -0.01382     1 3d0   0.72837     1 3d2+  0.64481
                                    1 3d0  -0.04663     1 3d2+ -0.04505     1 3d0  -0.01460     1 3d2+ -0.01347     2 1s   -0.07353
                                    2 1s   -0.03102     2 2pz   0.18885     2 2pz   0.02030     3 1s    0.05152     3 1s    0.02723
                                    3 2pz   0.09105     3 2py  -0.17769     3 2pz   0.01490     3 2py  -0.03324
   15.1     0.00702      1.64810    1 1s    0.02821     1 1s    0.47570     1 1s    0.13855     1 1s    0.10461     1 1s   -0.14366
                                    1 2pz   0.15146     1 2pz  -0.06111     1 2pz  -0.06387     1 3d0  -0.08912     1 3d2+  0.05468
                                    1 3d0  -0.62661     1 3d2+  0.94303     1 3d0  -0.02059     1 3d2+  0.05284     1 3d0   0.18647
                                    1 3d2+ -0.27293     1 5g4+ -0.01149     2 2pz   0.04159     2 2pz  -0.02425     3 1s   -0.04064
                                    3 1s    0.05057     3 2pz  -0.02522     3 2py   0.12679     3 2py  -0.02574

    3.2     2.00000     -0.57802    1 2px  -0.02755     1 2px   0.03860     1 2px   0.05174     1 2px   0.01176     1 3d1+ -0.02536
                                    2 2px   0.01225     3 2px   0.91801     3 2px   0.06759     3 3d2- -0.02061
    4.2     1.99203     -0.73067    1 2px   0.01399     1 3d1+  0.99887     1 3d1+ -0.01773     2 2px   0.07568     3 2px   0.02551
    5.2     1.00789     -0.38018    1 2px   0.01077     1 2px   0.02660     1 2px  -0.02725     1 3d1+  0.12232     1 3d1+ -0.01168
                                    2 2px  -1.02396     2 2px  -0.01012     2 2px   0.05315     2 3d1+  0.01395     3 2px   0.03576

    6.3     2.00000     -0.58095    1 2py  -0.04474     1 2py  -0.12768     1 2py   0.12764     1 2py  -0.01187     1 2py   0.04272
                                    1 3d1-  0.03602     2 2py   0.02582     3 1s   -0.04768     3 1s    0.01448     3 2py  -0.23331
                                    3 2pz   0.89454     3 2py  -0.02025     3 2pz   0.06073     3 3d1- -0.01732
    7.3     1.99320     -0.75558    1 2py  -0.02323     1 2py   0.04191     1 3d1-  1.00223     1 3d1- -0.02815     1 3d1- -0.02280
                                    2 2py   0.05903     3 1s    0.01752     3 2py  -0.09989     3 2pz  -0.10961     3 2py  -0.01252
```

```
                                3 2pz  -0.02838
8.3     1.00680    -0.37411     1 2py  -0.02980     1 2py   0.02511     1 2py   0.01141     1 3d1- -0.09597     1 3d1-  0.01257
                                2 2py   1.03253     2 2py   0.01040     2 2py  -0.06159     2 3d1- -0.01225     3 1s   -0.01125
                                3 1s   -0.01203     3 2py   0.04413     3 2pz  -0.05008

1.4     2.00000    -0.56999     1 3d2- -0.02995     1 3d2-  0.01107     1 3d2-  0.03621     3 2px   0.93491     3 2px   0.06368
                                3 3d2- -0.01622
2.4     1.99991    -0.74991     1 3d2-  1.01278     1 3d2- -0.02247     1 3d2- -0.02434     3 2px  -0.05299     3 2px  -0.02471
```

Spin population: Individual basis function populations

Symmetry no. 1

```
1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 1s     1 2pz    1 2pz    1 2pz
-0.00000 -0.00000  0.00004  0.02396  0.00614  0.00011  0.00188 -0.00000  0.00002 -0.00510

1 2pz    1 2pz    1 2pz    1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0    1 3d2+   1 3d0
0.00692  0.00006  0.00045  0.48972  0.38566  0.00825  0.00514  0.00146  0.00076 -0.00040

1 3d2+   1 4f0    1 4f2+   1 4f0    1 4f2+   1 5g0    1 5g4+   1 5g2+   2 1s     2 1s
0.00070 -0.00000 -0.00000  0.00002  0.00000  0.00000  0.00000  0.00000  0.00000  0.00170

2 1s     2 1s     2 2pz    2 2pz    2 2pz    2 3d0    2 3d2+   2 3d0    2 3d2+   2 4f0
0.00004 -0.00048  0.03368  0.00036  0.00018  0.00002  0.00000  0.00012 -0.00000  0.00003

2 4f2+   3 1s     3 1s     3 1s     3 1s     3 2pz    3 2py    3 2pz    3 2py    3 2pz
0.00000  0.00000  0.00136 -0.00001  0.00032  0.00616  0.02638 -0.00003  0.00032  0.00024

3 2py    3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 3d1-   3 4f0    3 4f2+   3 4f1-
0.00373  0.00000  0.00001  0.00000  0.00002  0.00001  0.00001  0.00000  0.00000  0.00000

3 4f3-
0.00001


 Symmetry no. 2

1 2px    1 2px    1 2px    1 2px    1 2px    1 2px    1 3d1+   1 3d1+   1 3d1+   1 3d1+
0.00000  0.00001 -0.00397  0.00332  0.00031  0.00129  0.01651  0.00183  0.00070 -0.00027

1 4f1+   1 4f3+   1 4f1+   1 4f3+   1 5g1+   1 5g3+   2 2px    2 2px    2 2px    2 3d1+
-0.00000  0.00000  0.00005  0.00000 -0.00000  0.00000  1.00641  0.00942 -0.03680  0.00001

2 3d1+   2 4f1+   2 4f3+   3 2px    3 2px    3 2px    3 3d1+   3 3d2-   3 3d1+   3 3d2-
0.00013  0.00003  0.00000  0.00102 -0.00002  0.00003  0.00000  0.00000 -0.00000 -0.00000

3 4f1+   3 4f3+   3 4f2-
0.00000 -0.00000  0.00000


 Symmetry no. 3

1 2py    1 2py    1 2py    1 2py    1 2py    1 2py    1 3d1-   1 3d1-   1 3d1-   1 3d1-
0.00000  0.00000 -0.00376  0.00227  0.00042  0.00147  0.01140  0.00183  0.00070 -0.00085

1 4f1-   1 4f3-   1 4f1-   1 4f3-   1 5g1-   1 5g3-   2 2py    2 2py    2 2py    2 3d1-
0.00000  0.00000  0.00007  0.00000  0.00000  0.00000  1.01572  0.00971 -0.04214  0.00001

2 3d1-   2 4f1-   2 4f3-   3 1s     3 1s     3 1s     3 1s     3 2py    3 2pz    3 2py
0.00008  0.00003  0.00000  0.00000  0.00005  0.00000 -0.00012  0.00150  0.00169  0.00003

3 2pz    3 2py    3 2pz    3 3d1-   3 3d0    3 3d2+   3 3d1-   3 3d0    3 3d2+   3 4f1-
-0.00004  0.00002 -0.00010 -0.00000  0.00000  0.00000  0.00000  0.00001 -0.00001  0.00000

3 4f3-   3 4f0    3 4f2+
-0.00000  0.00000  0.00000


 Symmetry no. 4

1 3d2-   1 3d2-   1 3d2-   1 3d2-   1 4f2-   1 4f2-   1 5g2-   1 5g4-   2 3d2-   2 3d2-
0.00003  0.00000  0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000

2 4f2-   3 2px    3 2px    3 2px    3 3d2-   3 3d1+   3 3d2-   3 3d1+   3 4f2-   3 4f1+
0.00000 -0.00000 -0.00000 -0.00000  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
```

```
3 4f3+
0.00000
```

Population analysis by basis function type

```
 Unique atom        s        p        d        f        g    Total    Charge
   1  CU      0.03212  0.00369  0.92320  0.00014  0.00000  0.95915  +28.04085
   2  O       0.00126  1.99653  0.00036  0.00009  0.00000  1.99823  + 6.00177
   3  F1      0.00080  0.02047  0.00003  0.00001  0.00000  0.02131  + 8.97869
```

AIM Charges ($^4A_2$)

```
  Total result:
    #Basin       Integral(a.u.)     Vol(Bohr^3)   Vol(rho > 0.001)
       1         9.8048780325       1201.646       125.253
       2        27.4497199676        493.466        86.898
       3         9.8048781057       1201.650       125.253
       4         7.9403643884       1260.310       114.605
   Sum of above integrals:        54.99984049
   Sum of basin volumes (rho > 0.001):     452.010 Bohr^3

   Normalization factor of the integral of electron density is    0.999997
   The atomic charges after normalization and atomic volumes:
       1 (Cu)   Charge:    1.550201     Volume:    86.898 Bohr^3
       2 (O )   Charge:    0.059613     Volume:   114.605 Bohr^3
       3 (F )   Charge:   -0.804906     Volume:   125.253 Bohr^3
       4 (F )   Charge:   -0.804906     Volume:   125.253 Bohr^3
```

Summary of Natural Population Analysis:

```
                                     Natural Population
             Natural    -----------------------------------------------
  Atom No    Charge         Core      Valence    Rydberg      Total
 -----------------------------------------------------------------------
    Cu  1    1.66653     17.99968      9.28501    0.04878     27.33347
     O  2    0.06271      2.00000      5.93162    0.00567      7.93729
     F  3   -0.86462      2.00000      7.85641    0.00821      9.86462
     F  4   -0.86462      2.00000      7.85641    0.00821      9.86462
 =======================================================================
 * Total *   0.00001     23.99968     30.92946    0.07086     54.99999
```