Iridium Oxyfluorides

Yan Lu, Sebastian Riedel

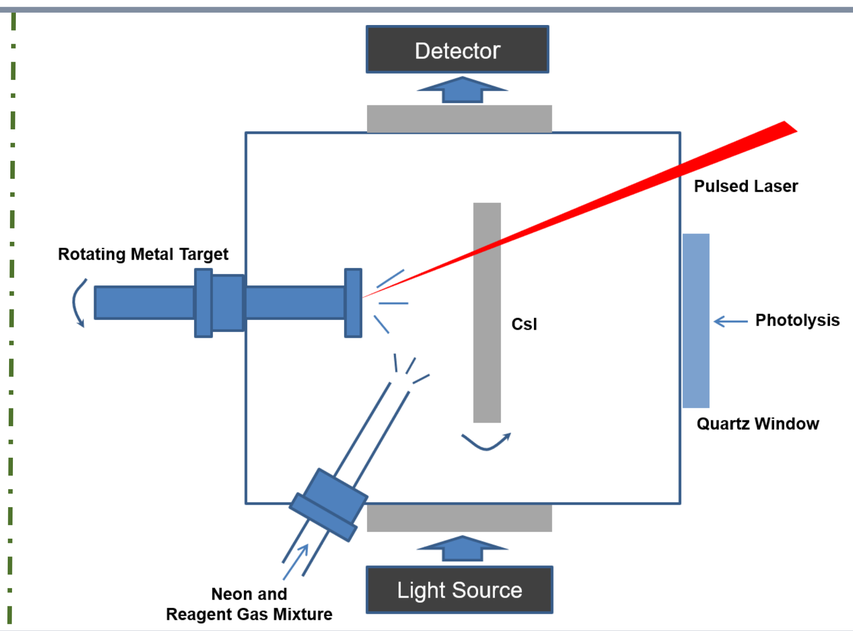
E-Mail: yan.lu@fu-berlin.de Freie Universität Berlin, Institute of Chemistry and Biochemistry – Inorganic Chemistry, Berlin, Germany.

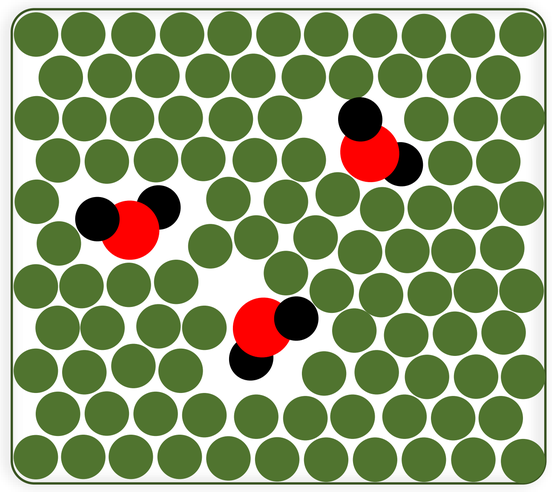
Abstract

The novel iridium oxyfluorides were prepared for the first time by the two methods: laser-ablated iridium metal atoms with OF_2, and iridium dioxide (IrO_2) with F_2 in excess neon or argon under cryogenic conditions. The assignments of the main vibrational absorptions of these products were confirmed by a joint analysis of IR-matrix-isolation spectroscopy together with $^{18}OF_2$ substitution and the state-of-the art quantum-chemical calculations of frequencies and thermal stabilities. The closed-shell singlet OIrF molecule with linear geometry possess terminal oxo ligand with triple bond character consisting of two covalent bonds and a dative bond arising from the oxygen $2p_\pi$ lone pair donation to the empty Ir 5*d* orbital. For the $^2B_1$ ground state of the oxo difluoride $OIrF_2$ with a planar T-shaped structure, the single unpaired electron is located mainly at the antibonding O–Ir π^* orbital.

Methods

1. Laser ablation processes
2. Matrix-isolation IR spectroscopy
3. Quantum chemical calculations





Background

All preparation of iridium oxyfluorides failed over the years

1929

$OIrF_4$ has been first proposed as **residue in the reaction of iridium hexafluoride and the alkali** of the glass.

Z. Anorg. Allg. Chem. **1929,** *179*, 161.

1956

1) The **$OIrF_4$** has been found to be **ill-founded** and the residue was identified to **a complex salt of quinquevalent iridium**.

2) **Fluorination of iridium dioxide IrO_2** with temperature no more than 350 °C.

J. Chem. Soc. **1956**, 4481.

1978

1) **Oxygen-fluorine exchange reaction**

$IrF_6 + B_2O_3 \rightarrow IrF_5 + BF_3 + O_2 +$ an involatile iridium-containing solid

J. Fluorine Chem. **1978**, *12*, 505.

2) **Hydrolysis reaction**

$IrF_6 \xrightarrow[\text{liquid HF}]{} H_3O^+IrF_6^-$

J. Fluorine Chem. **1978**, *11*, 39.

Results

$Ir + OF \longrightarrow OIrF \quad \Delta E = -778.3$

$Ir + OF_2 \longrightarrow OIrF_2 \quad \Delta E = -929.7$

$OIrF + F \longrightarrow OIrF_2 \quad \Delta E = -307.3$

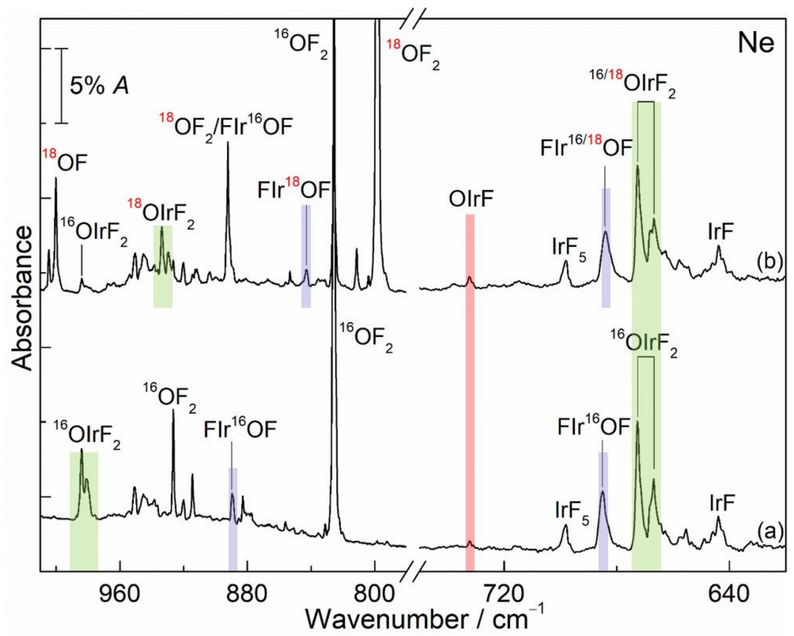
$Ir + OF_2 \longrightarrow FOIrF \quad \Delta E = -540.8$

$FOIrF \longrightarrow OIrF_2 \quad \Delta E = -389.0$

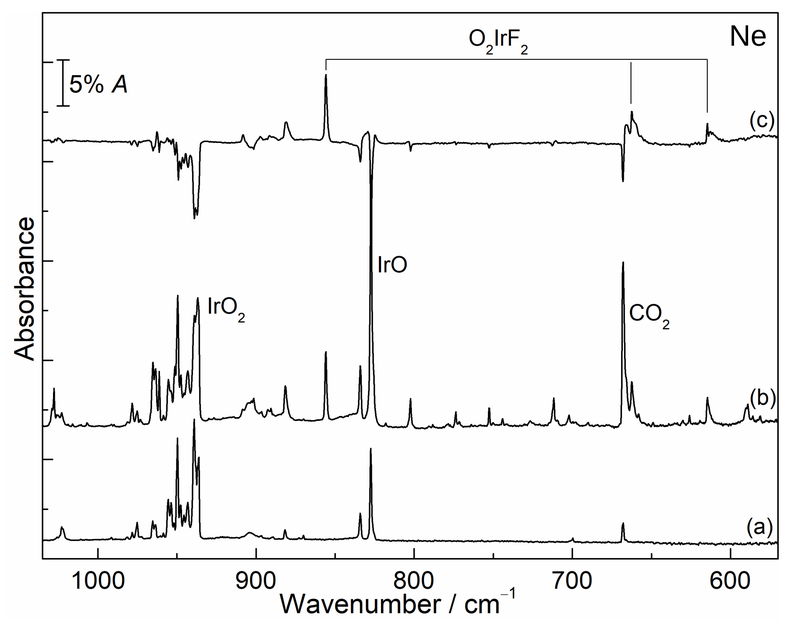
$IrO_2 + 2F \longrightarrow O_2IrF_2 \quad \Delta E = -548.4$

$IrO_2 + F_2 \longrightarrow O_2IrF_2 \quad \Delta E = -401.3$

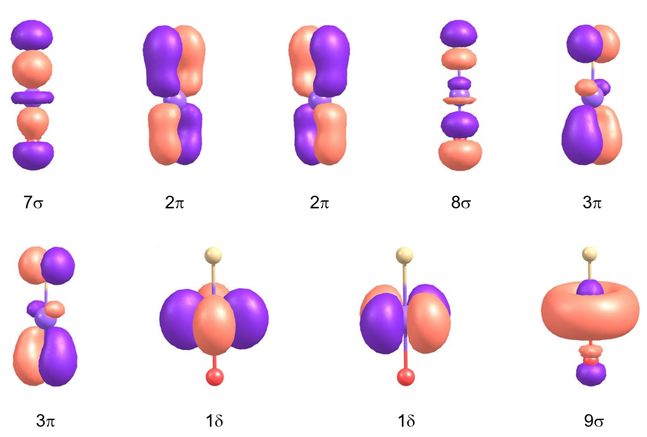
Computed thermochemical stability of iridium oxyfluorides (298.15 K, kJ mol^{-1}) at CCSD(T) level.



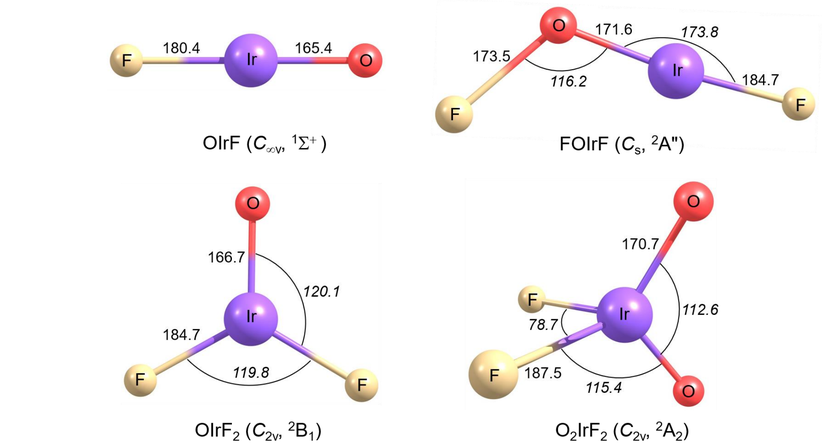
IR spectra in neon matrix at 5 K. (a) IR spectrum of reaction products of laser-ablated Ir atoms with 0.02% $^{16}OF_2$. (b) IR spectrum of reaction products of laser-ablated Ir atoms with 0.1% $^{18}OF_2$.



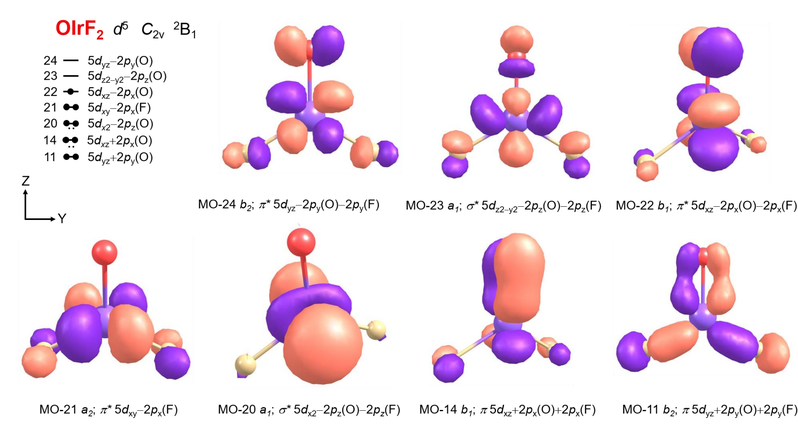
IR spectra in neon matrix at 5 K. (a) IR spectrum of reaction products of laser-ablated IrO_2. (b) IR spectrum of reaction products of laser-ablated IrO_2 with 1% F_2. (c) Difference IR spectrum obtained after annealing to 10 K



Molecular orbitals of OIrF computed at the B3LYP/aug-cc-pVTZ-PP level.



Optimized structures of OIrF, $OIrF_2$, FOIrF and O_2IrF_2 at the CCSD(T)/aug-cc-pVTZ-PP level. Selected bond lengths in pm and angles in deg (in italics) are shown.



Selected molecular orbitals of $OIrF_2$ ($^2B_1$, C_{2v}). (B3LYP/AVTZ(-PP), Kohn-Sham orbitals with α spin)

Reference Y. Lu, S. Riedel, unpublished work.

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