Group 13 Oxyfluoride radicals: A Combined Matrix-Isolation and Quantum-Chemical Study

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Herein, we firstly show the reaction between laser-ablated group 13 atoms M (M = B, Al, Ga, In) with OF_2 to form OBF, OAlF, OGaF, OInF molecules and $^{\bullet}OBF_2$, $^{\bullet}OAlF_2$, $^{\bullet}OGaF_2$, $^{\bullet}OInF_2$ oxygen-center radicals as well as MF, MF_2, MF_3 fluorides. These compounds have been characterized by matrix-isolation spectroscopy in neon and argon matrices at 4 K aided by quantum-chemical calculations with DFT and ab initio methods. The calculations revealed the linear structure for OMF molecules in the singlet state. Moreover, the orbitals of OMF exhibits the multiple bond characteristics derived from two covalent bonds and a dative bond formed by oxygen $2p_p$ lone pair donating electrons to the M atoms n*p* (n = 2, 3, 4, 5) empty orbital. While the $^{\bullet}OMF_2$ radicals have a $^2B_2$ ground state with C_{2v} symmetry, with the unpaired electron located mainly at the terminal oxygen atom. Furthermore, isotopic substitution experiments with $^{18}OF_2$ were performed to support these novel findings.

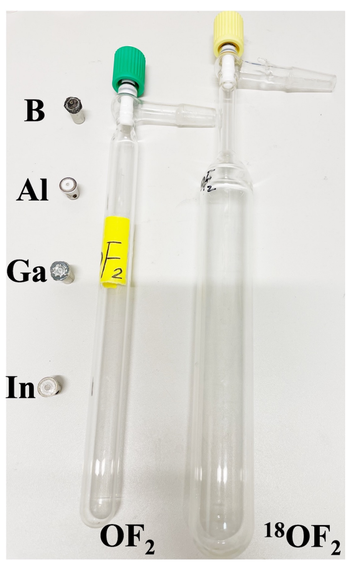
Introduction

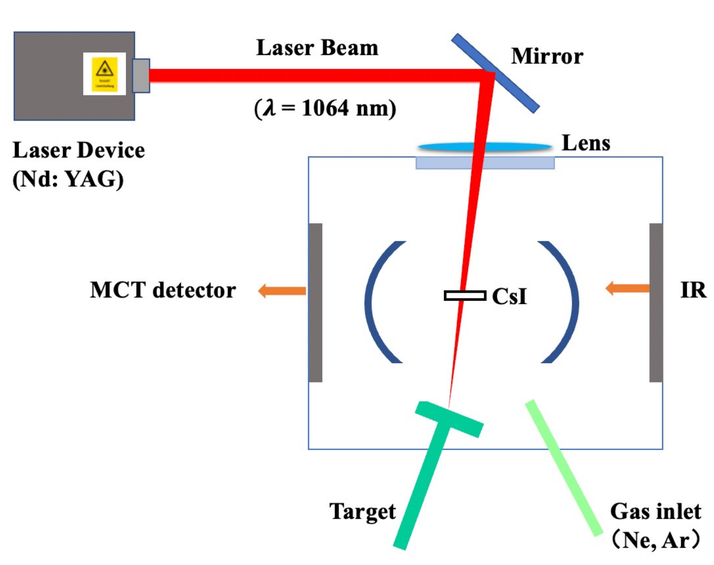
- Oxygen radicals play important roles in chemistry, biology and atmosphere, the most known were singlet oxygen radical ($0_2^{\cdot\cdot}$), alkoxyradical ($RO^{\bullet}$) and nitric oxide ($NO^{\bullet}$) species;
- However, little attention has been paid to investigate group 13 containing oxygen radical;
- The only known $^{\bullet}OMX_2$ (M = group 13, X = halogen) radicals, $^{\bullet}OBF_2$, was firstly observed in the emission spectrum BF_3/O_2 mixture discharge[1].

Problem Formulation

Whether such an unusual compound with group 13 in the formal oxidation state +4 can be isolated in matrix isolation? ? ?

Method

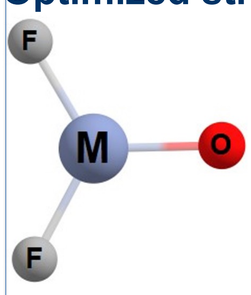




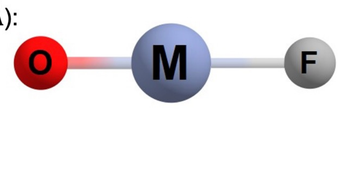
Reaction process

$$M^* + OF \rightarrow OMF$$
$$M^* + OF_2 \rightarrow OMF_2 \ (M = B, Al, Ga, In)$$

Optimized structures



- M-O bond length[a] (Å):
  B-O: 1.370
  Al-O: 1.740
  Ga-O: 1.781
  Al-O: 1.990



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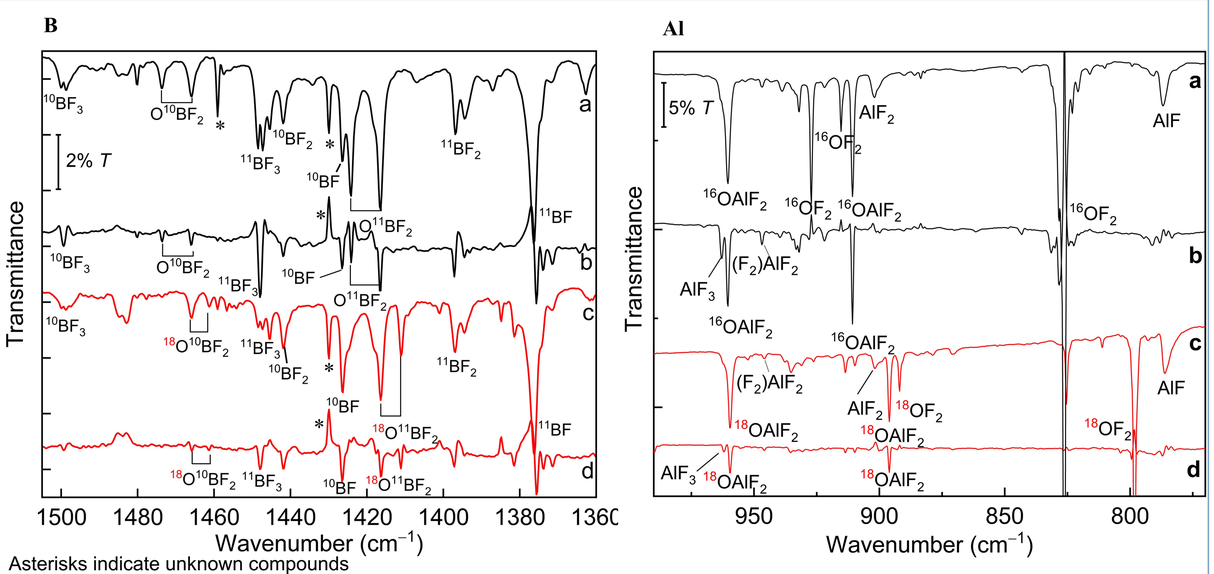
OMF_2 C_{2v} X^2B_2 OMF $C_{\infty v}$ X^1A'

[a]calculated under CCSD(T)/aug-cc-pVTZ-PP

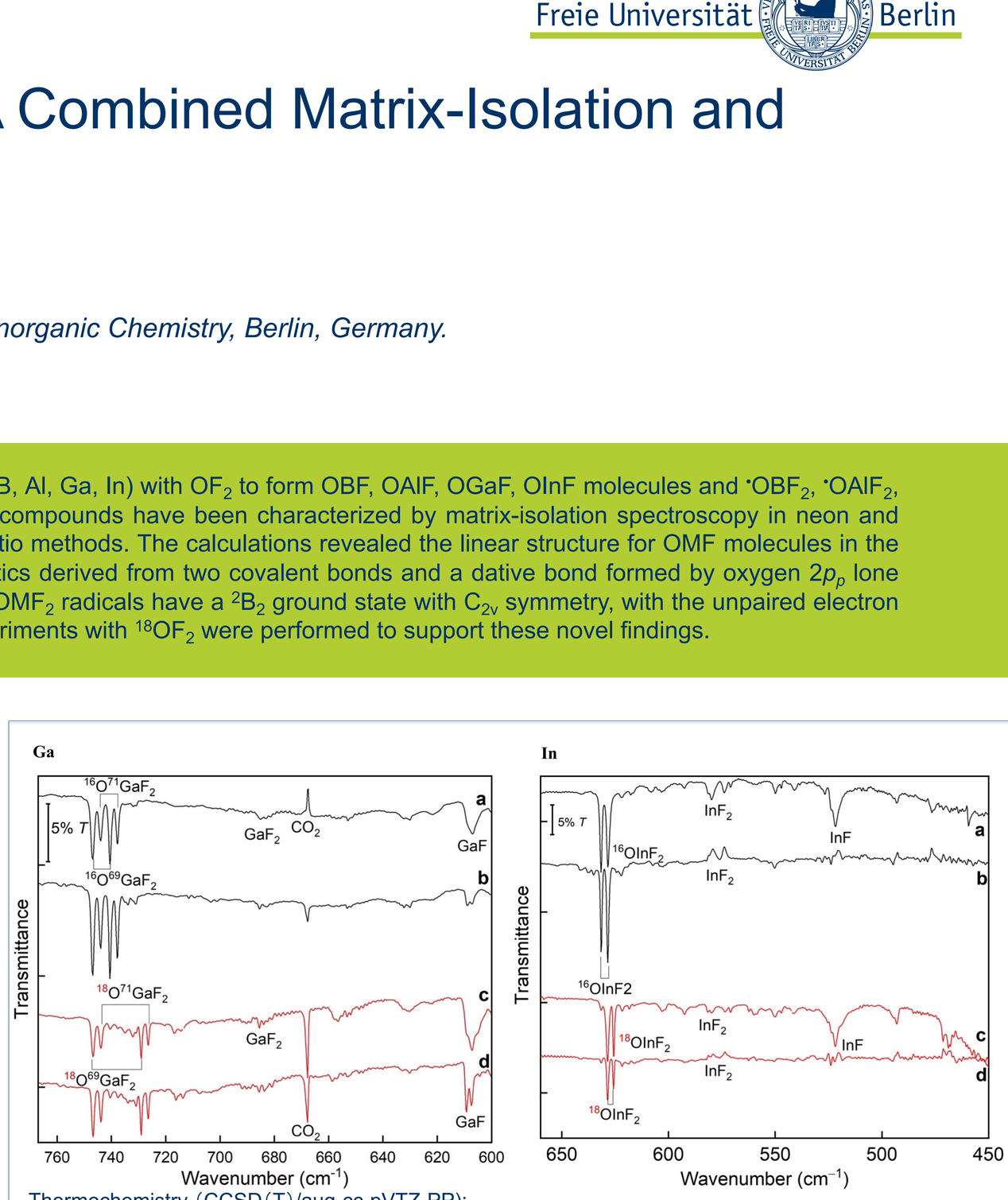
IR spectra (a) codeposition of M (M = B, Al, Ga, In) with 0.05% OF_2 in Neon, (b) after irradiation, (c) M + 0.05% $^{18}OF_2$, (d) after irradiation



Asterisks indicate unknown compounds

Thermochemistry (CCSD(T)/aug-cc-pVTZ-PP):

B + OF → OBF ΔH = -1233.8 KJ mol^{-1} B + OF_2 → OBF_2 ΔH = -1378.9 KJ mol^{-1}
Al + OF → OAlF ΔH = -843.9 KJ mol^{-1} Al + OF_2 → $OAlF_2$ ΔH = -1155.9 KJ mol^{-1}



Thermochemistry (CCSD(T)/aug-cc-pVTZ-PP):

Ga + OF → OGaF ΔH = -364.4 KJ mol^{-1} Ga + OF_2 → $OGaF_2$ ΔH = -380.8 KJ mol^{-1}
In + OF → OInF ΔH = -158.2 KJ mol^{-1} In + OF_2 → $OInF_2$ ΔH = -109.7 KJ mol^{-1}

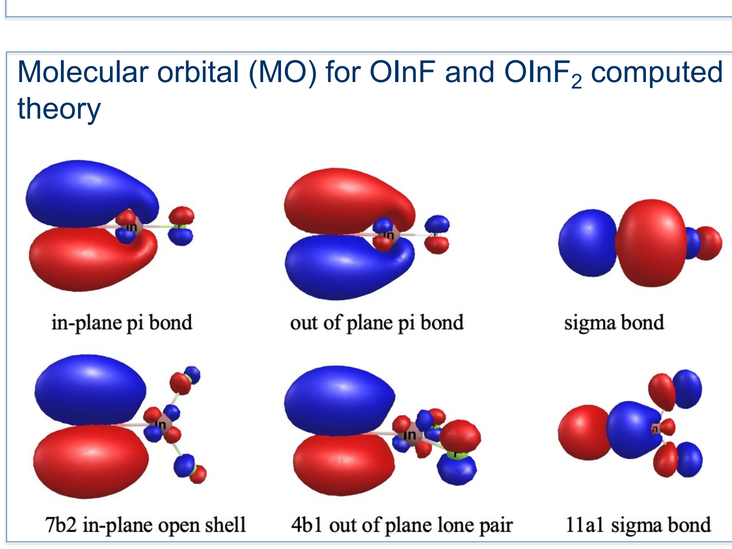
IR band positions in matrix and calculated vibrational frequencies[b]

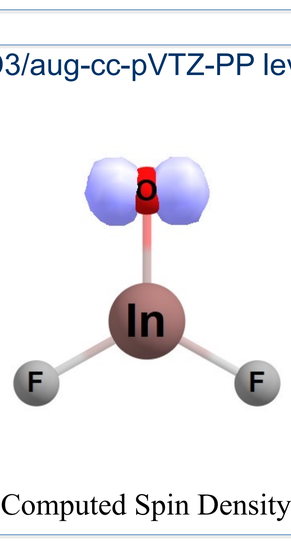
	OBF	OBF_2	OAlF	$OAlF_2$	$O^{69}GaF$	$O^{69}GaF_2$	OInF	$OInF_2$
Calculated	504.3 2111.3	653.2 1405.9 1416.7	733.1 1161.9	669.3 898.6 940.7	676.0 942.3	638.8 718.9 722.6	588.4 780.9	652.4 603.9 607.8
$\Delta\nu(^{16/18}O)$	3.9 27.4	2.1 0.0 13.2	15.3 25.3	15.7 13.8 0.0	8.2 34.4	19.7 12.3 0.0	5.6 32.7	22.4 0.1 7.0
Exp. argon	495.4 2064.8	649.8 1409.5 1416.8	– 1147.9	– 895.3 946.4	690.2 943.4	– 733.1 736.1	598.4 782.6	– 614.9 619.9
$\Delta\nu(^{16/18}O)$	3.7 25.9	2.1 0.2 12.9	– 23.7	– 12.7 0.0	9.1 33.4	– 13.9 0.0	5.6 32.4	– 0.7 6.5

[b]calculated under B3LYP-D3/aug-cc-pVTZ-PP

The calculated vibrational stretching and the oxygen isotopic shift are in good agreement with the corresponding experimental values

Molecular orbital (MO) for OInF and $OInF_2$ computed at the B3LYP-D3/aug-cc-pVTZ-PP level of theory





Computed Spin Density.

Conclusion

- Report the shortest M – O bond length in the OMF (M= B, Al, Ga, In) molecules;
- Report firstly the novel group 13 oxofluoride radicals $^{\bullet}OMF_2$;
- Identified the oxygen radical characteristic for the $^{\bullet}OMF_2$ molecules by the computed spin density and molecular orbital profiles.

References
[1] C. W. Mathews and K. K. Innes, *J. Mol. Spectrosc.* **1965**, *15*, 199.

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