Supporting Information

A Combined Quantum-Chemical and Matrix-Isolation Study on Molecular Manganese Fluorides

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Table S1. Calculated and experimental structural parameters of molecular manganese fluorides.[a]

Molecule	Parameter	B3LYP	CCSD(T)	Exp.
MnF ($C_{\infty v}$, $^7\Sigma^+$)	$d_{Mn\text{-}F}$	184.3	185[b]	183.9[c]
MnF_2 ($D_{\infty h}$, $^6\Sigma^+_g$)	$d_{Mn\text{-}F}$	180.1	181.6	181.1[d]
MnF_3 (C_{2v}, $^5A_1$)	$d_{Mn\text{-}F(1)}$	173.3	173.0	172.8[e]
	$d_{Mn\text{-}F(2)}$	175.6	175.3	175.4[e]
	$\measuredangle_{F(1)\text{-}Mn\text{-}F(2)}$	106.7	106.3	106.4[e]
MnF_4 (C_{2v}, $^4B_2$)	$d_{Mn\text{-}F(1)}$	173.6	173.0	
	$d_{Mn\text{-}F(2)}$	169.9	169.2	
	$\measuredangle_{F(1)\text{-}Mn\text{-}F(1)}$	136.7	138.9	
	$\measuredangle_{F(2)\text{-}Mn\text{-}F(2)}$	107.0	105.6	
MnF_5 (D_{3h}, $^3A'_2$)	$d_{Mn\text{-}F(ax)}$	174.8	174.1	
	$d_{Mn\text{-}F(eq)}$	167.9	167.4	
MnF_6 (D_{4h}, $^2B_{2g}$)	$d_{Mn\text{-}F(ax)}$	172.1		
	$d_{Mn\text{-}F(eq)}$	173.4		
MnF_6 (D_{3d}, $^2A_{1g}$)	$d_{Mn\text{-}F}$	172.7		
	$\measuredangle_{F\text{-}Mn\text{-}X}$[f]	54.9		
MnF_7 (C_{2v}, $^1A_1$)	$d_{Mn\text{-}F(1)}$	193.0		
	$d_{Mn\text{-}F(2)}$	175.4		
	$d_{Mn\text{-}F(3)}$	175.3		
	$\measuredangle_{F(1)\text{-}Mn\text{-}F(2)}$	74.8		
	$\measuredangle_{F(3)\text{-}Mn\text{-}F(3)}$	77.4		
MnF_7 (D_{5h}, $^1A'_1$)	$d_{Mn\text{-}F(ax)}$	171.3		
	$d_{Mn\text{-}F(eq)}$	180.4		

a) Bond lengths in pm, angles in °
b) 6-311++G(3df,2d) basis set, Ref. 1
c) Rotational spectroscopy, Ref. 2
d) Gas phase electron diffraction, Ref. 3
e) Gas phase electron diffraction, Ref. 4
f) Angle between the Mn-F bond and the six-fold axis

Table S2. Calculated IR wavenumbers of Mn-F stretching modes of MnF_6 and MnF_7.[a]

Molecule	Mode	B3LYP	
MnF_6 (D_{4h}, $^2B_{2g}$)	E_u	681.4	(97)
	A_{2u}	739.2	(257)
MnF_6 (D_{3d}, $^2A_{1g}$)	E_u	728.6	(207)
	A_{2u}	736.1	(207)
MnF_7 (C_{2v}, $^1A_1$)	A_1	643.1	(7)
	A_1	662.8	(61)
	B_1	665.8	(104)
	B_2	682.1	(123)
MnF_7 (D_{5h}, $^1A'_1$)	B	614.4	(102)
	A''_2	745.3	(230)

a) Values in cm^{-1}, IR intensities in km mol^{-1} in parentheses

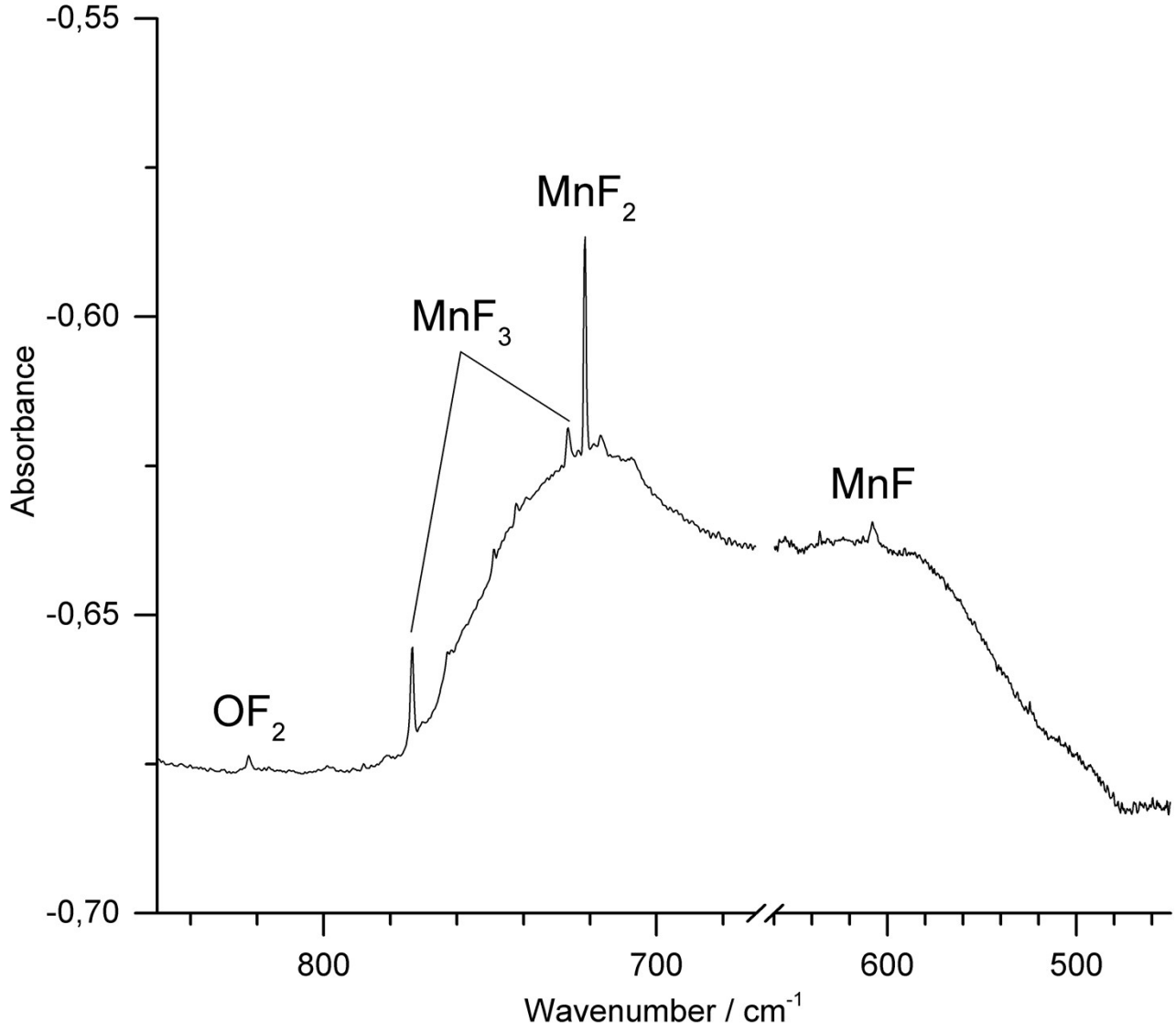

Figure S1. IR spectrum in the 450 – 850 cm^{-1} region of the Ne matrix-isolated (5 K) reaction products of laser ablated manganese atoms in the presence of F_2 (0.2%) after 1 h of sample deposition. The region of the bending mode of atmospheric CO_2 (660 – 670 cm^{-1}) was omitted for a better representation.

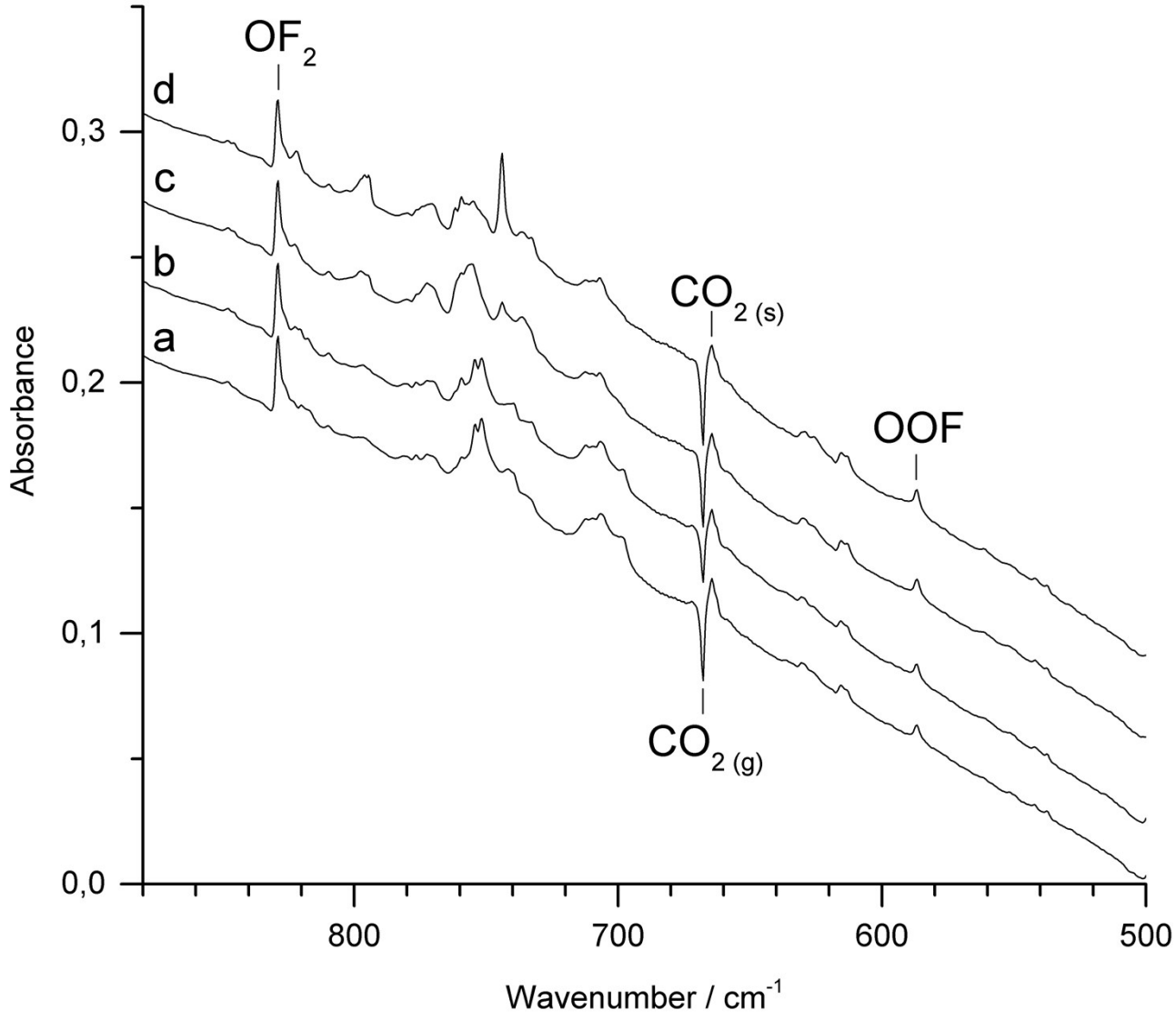

Figure S2. IR spectra in the 500 – 880 cm^{-1} region of the reaction products of laser ablated manganese atoms and elemental fluorine isolated in solid fluorine at 12 K. (a) After 1 h of deposition. (b) After annealing to 25 K. (c) After 10 min of broad band UV irradiation. (d) After annealing to 30 K.

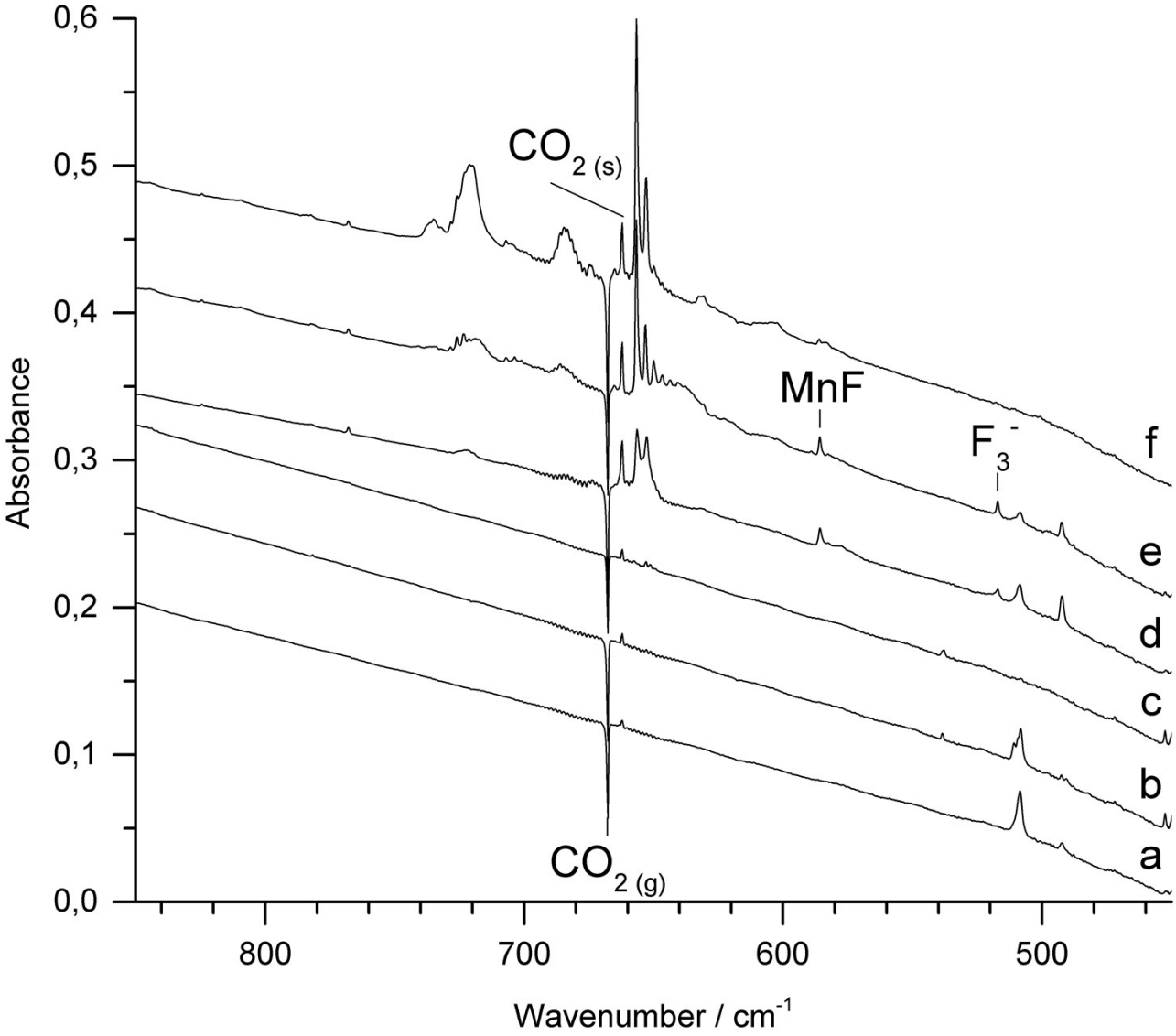

Figure S3. IR spectra in the 450 – 850 cm^{-1} region of the nitrogen matrix-isolated (12 K) reaction products of laser ablated manganese atoms (a – c). Spectra (d – f) in the presence of F_2 (3%). (a) After 1 h of deposition. (b) After annealing to 20 K. (c) After 15 min of broad band UV irradiation. (d) After 1 h of deposition. (e) After annealing to 25 K. (f) After 15 min of broad band UV irradiation.

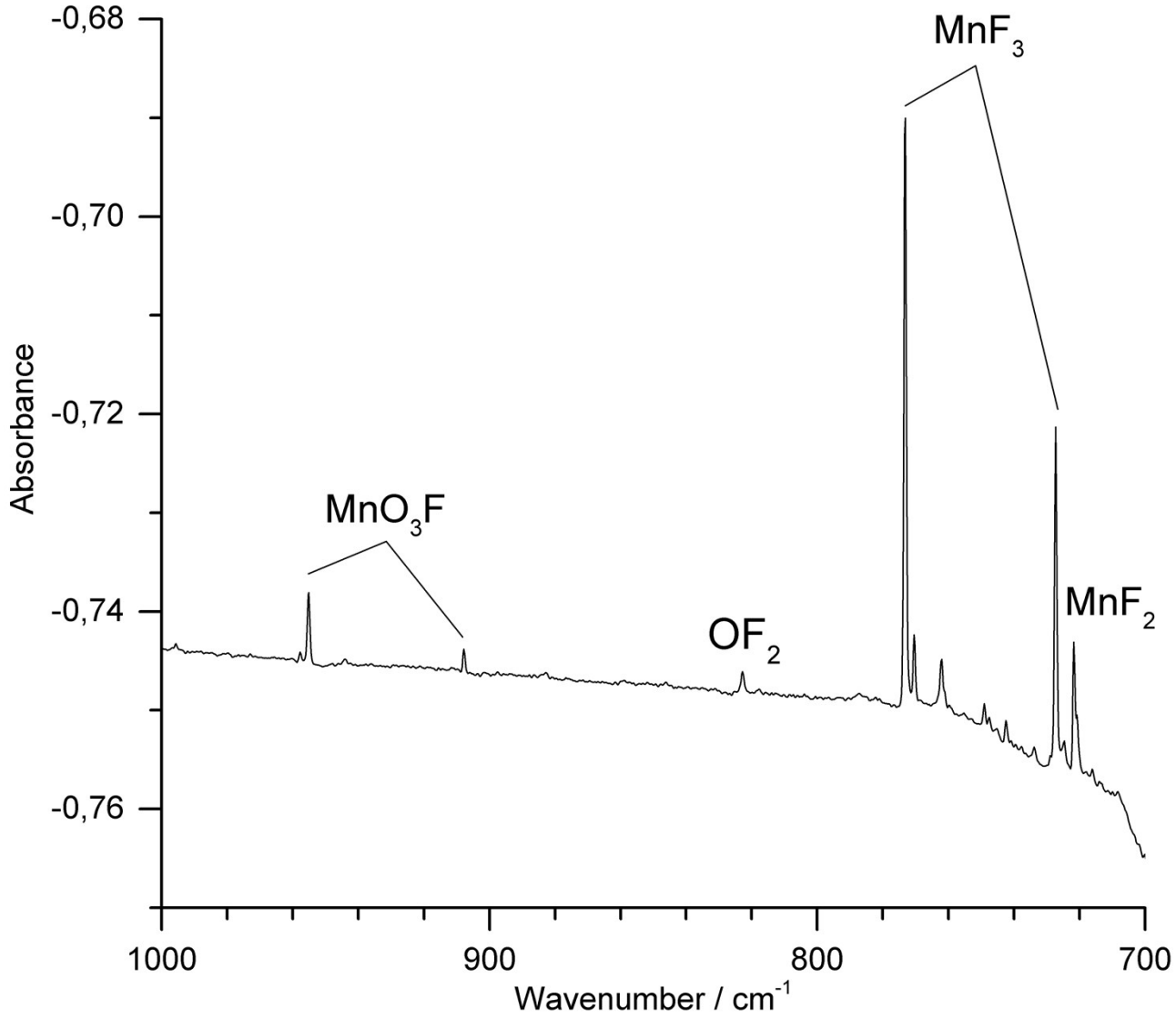

Figure S4. IR spectrum in the 700 – 1000 cm^{-1} region of the Ne matrix-isolated (5 K) products of laser ablated solid MnF_3 after 15 min of deposition.

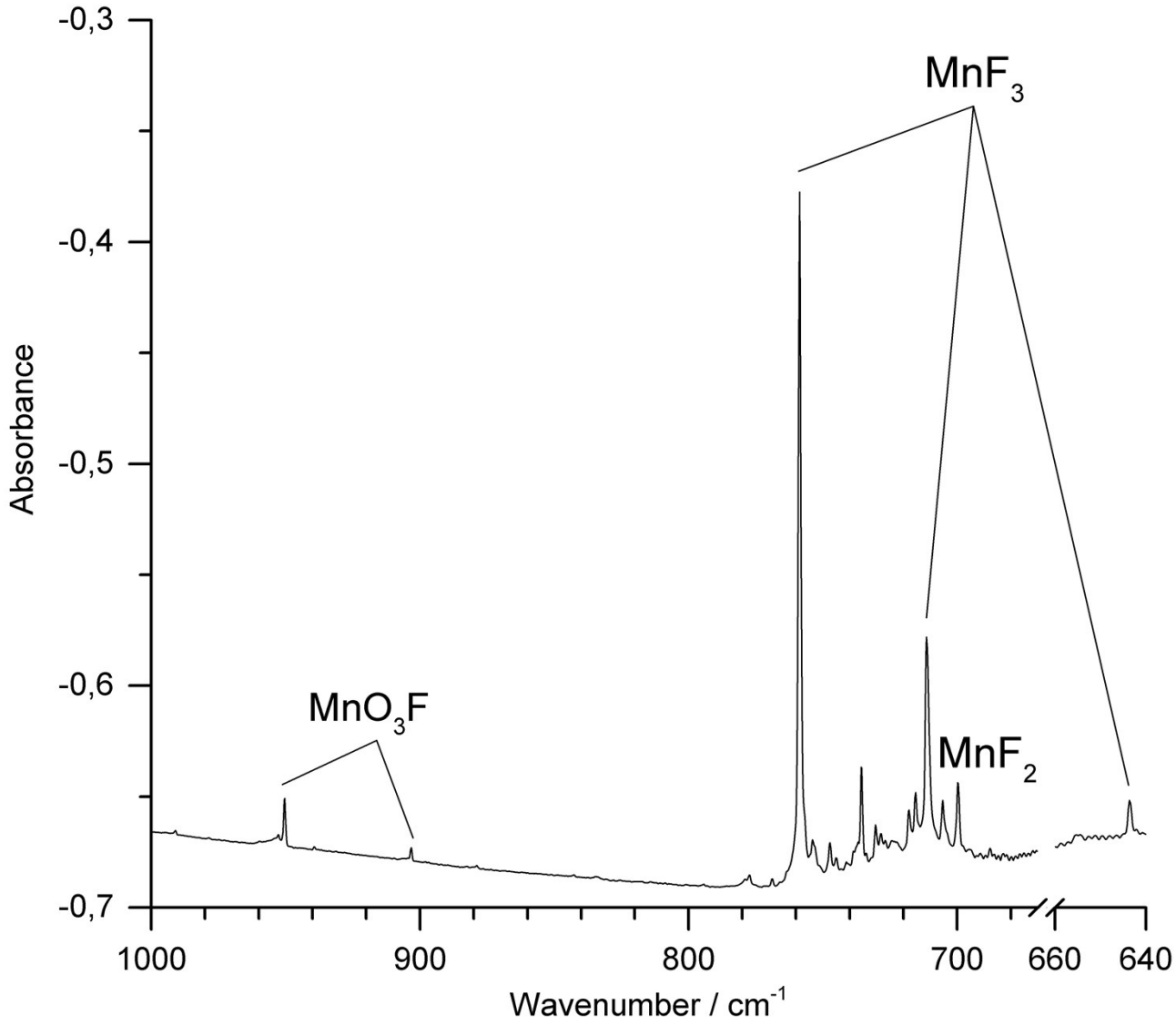

Figure S5. IR spectrum in the 640 – 1000 cm^{-1} region of the Ar matrix-isolated (12 K) products of laser ablated solid MnF_3 after 15 min of deposition. The region of the bending mode of atmospheric CO_2 (660 – 670 cm^{-1}) was omitted for a better representation.

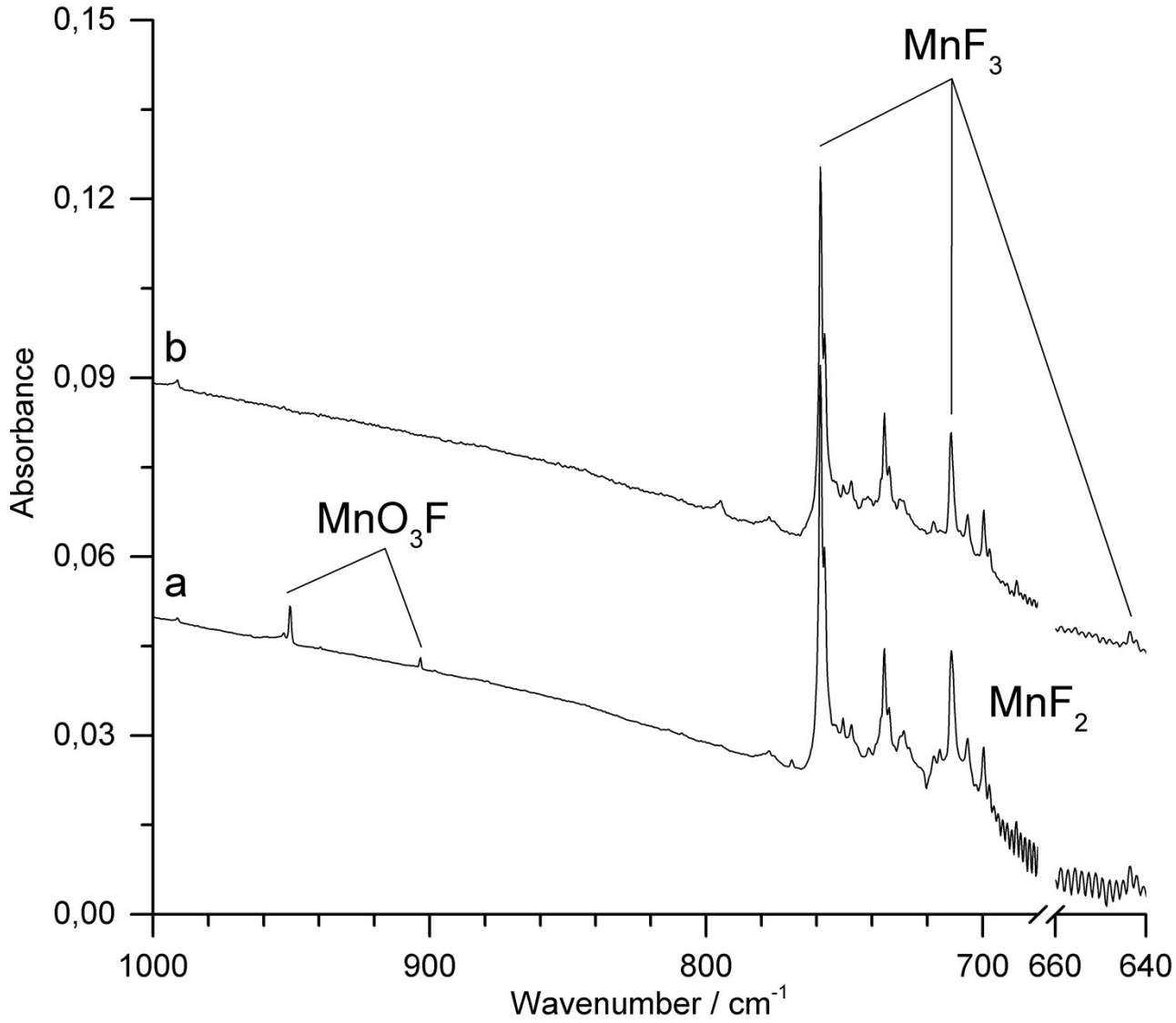

Figure S6. IR spectra in the 640 – 1000 cm^{-1} region of the Ar matrix-isolated (12 K) products of laser ablated solid MnF_3 in the presence of F_2 (1%). a) After 15 min of deposition. b) After 15 min of $\lambda = 455 \pm 10$ nm irradiation. The region of the bending mode of atmospheric CO_2 (660 – 690 cm^{-1}) was omitted for a better representation.

Calculated x,y,z-coordinates and energies of molecular manganese fluorides MnF_x (x = 2 – 7) at the B3LYP/aug-cc-pVTZ level

MnF_2 ($D_{\infty h}$, $^6\Sigma^+_g$)

E(UB3LYP) = -1350.9426464 a.u. ZPE = 0.0035288 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1350.965062 a.u.

Mn	0.000000	0.000000	0.000000
F	1.801200	0.000000	0.000000
F	-1.801200	0.000000	0.000000

MnF_3 (C_{2v}, $^5A_1$)

E(UB3LYP) = -1450.8307513 a.u. ZPE = 0.0060542 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1450.854622 a.u.

Mn	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.733174
F	1.681947	0.000000	-0.504001
F	-1.681947	0.000000	-0.504001

MnF_4 (C_{2v}, $^4B_2$)

E(UB3LYP) = -1550.6883439 a.u. ZPE = 0.0086835 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1550.711944 a.u.

Mn	0.000000	0.000000	0.000000
F	1.363394	0.000000	1.008527
F	0.000000	-1.613114	-0.641121
F	-1.363394	0.000000	1.008527
F	0.000000	1.613114	-0.641121

MnF_5 (D_{3h}, $^3A'_2$)

E(UB3LYP) = -1650.5049658 a.u. ZPE = 0.0126081 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1650.522815 a.u.

Mn	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.747914
F	1.678729	0.000000	0.000000
F	-0.839365	-1.453822	0.000000
F	-0.839364	1.453822	0.000000
F	0.000000	0.000000	-1.747914

MnF_6 (D_{4h}, $^2B_{2g}$)

E(UB3LYP) = -1750.2539088 a.u. ZPE = 0.0143694 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1750.271090 a.u.

Mn	0.000000	0.000000	0.000000
F	0.000000	0.000000	1.720635
F	1.733559	0.000000	0.000000
F	0.000000	-1.733559	0.000000
F	-1.733559	0.000000	0.000000
F	0.000000	1.733559	0.000000
F	0.000000	0.000000	-1.720635

MnF_6 (D_{3d}, $^2A_{1g}$)

E(UB3LYP) = -1750.2540051 a.u. ZPE = 0.0165587 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1750.269107 a.u.

Mn	0.000000	0.000000	0.000000
F	0.993217	0.000000	1.413157
F	0.993217	1.223830	-0.706579
F	0.993217	-1.223830	-0.706579
F	-0.993217	-1.223830	0.706579
F	-0.993217	0.000000	-1.413157
F	-0.993217	1.223830	0.706579

MnF_7 (C_{2v}, $^1A_1$)

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E(UB3LYP) = -1849.9461326 a.u. ZPE = 0.0170604 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1849.962171 a.u.
Mn     0.000000     0.000000    -0.161790
 F     0.000000     0.000000     1.768226
 F     1.096055     0.000000    -1.530027
 F    -1.096055     0.000000    -1.530027
 F     1.133235    -1.256520     0.299102
 F     1.133235     1.256520     0.299102
 F    -1.133235     1.256520     0.299102
 F    -1.133235    -1.256520     0.299102
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MnF_7 (D_{5h}, $^1A'_1$)

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E(UB3LYP) = -1849.9440347 a.u. ZPE = 0.0168704 a.u.
Sum of electronic and thermal Free Energies at 298.15 K = -1849.959484 a.u.
Mn     0.000000     0.000000     0.000000
 F     0.000000     0.000000     1.804134
 F     1.715833     0.000000     0.557508
 F     0.000000    -1.712576     0.000000
 F    -1.715833     0.000000     0.557508
 F     0.000000     1.712576     0.000000
 F     1.060443     0.000000    -1.459575
 F    -1.060443     0.000000    -1.459575
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