Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

"Reactions of oxygen atoms with fluoroform and its radiolysis products: matrix isolation and *ab initio* study"

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Table S1. Absorption maxima in the IR spectra of **CHF_3**, **N_2O**, **H_2O**, **$CHF_3\cdots H_2O$** and **$CHF_3\cdots N_2O$** (tentative) in solid argon, krypton and xenon. See text for the reference data.

	Ar	**Kr**	**Xe**
CHF_3	509.9, 700.5, 1136, 1148, 1211.2, 1376.5, 2274.6, 3044.5	509.3, 699.9, 1133.7, 1144.1, 1209.9, 1373.0, 2268.5, 3036.6	507.9, 698.2, 1131.1, 1139.8, 1206.9, 1369.8, 2260.7, 3026.1
N_2O	589.0, 1283.0, 2218.5, 2228.2, 2259.5, 3473.7	585.0, 1160.3, 1283.6, 2220.4, 3477.0	584.3, 1158.5, 1280.0, 2219.3, 2223.1, 3467.0
H_2O	1594.6, 1608.5, 1624.3, 3711.4, 3756.0, 3776.7	1605.8, 1620.8, 1640.6, 3700.4, 3747.1, 3765.9,	1592.9, 1604.6, 1629.0, 3693.6, 3740.4, 3762.4
$CHF_3\cdots N_2O$	584.5, 1139.6, 1141.7, 1286.0, 1371.5, 2222.8, 2224.2, 2232.0, 3483.5	1128.2, 1138.8, 1287.0, 1370.5, 1376.5, 2224.5, 2215.9, 3039.3, 3050.2, 3469.6, 3485.1	1126.8, 1135.3, 1143.0, 1204.6, 1277.0, 1367.0, 1373.1, 2214.8, 3038.8, 3471.5, 3474.4
$CHF_3\cdots H_2O$	698.0, 1127.6, 1136.0, 1138.2, 1370.6, 1387.6, 3064.6	697.1, 1116.2, 1124.0, 1129.1, 1139.5, 1158.5, 1207.1, 1377.1, 1383.6, 1593.0, 3041.7, 3052.3, 3718.6	696.1, 1123.2, 1128.4, 1389.2, 1586.9, 3042.3, 3054.7, 3689.4, 3701.2

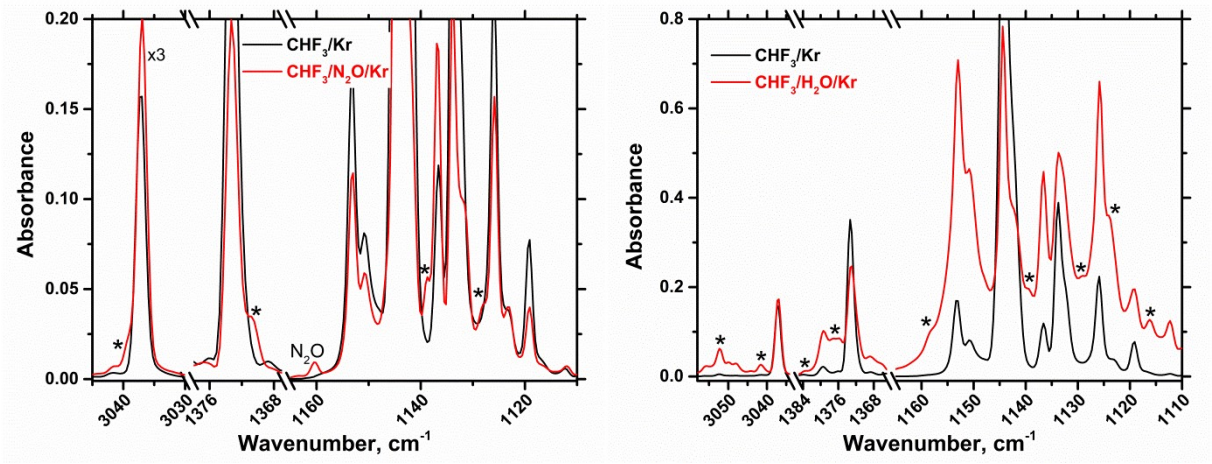

Figure S1. Fragments of FTIR spectra of the deposited CHF_3/Kr (1/1000), CHF_3/N_2O/Kr (1/1/1000), CHF_3/H_2O/Kr (1/1/1000) samples (the bands of $CHF_3\cdots N_2O$ and $CHF_3\cdots H_2O$ complexes are marked by asterisks).

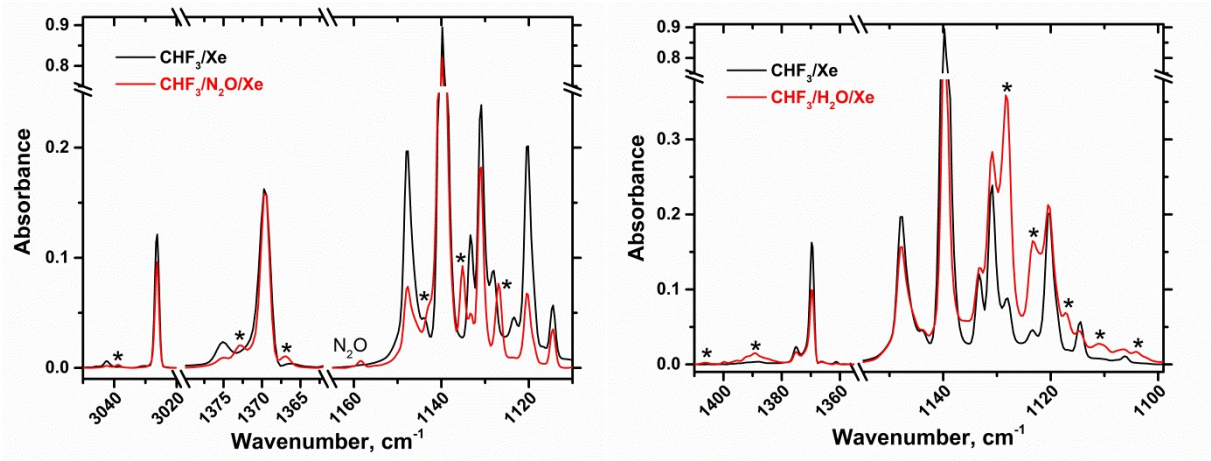

Figure S2. Fragments of FTIR spectra of the deposited CHF_3/Xe (1/1000), CHF_3/N_2O/Xe (1/1/1000), CHF_3/H_2O/Xe (1/1/1000) samples (the bands of $CHF_3\cdots N_2O$ and $CHF_3\cdots H_2O$ complexes are marked by asterisks).

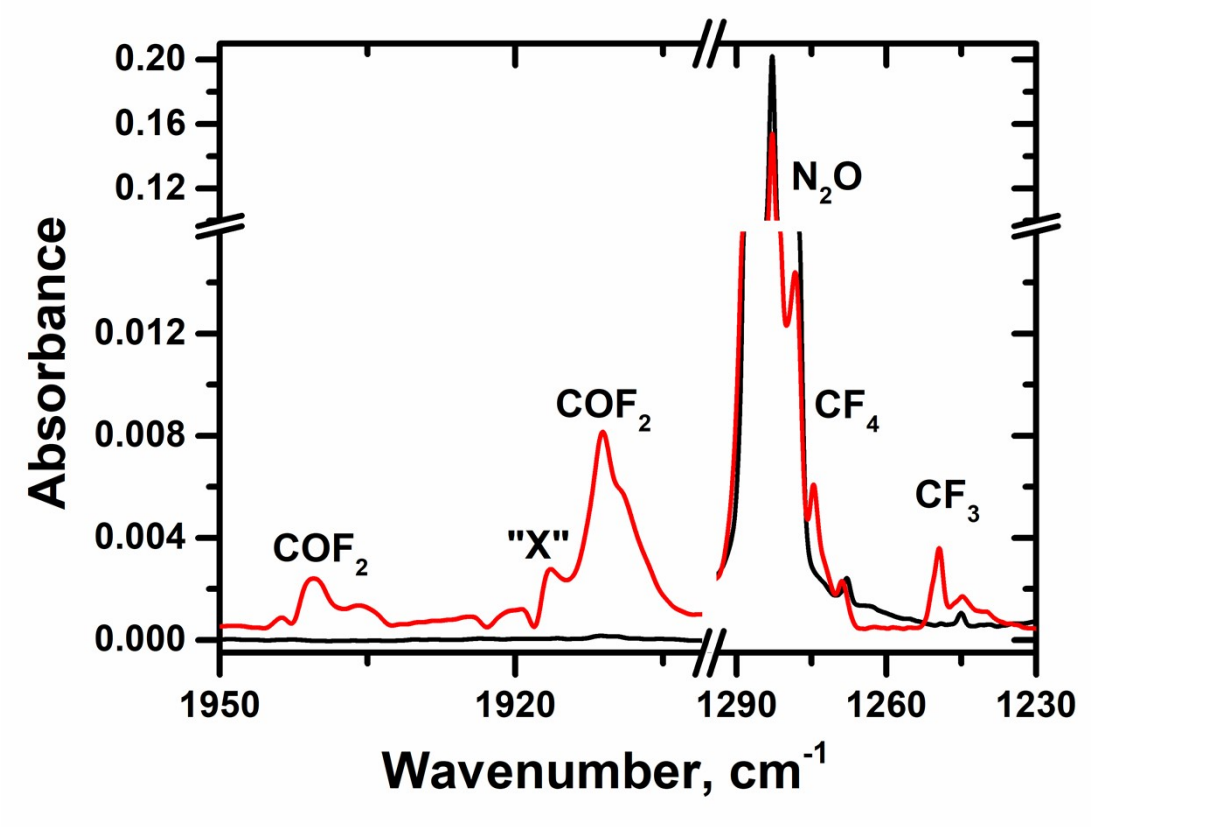

Figure S3. Fragments of the FTIR spectra of CHF_3/N_2O/Ar (1/1/1000) sample: after deposition (black line) and after irradiation with UV-light (red line).

Table S2. Calculated harmonic frequencies in cm^{-1} and IR intensities in km/mol (indicated in parentheses) of **$COF_2\cdots HF$** complexes at the CCSD(T)/L2a_3 level of theory.

Mode number	**Mode type**	**COF_2**	**HF**	**Complex A**	**Complex B**	**Complex C**
1	Intermol	-	-	32.2 (2)	18.4 (3)	14.1 (6)
2	Intermol	-	-	40.4 (1)	24.5 (1)	25.8 (4)
3	Intermol	-	-	156.6 (6)	83.3 (1)	93.6 (3)
4	Intermol	-	-	515.8 (128)	216.1 (106)	242.3 (144)
5	Intermol	-	-	529.8 (109)	253.5 (126)	251.1 (125)
6	CF_2 s-bend	583.7 (5)	-	590.4 (0)	584.9 (8)	584.6 (6)
7	CF_2 a-bend	621.6 (7)	-	640.4 (18)	621.2 (7)	619.9 (6)
8	CO bend.	779.3 (34)	-	786.4 (41)	772.5 (36)	771.1 (36)
9	CF_2 s-str	971 (60)	-	991.3 (49)	962.8 (71)	960.3 (79)
10	CF_2 a-str	1260.3 (408)	-	1306.9 (399)	1249.2 (454)	1237.5 (402)
11	CO str	1961.8 (443)	-	1936.0 (541)	1970.4 (420)	1976.9 (460)
12	HF str	-	4128.8 (104)	3982.3 (589)	4111.7 (256)	4110.9 (258)

Table S3. Absolute, ZPVE-corrected and relative energies of reagents, intermediates and transition states for reactions (8, 9) and (10, 11) calculated at the MP2/CBS level of the theory.

Structure	**E(CBS), a.u.**	**E(CBS)+ZPVE, a.u.**	**$E_{rel,}$ kcal/mol**
CHF_3+O/Ar	-940.00675	-939.9789425	0.0
TS1 (8)	-939.99444	-939.9691116	6.2
CF_3OH/Ar	-940.25819	-940.2286749	-156.7
TS2 (9)	-940.18433	-940.1606574	-114.0
COF_2 + HF/Ar	-940.24968	-940.2242409	-153.9
TS3 (10)	-939.95123	-939.9248	31.6
CHF_2OF/Ar	-940.09632	-940.06744	-57.9
TS4 (11)	-940.00979	-939.98809	-8.1
COF_2…HF/Ar	-940.25227	-940.22585	-157.3

Table S4. Calculated harmonic frequencies in cm^{-1} and IR intensities in km/mol (indicated in parentheses) and optimized molecular geometries (in angstroms) of **CF_3OH/Ar** and **CHF_2OF/Ar** at the MP2(T)/L3a_3 level of theory.

Mode number	CF_3OH/Ar	CHF_2OF/Ar
1	24.2 (0)	22.4 (1)
2	25.7 (1)	25.9 (2)
3	62.6 (1)	39 (0)
4	270.7 (86)	134 (1)
5	445.4 (4)	301 (4)
6	457.2 (14)	467.5 (1)
7	607.8 (13)	559.3 (7)
8	627.2 (2)	663 (13)
9	641.1 (4)	992.2 (13)
10	909.7 (5)	1127.6 (122)
11	1127.3 (162)	1156.3 (222)
Mode number	**CF_3OH/Ar**	**CHF_2OF/Ar**
12	1190.3 (361)	1203.6 (169)
13	1308.3 (480)	1387.2 (54)
14	1426.2 (232)	1412.5 (20)
15	3832.4 (180)	3188.5 (15)

CF_3OH/Ar

Atom	x	y	z
6	0.0810792	-0.74729538	-0.06670255
9	0.55604577	-1.96678377	-0.23932074
9	-0.49770893	-0.68129376	1.14038696
9	-0.88977001	-0.53580385	-0.96622472
1	0.74528288	1.0144924	-0.0686388
8	1.09281257	0.12474949	-0.1947695
18	-1.08774149	2.79193483	0.39526931

CHF_2OF/Ar

Atom	x	y	z
6	-0.38946516	0.03137185	0.00059441
9	0.49065492	2.14630145	-0.0123873

9	-0.89455858	-0.55974861	1.0900375
9	-0.89879851	-0.57130727	-1.08050986
1	-0.69955412	1.24693808	-0.00527302
8	0.8294108	0.3667607	-0.00357254
18	1.56231065	-2.6603162	0.01111081

Table S5. Absolute, ZPVE-corrected and relative energies of reagents, intermediates and transition states for reactions (12) and (13) calculated at the MP2/CBS level of the theory.

Structure	**E(CBS), a.u.**	**E(CBS)+ZPVE, a.u.**	**E_{rel}, kcal/mol**
CF_2+O/Ar	-839.51712	-839.50745	0.0
TS5 (12)	-839.49726	-839.48759	12.5
CFOF/Ar	-839.67263	-839.66004	-95.8
TS6 (13)	-839.65928	-839.64873	-88.7
COF_2/Ar	-839.85518	-839.84085	-209.2

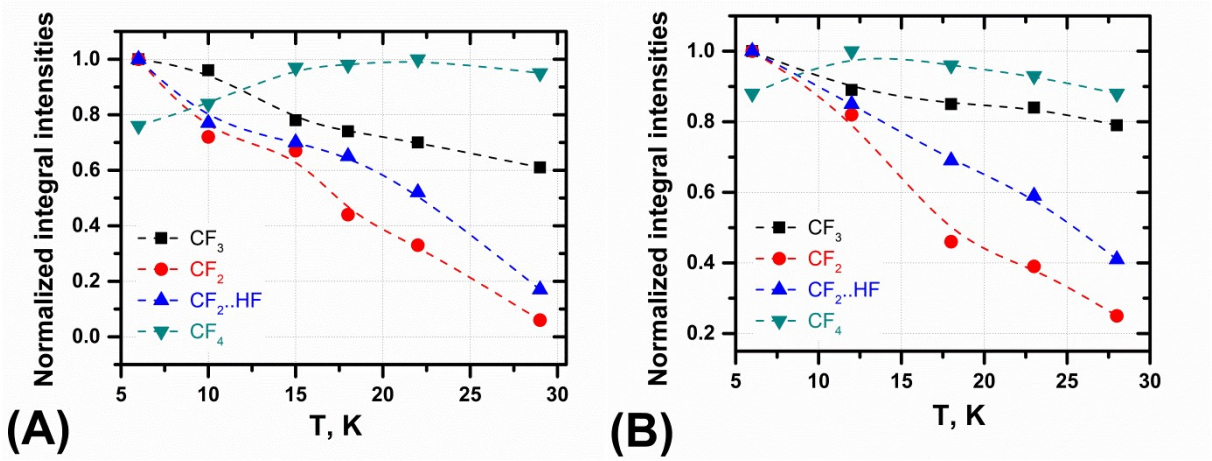

Figure S4. Relative product yields as a function of annealing temperature in the irradiated samples: a) CHF_3/N_2O/Ar (1/1/1000) and b) CHF_3/H_2O/Ar (1/1/1000).

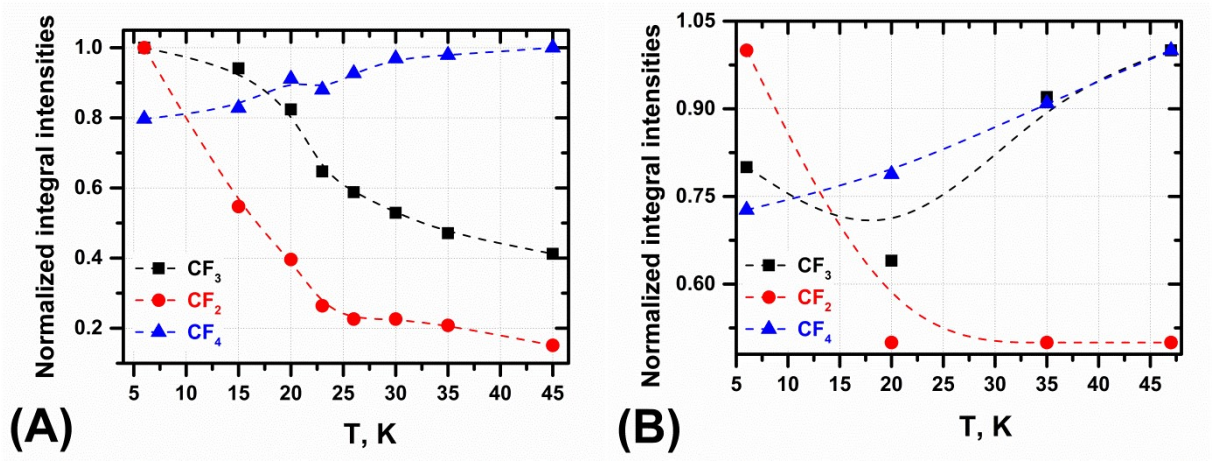

Figure S5. Relative product yields as a function of annealing temperature in the irradiated samples: a) $CHF_3/N_2O/Kr$ (1/1/1000) and b) $CHF_3/N_2O/Xe$ (1/1/1000).

Table S6. Optimized molecular geometries (in angstroms) and energies (in atomic units) for **COF_2**, **HF** and their complexes (**A**, **B**, **C**) at the CCSD(T)/L2a_3 level of theory.

E –energy,

ZPVE – Zero-point vibrational energy,

E0 = E + ZPVE,

COF_2

Atom	x	y	z
6	0.03855523	-0.08550384	-0.00200240
9	0.68817731	1.05689980	0.01452989
9	-1.24770950	0.18397333	0.01452990
8	0.52097697	-1.15536929	-0.02705740

E = -312.718303 E0 = -312.704229

HF

Atom	x	y	z
1	-0.45951778	-0.00000000	0.00000000
9	0.45951778	0.00000000	0.00000000

E = -100.367418 E0 = -100.358012

$COF_2\cdots HF$ (A)

Atom	x	y	z
6	-0.24191789	-0.17301332	-0.00072073
9	0.92131672	-0.76442412	-0.00345656
9	-0.05791289	1.11938917	0.00559558
8	-1.28608429	-0.72255256	-0.00352639
1	-2.96481842	0.04223628	-0.00000695
9	-3.77058322	0.49836455	0.00211507

E = -413.093659 E0 = -413.067440

$COF_2\cdots HF$ (B)

Atom	x	y	z
6	-0.08801584	-0.07190240	0.00276945
9	0.72080376	-1.09837612	-0.03417394
9	0.65917860	1.02386725	0.03894093
8	-1.25986168	-0.09184251	0.00445985
1	-0.16444388	2.93010749	0.10617691
9	-0.34220916	3.83229728	0.13756974

E = -413.087823 E0 = -413.063063

$COF_2\cdots HF$ (C)

Atom	x	y	z
6	-0.13245184	-0.02888491	0.00153160
9	0.64125842	-1.08484718	0.01376104
9	0.65478136	1.04010826	0.03927970
8	-1.30248840	-0.00778059	-0.03556604
1	2.69923573	1.07711504	0.10476114
9	3.60829257	0.93769486	0.13197550

E = -413.087713 E0 = -413.062909

Table S7. Optimized molecular geometries (in angstroms) and energies (in atomic units) for **CHF_3+O/Ar**, **CHF_2OF/Ar**, **CF_3OH/Ar**, **COF_2 + HF/Ar**, **COF_2···HF/Ar**, **CF_2 + O/Ar**, **CFOF/Ar**, **COF_2/Ar** and **TS1-TS6** at the MP2/L2a_3 level of theory.

E –energy,

ZPVE – Zero-point vibrational energy,

E0 = E + ZPVE,

CHF_3+O/Ar

Atom	x	y	z
6	-0.041905	-1.24507136	-0.03368618
9	0.91822985	-0.33055762	-0.01026055
9	0.07878629	-2.02584466	1.04378593
9	0.11548268	-2.00898477	-1.11848002
1	-1.01898166	-0.77382291	-0.04659343
8	3.1347114	-2.94056236	0.00688066
18	2.12861516	-4.28304516	-0.02058326

E = -939.925327 E0 = -939.897771

CHF_2OF/Ar

Atom	x	y	z
6	-0.58584294	0.25716669	-0.09879497
9	0.94352245	1.736373	0.47001673
9	-0.67753099	-0.31545455	1.10512645
9	-0.86192356	-0.65146052	-1.03242731
1	-1.25403979	1.11112885	-0.14967929
8	0.73269743	0.61503907	-0.37896502
18	1.70311741	-2.75279256	0.08472341

E = -940.021924 E0 = -939.993037

CF_3OH/Ar

Atom	x	y	z
6	0.0810792	-0.74729538	-0.06670255
9	0.55604577	-1.96678377	-0.23932074
9	-0.49770893	-0.68129376	1.14038696
9	-0.88977001	-0.53580385	-0.96622472
1	0.74528288	1.0144924	-0.0686388
8	1.09281257	0.12474949	-0.1947695
18	-1.08774149	2.79193483	0.39526931

E = -940.182918 E0 = -940.153403

COF_2 + HF/Ar

Atom	x	y	z
6	0.57098868	-0.81510749	-0.81056058
9	1.13132074	-1.73177849	-0.06147905
9	-1.15472832	-0.15976241	1.19633922
9	-0.39550444	-1.38223559	-1.48852647
1	-0.92403861	0.73277759	1.16812061
8	0.89398697	0.31428325	-0.87950794
18	-0.12202498	3.04182314	0.87561417

E = -940.174963 E0 = -940.149528

COF_2···HF/Ar

Atom	x	y	z
6	-0.45979823	-0.75063712	0.46155348
9	0.37741327	2.70736426	0.10002423
9	-0.4498767	-2.02436893	0.73917894
9	-1.45777655	-0.50516562	-0.34108431
1	0.38735957	1.83211626	0.40377915
8	0.30890567	0.04430658	0.87465532
18	1.29377294	-1.30361542	-2.23810682

E = -940.177542 E0 = -940.151118

CF_2 + O/Ar

Atom	x	y	z
6	-0.1082169	-0.62068215	-0.65341957

9	-0.33136645	-1.19629833	0.48784781
9	1.16083782	-0.78296725	-0.86971711
8	0.19298947	1.82095896	0.42105373

E = -839.455501 E0 = -839.445826

CFOF/Ar

Atom	x	y	z
6	-0.13637279	0.09268593	-1.10972076
9	0.15731572	-1.58705388	0.78385982
9	1.05709123	0.51703196	-1.01544215
8	-0.77759158	-0.70540376	-0.56734798

E = -839.613072 E0 = -839.600482

COF_2/Ar

Atom	x	y	z
6	0.00072319	-0.44206237	-0.50407804
9	0.48032875	-1.24762543	0.41553394
9	0.99348423	0.2989103	-0.93999614
8	-1.113575	-0.39429944	-0.87141853

E = -839.794519 E0 = -839.780192

TS1

Atom	x	y	z
6	-0.07603014	-0.88660921	-0.10846421
9	1.17292798	-1.10386636	-0.48094095
9	-0.21799494	-1.18662137	1.17047087
9	-0.88275374	-1.66910663	-0.82714993
1	-0.39111434	0.17901173	-0.32044747
8	0.04103769	1.42361479	0.10590127
18	0.35392749	3.24357706	0.46063042

E = -939.919141 E0 = -939.893817

TS2

Atom	x	y	z
6	0.22842128	-0.81911545	-0.44504552
9	0.93745265	-1.72923177	0.14896865

9	-0.82285884	-0.24652244	0.81999268
9	-0.59168545	-1.37947613	-1.28009677
1	-0.12794771	0.57465833	0.27740145
8	0.65739742	0.34616127	-0.61886607
18	-0.28077933	3.2535262	1.09764559

E = -940.109091 E0 = -940.085416

TS3

Atom	x	y	z
6	-0.71154449	0.39098585	-0.00908534
9	0.60356843	1.52130233	0.02214947
9	-0.81942067	-0.2947425	1.07007251
9	-0.78234844	-0.27783056	-1.10184024
1	-1.3668802	1.25121872	-0.01357115
8	1.2726746	0.17770985	0.02312601
18	1.80395077	-2.7686437	0.00914876

E = -939.876451 E0 = -939.850014

TS4

Atom	x	y	z
6	-0.38946516	0.03137185	0.00059441
9	0.49065492	2.14630145	-0.0123873
9	-0.89455858	-0.55974861	1.0900375
9	-0.89879851	-0.57130727	-1.08050986
1	-0.69955412	1.24693808	-0.00527302
8	0.8294108	0.3667607	-0.00357254
18	1.56231065	-2.6603162	0.01111081

E = -939.935689 E0 = -939.913990

TS5

Atom	x	y	z
6	-0.21258079	-0.78436009	-0.3457359
9	-0.0745015	-1.19047372	1.00698731
9	1.04795045	-0.75184977	-0.77098259
8	-0.29333501	0.59649636	0.55607687

E = -839.434937 E0 = -839.425272

TS6

Atom	x	y	z
6	-0.09603622	0.03063191	-0.93837751
9	0.31775521	-1.52205435	0.65343067
9	1.06650196	0.43742911	-0.93576822
8	-0.96516333	-0.63453875	-0.61801807

E = -839.599072 E0 = -839.588521

Table S8. Vibrational features (harmonic frequencies in cm^{-1}, and IR intensities in km/mol, in parentheses) of **CHF_3+O/Ar**, **CHF_2OF/Ar**, **CF_3OH/Ar**, **COF_2 + HF/Ar**, **$COF_2\cdots$HF/Ar**, **CF_2 + O/Ar**, **CFOF/Ar**, **COF_2/Ar** and **TS1**-**TS6** calculated at the MP2/L2a_3 level of theory.

Mode	CHF_3+O/Ar	CHF_2OF/Ar	CF_3OH/Ar	COF_2+HF/Ar	$COF_2\cdots$HF/Ar
1	13.2 (0)	22.4 (1)	24.2 (0)	15.3 (0)	10.5 (1)
2	38.4 (12)	25.9 (2)	25.7 (1)	36.4 (0)	34.2 (2)
3	63.5 (5)	39 (0)	62.6 (1)	50.6 (8)	40.2 (0)
4	72.5 (1)	134 (1)	270.7 (86)	61.9 (0)	45.1 (0)
5	119.6 (15)	301 (4)	445.4 (4)	81.6 (7)	59.8 (1)
6	509.7 (2)	467.5 (1)	457.2 (14)	113.2 (3)	154 (5)
7	512.3 (2)	559.3 (7)	607.8 (13)	239.3 (104)	516.4 (125)
8	629.6 (3)	663 (13)	627.2 (2)	305.3 (162)	527.4 (118)
9	703.3 (15)	992.2 (13)	641.1 (4)	589.4 (5)	593.5 (0)
10	1142.6 (153)	1127.6 (122)	909.7 (5)	623.4 (7)	640.1 (16)
11	1158.7 (283)	1156.3 (222)	1127.3 (162)	783.2 (43)	788.4 (52)
12	1172.1 (286)	1203.6 (169)	1190.3 (361)	979.5 (60)	994.3 (49)
13	1409.8 (15)	1387.2 (54)	1308.3 (480)	1266.9 (397)	1299.3 (378)
14	1433.1 (40)	1412.5 (20)	1426.2 (232)	1949.7 (454)	1934.1 (495)
15	3229.6 (5)	3188.5 (15)	3832.4 (180)	4069 (277)	3961.5 (606)

Mode	TS1	TS2	TS3	TS4
1	584.2i (917)	1756.8i (356)	754.4i(62)	2858.2i (2004)
2	59 (0)	8.8 (0)	18.6 (4)	64.4i (1)
3	71 (0)	29.1 (0)	24.4 (5)	40.8 (0)
4	206.1 (23)	41.4 (0)	55.6 (1)	54 (1)
5	223.2 (12)	257.9 (0)	78.2 (0)	164.3 (3)
6	266.4 (10)	367.9 (58)	342.4 (93)	374 (1)
7	513.6 (4)	567.1 (52)	370.8 (3)	533.4 (6)
8	528.7 (4)	575.7 (0)	603.1 (48)	539.4 (7)
9	717.2 (16)	711.4 (111)	640.3 (323)	588.8 (3)
10	1107.7 (291)	881.4 (432)	920.6 (44)	740.4 (64)
11	1126.3 (59)	894.9 (22)	1181.2 (164)	1010.3 (203)
12	1192.5 (261)	993.7 (272)	1338.3 (223)	1067.9 (42)
13	1271.5 (267)	1341.3 (436)	1339.9 (14)	1194.3 (227)
14	1462 (151)	1652 (765)	1468 (114)	1437.7 (35)
15	2370.7 (1525)	2069.4 (149)	3223.4 (10)	1779.4 (222)

Mode	CF_2 + O/Ar	TS5	CFOF/Ar	TS6	COF_2/Ar
1	32.1 (7)	556.5i (204)	31.9 (7)	923.9i (1190)	35.2 (0)
2	82.2 (1)	83 (14)	39.5 (0)	34.3 (27)	36 (1)
3	88.9 (1)	175.3 (9)	51.9 (1)	47.9 (0)	49.5 (0)
4	97.9 (25)	368.4 (30)	150 (2)	58.2 (4)	586.9 (5)
5	234.3 (3)	462.9 (19)	477 (9)	225.6 (37)	620.7 (6)
6	633.5 (4)	553.4 (86)	513.2 (20)	383.4 (16)	782.1 (44)
7	678.4 (2)	619.8 (200)	732.3 (1)	473.6 (73)	972.4 (60)
8	1139 (364)	872.1 (247)	1205.3 (184)	1107.3 (206)	1248.5 (387)
9	1260.8 (114)	1107.6 (152)	2325.2 (424)	2301.4 (192)	1957.6 (406)

Table S9. Optimized molecular geometries (in angstroms), energies (in atomic units), and singlet transition energies (in eV) for **CF_3OH** and **CHF_2OF** at the CIS(2)/L2a_3 level of theory.
E –energy

CF_3OH

Atom	x	y	z
6	0.08021644	-0.7519748	-0.06686499
9	0.57686568	-1.96887147	-0.24334086
9	-0.50417456	-0.69767988	1.1465192
9	-0.89840753	-0.55138319	-0.97175175
1	0.7218652	1.02326785	-0.06367431
8	1.08386079	0.13756376	-0.19221864

E = -413.0766421153

Transition	Energy
$S_0 \rightarrow S_1$	10.178
$S_0 \rightarrow S_2$	12.040
$S_0 \rightarrow S_3$	13.114
$S_0 \rightarrow S_4$	13.604
$S_0 \rightarrow S_5$	13.841

CHF_2OF

Atom	x	y	z
6	-0.58814111	0.2572475	-0.09916375
9	0.94890285	1.74647154	0.48256054
9	-0.67612003	-0.31723623	1.11121872
9	-0.86281302	-0.65923661	-1.0371685
1	-1.25700835	1.11147044	-0.15043751
8	0.7363548	0.6105102	-0.39214729

E = -412.9210109962

Transition	Energy
$S_0 \rightarrow S_1$	5.8117
$S_0 \rightarrow S_2$	7.560
$S_0 \rightarrow S_3$	9.544
$S_0 \rightarrow S_4$	10.258
$S_0 \rightarrow S_5$	11.310