Supporting information

Computational Study of Oxygen Atom (^{3}P and ^{1}D) Reaction with CF_3CN

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Table S1: The moment of inertia (I_a, I_b and I_c), rotational constants, rotational symmetry number, optical isomers number of various species involved in the reactions.

species	I_a, I_b, I_c (amu bohr^2)	Rotational Constants (GHZ)	$N_{rotational\ symmetry}$	$N_{optical\ isomers}$
$CF_3CN(^1A_1)$	320.64107 614.58339 614.58339	5.62854 2.93653 2.93653	3	1
$CF_2CN(^2A')$	164.70663 443.80055 607.21306	10.95731 4.06656 2.97217	1	1
$OF(^2\Pi)$	0.00000 56.75885 56.75885	31.796649	1	1
$CF_3(^2A_1)$	167.75373 167.75373 324.16953	10.75828 10.75828 5.56728	3	1
$NCO(^2\Pi)$	0.00000 153.65536 153.65536	11.745384	1	1
$CNO(^2\Pi)$	0.00000 145.14571 145.14571	12.433996	1	1
$CF_3O(^2A')$	300.31860 310.73048 326.59300	6.00942 5.80806 5.52596	1	1
$CN(^2\Sigma^+)$	0.00000 31.37215 31.37215	57.526852	1	1
$CF_2NCO(^2A)$	168.98003 860.74611 1020.81056	10.68020 2.09672 1.76795	1	1
$CF_2(^3B_1)$	14.49112 176.28439 190.77551	124.54118 10.23767 9.46003	2	1
$CNOF(^3A'')$	137.98591 157.92360 295.90951	13.07917 11.42794 6.09896	1	2
$F_2CO(^3A'')$	151.27248 173.35596	11.93040 10.41061	1	1

	312.28608	5.77913		
FCN(^{3}A′)	12.98325 146.78769 159.77094	139.00538 12.29491 11.29580	1	1
CF_3C(^{2}A″)	290.12794 305.68236 333.83748	6.22050 5.90398 5.40605	1	1
NO(^{2}Π)	0.00000 35.14144 35.14144	51.356499	1	1
CF_3N(^{1}A′)	262.53805 307.66739 356.46665	6.87421 5.86588 5.06286	1	1
CO($^1\Sigma^+$)	0.00000 31.12996 31.12996	57.974423	1	1
CF_2($^1A_1$)	20.82720 145.18110 166.00829	86.65311 12.43097 10.87139	2	1
CNOF(^{1}A′)	98.51675 185.80500 284.32176	18.31913 9.71309 6.34753	1	2
F_2CO($^1A_1$)	154.31434 154.54982 308.86416	11.69523 11.67741 5.84316	2	1
FCN($^1\Sigma$)	0.00000 170.31936 170.31936	10.596219	1	1
IM1($CF_3C(O)N$)(^{3}A″)	456.92196 715.38762 850.03460	3.94978 2.52275 2.12314	1	1
IM2(CF_3CNO)(^{3}A)	348.06152 966.04496 994.25917	5.18512 1.86818 1.81516	1	1
IM3(CF_3OCN)(^{3}A″)	357.48518 796.57682 834.11739	5.04844 2.26562 2.16365	1	1
IM4 ($F_2C(O)CNF$)(^{3}A)	411.77376 675.62574 886.33317	4.38285 2.67121 2.03619	1	1
IM5(F_2COCNF)(^{3}A)	460.28174 695.25179 852.86631	3.92095 2.59581 2.11609	1	1
IM6($F_2CC(F)NO$)(^{3}A″)	476.79586	3.78514	1	1

	717.13996 1193.93582	2.51658 1.51159		
IM7(F_2CONCF)(^3A)	437.96149 662.17182 817.50892	4.12078 2.72549 2.20761	1	1
1-IM1($CF_3C(O)N$)($^1A'$)	409.59507 788.24268 876.96962	4.40616 2.28958 2.05793	1	1
1-IM2($FOCF_2CN$)($^1A'$)	382.94504 898.20829 962.36857	4.71279 2.00927 1.87531	1	1
1-IM3(CF_3OCN) ($^1A'$)	327.88312 930.25796 940.48309	5.50422 1.94004 1.91895	1	1
1-IM4(CF_3CNO)(^1A)	320.50806 1224.61049 1224.69503	5.63088 1.47373 1.47363	1	1
1-IM5(CF_3NCO)($^1A'$)	322.43315 1053.57795 1056.09805	5.59726 1.71296 1.70888	1	1
1-IM6($F_2C(N)COF$)(^1A)	404.02669 671.56743 866.27953	4.46689 2.68736 2.08332	1	1
1-IM7($CF_3NC(O)$)(^1A)	365.95731 754.17771 788.84779	4.93156 2.39299 2.28782	1	1
1-IM8(CF_3ONC)($^1A'$)	329.33416 892.23305 904.65064	5.47997 2.02272 1.99496	1	1
1-IM9(F_2CNCOF)(^1A)	311.03297 1089.30136 1173.83375	5.80241 1.65679 1.53748	1	1
TS1($^3A''$)	565.61937 1056.95182 1298.94391	3.19073 1.70750 1.38939	1	1
TS1′($^3A'$)	570.47780 1051.62885 1298.61032	3.16356 1.71614 1.38975	1	1
TS2($^3A''$)	478.16049 781.91109 939.33154	3.77434 2.30812 1.92130	1	1
TS3($^3A''$)	472.09909 790.78029 940.82061	3.82280 2.28223 1.91826	1	1

TS4(^{3}A)	366.34998 1066.73875 1111.66711	4.92628 1.69183 1.62345	1	1
TS5(^{3}A)	369.90679 1299.74386 1346.91291	4.87891 1.38854 1.33991	1	1
TS6(^{3}A)	340.27897 1084.81923 1085.87758	5.30371 1.66363 1.66201	1	1
TS7(^{3}A′)	513.58771 636.25852 836.11213	3.51399 2.83649 2.15849	1	1
TS8 (^{3}A″)	374.30789 919.10262 971.96441	4.82154 1.96359 1.85680	1	1
TS9(^{3}A)	469.33654 746.61072 851.87339	3.84530 2.41725 2.11856	1	1
TS10(^{3}A)	440.10426 792.26837 955.29143	4.10071 2.27794 1.88920	1	1
TS11(^{3}A)	426.95309 672.99342 865.79759	4.22702 2.68166 2.08448	1	1
TS12(^{3}A′)	463.13620 869.99102 1019.51739	3.89678 2.07444 1.77019	1	1
TS13(^{3}A′)	414.66477 1119.80995 1215.49595	4.35229 1.61165 1.48478	1	1
TS14(^{3}A)	478.67440 628.29844 892.18349	3.77029 2.87243 2.02284	1	1
TS15(^{3}A)	434.80443 659.80768 825.61653	4.15070 2.73525 2.18593	1	1
1-TS1(^{1}A′)	411.82142 903.41082 1003.05536	4.38234 1.99770 1.79924	1	1
1-TS2(^{1}A)	355.70412 915.20057 961.37811	5.07371 1.97196 1.87724	1	1
1-TS3(^{1}A′)	454.57177 704.41056	3.97020 2.56206	1	1

	839.43652	2.14994		
1-TS4(^{1}A)	434.61175 781.86364 836.81473	4.15254 2.30826 2.15668	1	1
1-TS5(^{1}A′)	443.68815 668.02719 794.13706	4.06759 2.70160 2.27258	1	1
1-TS6(^{1}A)	368.55201 811.28664 850.90915	4.89684 2.22454 2.12096	1	1
1-TS7(^{1}A)	360.68466 779.27499 803.91455	5.00365 2.31592 2.24494	1	1
1-TS8(^{1}A)	423.49529 672.07819 864.30601	4.26154 2.68531 2.08808	1	1
1-TS9(^{1}A)	327.74821 948.00888 961.64426	5.50649 1.90372 1.87672	1	1
1-TS10(^{1}A)	428.95169 858.25927 1044.38009	4.20733 2.10279 1.72805	1	1

Table S2: The Z-matrix (Cartesian coordinates) of all species found on PESs at the B3LYP/6-311+G(d) level.

Species	Coordinates(Atom, X, Y, Z)			
$CF_3CN(^1A_1)$	C	0.000000	0.000000	-0.319481
	C	0.000000	0.000000	1.160162
	N	0.000000	0.000000	2.309784
	F	0.000000	1.255138	-0.785651
	F	1.086982	-0.627569	-0.785651
	F	-1.086982	-0.627569	-0.785651
$CF_2CN(^2A')$	C	0.176762	-0.330156	0.000000
	C	-0.199040	0.997971	0.000000
	N	-0.435434	2.139763	0.000000
	F	0.176762	-1.054735	1.099584
	F	0.176762	-1.054735	-1.099584
$OF(^2\Pi)$	O	0.000000	0.000000	-0.716233
	F	0.000000	0.000000	0.636652
$CF_3(^2A_1)$	C	0.000000	0.000000	0.327418
	F	0.000000	1.262025	-0.072760
	F	-1.092946	-0.631013	-0.072760
	F	1.092946	-0.631013	-0.072760
$NCO(^2\Pi)$	N	0.000000	0.000000	-1.263691
	C	0.000000	0.000000	-0.040546
	O	0.000000	0.000000	1.136139
$CNO(^2\Pi)$	C	0.000000	0.000000	-1.326595
	N	0.000000	0.000000	-0.119212
	O	0.000000	0.000000	1.099256
$CF_3O(^2A')$	C	-0.028349	0.031199	0.000000
	O	-0.447525	1.317536	0.000000
	F	1.311750	0.089171	0.000000
	F	-0.447525	-0.640557	1.079395
	F	-0.447525	-0.640557	-1.079395
$CN(^2\Sigma^+)$	C	0.000000	0.000000	-0.627824
	N	0.000000	0.000000	0.538135
$CF_2NCO(^2A)$	C	0.874937	-0.020827	0.289090
	C	-1.491616	-0.167517	-0.014493
	N	-0.337415	-0.538641	-0.080834
	O	-2.625789	0.079483	0.006625
	F	1.099937	1.255673	-0.064055
	F	1.907650	-0.781818	-0.062028
$CF_2(^3B_1)$	C	0.000000	0.000000	0.500288
	F	0.000000	1.139815	-0.166763
	F	0.000000	-1.139815	-0.166763

$CNOF(^3A'')$	C	0.000000	0.108847	0.000000
	N	1.363364	0.312686	0.000000
	O	-0.812477	0.986882	0.000000
	F	-0.338193	-1.192993	0.000000
$F_2CO(^3A'')$	C	-0.266859	0.214018	0.000000
	O	0.800576	1.038114	0.000000
	F	-0.266859	-0.532723	1.110008
	F	-0.266859	-0.532723	-1.110008
$FCN(^3A')$	C	0.000000	0.485424	0.000000
	N	1.223177	0.137740	0.000000
	F	-0.951360	-0.430747	0.000000
$CF_3C(^2A'')$	C	-0.068123	0.073430	0.000000
	F	1.286050	0.157667	0.000000
	F	-0.465238	-0.615830	1.082977
	F	-0.465238	-0.615830	-1.082977
	C	-0.465238	1.537561	0.000000
$NO(^2\Pi)$	N	0.000000	0.000000	-0.612284
	O	0.000000	0.000000	0.535749
$CF_3N(^1A')$	C	0.094448	0.094246	0.000000
	F	-0.374878	-1.224453	0.000000
	F	-0.374878	0.742554	1.071095
	F	-0.374878	0.742554	-1.071095
	N	1.365001	-0.415911	0.000000
$CO(^1\Sigma^+)$	O	0.000000	0.000000	0.483250
	C	0.000000	0.000000	-0.644333
$CF_2(^1A_1)$	C	0.000000	0.000000	0.599770
	F	0.000000	1.034386	-0.199923
	F	0.000000	-1.034386	-0.199923
$CNOF(^1A')$	C	0.000000	0.051095	0.000000
	N	-1.075767	0.716862	0.000000
	O	-0.474010	-1.107525	0.000000
	F	1.258049	0.392844	0.000000
$F_2CO(^1A_1)$	C	0.000000	0.000000	0.146461
	O	0.000000	0.000000	1.317347
	F	0.000000	1.066426	-0.634308
	F	0.000000	-1.066426	-0.634308
$FCN(^1\Sigma)$	C	0.000000	0.000000	-0.151259
	N	0.000000	0.000000	-1.304204
	F	0.000000	0.000000	1.115220
$IM1(CF_3C(O)N)(^3A'')$	C	-0.106498	0.539879	0.000000
	C	0.226518	-0.980667	0.000000
	N	-0.830979	-1.847382	0.000000
	O	1.376941	-1.393595	0.000000
	F	1.004313	1.269994	0.000000

	F	-0.830979	0.849734	1.089748
	F	-0.830979	0.849734	-1.089748
IM2(CF_3CNO)(^3A)	C	-0.712376	-0.024768	0.000363
	F	-0.416108	1.253200	-0.304252
	C	0.513103	-0.890282	0.013261
	N	1.749608	-0.655855	0.006956
	O	2.361917	0.428282	-0.000720
	F	-1.590283	-0.478665	-0.908918
	F	-1.321049	-0.035087	1.199317
IM3(CF_3OCN)($^3A''$)	C	0.467637	0.391832	0.000000
	O	-0.965297	0.472486	0.000000
	C	-1.720640	-0.624320	0.000000
	N	-1.289327	-1.850655	0.000000
	F	0.898729	1.641088	0.000000
	F	0.898729	-0.233343	1.085800
	F	0.898729	-0.233343	-1.085800
IM4 ($F_2C(O)CNF$)(^3A)	C	-0.674596	-0.001497	0.011012
	C	0.801344	0.112650	-0.039344
	N	1.479007	1.284045	-0.322211
	O	0.010191	0.098746	1.191129
	F	1.523108	-1.003539	-0.245241
	F	-1.488735	1.002901	-0.303747
	F	-1.278269	-1.159941	-0.240295
IM5(F_2COCNF)(^3A)	C	0.613293	-0.015159	0.063245
	C	-0.923252	-0.153450	-0.071458
	N	-1.483198	-1.279164	-0.098622
	O	0.779716	-0.468976	1.298929
	F	-1.589359	0.991722	-0.083890
	F	1.259163	-0.739848	-0.883432
	F	0.997353	1.272305	-0.105100
IM6($F_2CC(F)NO$)($^3A''$)	C	-0.605092	-0.596856	0.000000
	F	-1.911511	-0.752795	0.000000
	C	0.000000	0.622424	0.000000
	N	1.315665	0.874076	0.000000
	O	2.258088	0.085606	0.000000
	F	-0.772882	1.713466	0.000000
	F	0.057304	-1.733648	0.000000
IM7(F_2CONCF)(^3A)	C	-0.564481	-0.092855	0.028323
	F	-1.551993	0.050391	0.913769
	C	0.859829	-0.017663	0.550410
	N	0.986063	1.312157	-0.086935
	O	-0.289477	1.132277	-0.660099
	F	1.737154	-0.931330	0.165398
	F	-0.891686	-1.072417	-0.810618

1-IM1($CF_3C(O)N$)($^1A'$)	C	-0.037512	0.608460	0.000000
	C	0.144713	-0.897142	0.000000
	N	1.091858	-1.719552	0.000000
	O	-0.718854	-1.857562	0.000000
	F	1.155999	1.210024	0.000000
	F	-0.718854	0.985513	1.087366
	F	-0.718854	0.985513	-1.087366
1-IM2($FOCF_2CN$)($^1A'$)	C	-0.015433	0.222302	0.000000
	C	-1.489832	0.111725	0.000000
	N	-2.637957	0.045641	0.000000
	O	0.417673	-1.100855	0.000000
	F	1.848643	-1.053497	0.000000
	F	0.417673	0.886926	1.083830
	F	0.417673	0.886926	-1.083830
1-IM3(CF_3OCN) ($^1A'$)	C	-0.571929	0.366325	0.000000
	O	0.830112	0.448913	0.000000
	C	1.497029	-0.671384	0.000000
	N	2.144784	-1.626077	0.000000
	F	-1.007592	-0.270750	1.081913
	F	-1.007592	-0.270750	-1.081913
	F	-1.007592	1.610566	0.000000
1-IM4(CF_3CNO)(^1A)	C	-0.822769	0.001867	0.003002
	F	-1.253199	-0.994161	-0.793528
	C	0.634541	0.037967	0.060238
	N	1.793775	0.011149	0.017723
	O	2.985811	-0.004866	-0.007687
	F	-1.352055	-0.192679	1.224299
	F	-1.318472	1.155937	-0.479882
1-IM5(CF_3NCO)($^1A'$)	C	-0.645014	0.331278	0.000000
	C	1.580918	-0.518385	0.000000
	N	0.755952	0.374598	0.000000
	O	2.459673	-1.271365	0.000000
	F	-1.132759	1.573901	0.000000
	F	-1.132759	-0.305207	1.085747
	F	-1.132759	-0.305207	-1.085747
1-IM6($F_2C(N)COF$)(^1A)	C	0.681406	0.053557	-0.015902
	C	-0.765274	0.035857	-0.180911
	N	-0.205892	-0.413719	1.092452
	O	-1.032394	-1.259111	0.047789
	F	1.279533	1.204416	0.281593
	F	-1.672263	0.950058	-0.426680
	F	1.526464	-0.773092	-0.615870
1-IM7($CF_3NC(O)$)(^1A)	C	-0.570489	-0.000583	-0.013954
	C	1.787114	-0.711928	0.090669

	N	0.675673	-0.217227	-0.736555
	O	1.812805	0.548556	-0.047392
	F	-1.364170	-1.019727	-0.352098
	F	-1.136528	1.141597	-0.405505
	F	-0.447291	0.034486	1.321462
1-IM8(CF_3ONC)($^1A'$)	C	-0.553250	0.353216	0.000000
	O	0.852610	0.463726	0.000000
	C	2.160060	-1.665167	0.000000
	N	1.449176	-0.727373	0.000000
	F	-0.985406	-0.286004	1.080650
	F	-0.985406	-0.286004	-1.080650
	F	-0.985406	1.600175	0.000000
1-IM9(F_2CNCOF)(^1A)	C	1.085652	-0.064318	-0.032338
	C	-1.224137	-0.007517	-0.180759
	N	0.022534	-0.568625	-0.423103
	O	-1.706100	0.948477	-0.681308
	F	2.257418	-0.552028	-0.342550
	F	-1.902634	-0.792803	0.679055
	F	1.236546	0.991895	0.740247
TS1($^3A''$)	C	-0.739159	-0.179827	0.000000
	C	-0.922148	1.216627	0.000000
	N	-0.994567	2.372647	0.000000
	F	1.344740	-0.294639	0.000000
	F	-0.994567	-0.854057	1.092031
	F	-0.994567	-0.854057	-1.092031
	O	2.841171	-0.600570	0.000000
TS1′($^3A'$)	C	-0.741080	-0.193271	0.000000
	C	-0.925680	1.203271	0.000000
	N	-0.996789	2.359275	0.000000
	F	1.344018	-0.296678	0.000000
	F	-0.996789	-0.867669	1.091810
	F	-0.996789	-0.867669	-1.091810
	O	2.853016	-0.535847	0.000000
TS2($^3A''$)	C	0.072039	0.595245	0.000000
	C	-0.652498	-0.713527	0.000000
	N	-1.554287	-1.456117	0.000000
	O	0.837856	-2.029764	0.000000
	F	-0.824611	1.590633	0.000000
	F	0.837856	0.712496	1.087149
	F	0.837856	0.712496	-1.087149
TS3($^3A''$)	C	-0.685586	0.010524	0.000000
	C	1.355163	0.027566	-0.000002
	N	1.728863	1.211796	0.000000
	O	1.606068	-1.159791	-0.000001

	F	-1.092469	-0.607284	-1.089370
	F	-1.033740	1.277553	-0.000022
	F	-1.092463	-0.607246	1.089394
TS4(^{3}A)	C	-0.767291	0.001378	-0.000148
	C	0.535078	-0.707476	-0.004194
	N	1.712430	-0.834794	-0.003909
	O	2.657823	0.500096	0.001034
	F	-1.431188	-0.258160	1.133873
	F	-1.516846	-0.395851	-1.036636
	F	-0.591557	1.329497	-0.092221
TS5(^{3}A)	C	0.974374	0.008622	-0.002937
	C	-0.973061	-1.093939	-0.024760
	N	-1.966276	-0.385875	-0.011907
	O	-2.838711	0.464911	0.004945
	F	1.509281	-0.177138	1.198308
	F	1.743047	-0.524045	-0.942289
	F	0.799421	1.311599	-0.232688
TS6(^{3}A)	C	-0.409972	0.020524	-0.000091
	C	1.790056	-0.089368	0.000486
	N	2.950957	0.008419	0.000069
	F	-0.344827	1.310765	-0.013130
	F	-0.408758	-0.640550	-1.111425
	F	-0.409280	-0.617764	1.124520
	O	-2.308927	-0.014740	-0.000317
TS7(^{3}A′)	C	0.311515	0.492770	0.000000
	C	-1.036993	-0.190880	0.000000
	N	-1.460313	0.993097	0.000000
	O	-1.211180	-1.432526	0.000000
	F	0.898685	-1.469859	0.000000
	F	0.898685	0.884773	1.075210
	F	0.898685	0.884773	-1.075210
TS8 (^{3}A″)	C	-0.639492	0.370960	0.000000
	O	1.112062	0.479889	0.000000
	C	1.813974	-0.549597	0.000000
	N	1.686495	-1.822117	0.000000
	F	-1.027735	-0.257147	1.088345
	F	-1.027735	-0.257147	-1.088345
	F	-1.027735	1.624020	0.000000
TS9(^{3}A)	C	0.769780	0.047331	-0.036850
	C	-0.778220	0.010984	-0.177907
	N	-1.349072	1.315810	-0.191750
	O	-1.153989	-0.812845	-1.023532
	F	-0.868384	-0.424391	1.322050
	F	1.491122	1.095133	-0.047945

	F	1.457936	-1.010498	-0.071989
TS10(^{3}A)	C	0.861187	0.011516	-0.310338
	C	-0.901757	-0.112085	0.113815
	N	-1.363974	-1.222047	-0.642058
	O	-0.691563	-0.182456	1.327644
	F	-1.415346	1.054451	-0.418293
	F	1.647601	-0.983822	-0.096896
	F	1.470383	1.109081	-0.034545
TS11(^{3}A)	C	0.647870	-0.001911	0.052704
	C	-0.834222	-0.123937	-0.123840
	N	-1.467994	-1.277223	-0.264062
	O	0.158679	-0.157546	1.278975
	F	-1.527144	1.001503	-0.217640
	F	1.447437	-0.966940	-0.424623
	F	1.204666	1.182772	-0.241798
TS12(^{3}A′)	C	0.009757	0.986269	0.000000
	C	-0.281724	-1.140105	0.000000
	N	-1.467789	-1.555660	0.000000
	O	-1.175446	1.173222	0.000000
	F	0.789255	-1.903027	0.000000
	F	0.789255	1.086339	1.074997
	F	0.789255	1.086339	-1.074997
TS13(^{3}A′)	C	0.326075	-0.807572	0.000000
	F	0.506488	-1.512546	1.084160
	C	0.179854	0.516436	0.000000
	N	-0.105646	1.714677	0.000000
	O	0.506488	2.775162	0.000000
	F	-1.718305	-0.581265	0.000000
	F	0.506488	-1.512546	-1.084160
TS14(^{3}A)	C	-0.638773	0.128809	-0.052585
	F	-1.546009	-0.540254	-0.703829
	C	0.736992	0.178917	-0.492591
	N	1.244167	-1.099674	-0.129476
	O	0.268763	-1.317970	0.789179
	F	1.449621	1.252271	-0.146001
	F	-1.175677	1.109664	0.612492
TS15(^{3}A)	C	-0.570751	0.068645	-0.006896
	F	-1.521869	-0.337924	-0.861323
	C	0.865090	-0.064739	-0.488664
	N	1.037754	-1.316442	-0.005040
	O	-0.298852	-0.887392	0.985075
	F	1.728362	0.899577	-0.173513
	F	-0.944215	1.248435	0.493507
1-TS1(^{1}A′)	C	-0.137550	0.391352	0.000000

	C	-0.593820	-1.436927	0.000000
	N	-1.106750	-2.479365	0.000000
	O	0.835210	-0.433123	0.000000
	F	1.793617	1.147821	0.000000
	F	-0.593820	0.931311	1.072539
	F	-0.593820	0.931311	-1.072539
1-TS2(^{1}A)	C	0.693898	-0.022509	-0.027991
	C	-0.611745	0.429647	-0.650262
	N	-1.670529	0.650824	0.026982
	O	-2.309219	-0.473924	-0.052868
	F	0.529416	-0.830778	1.020271
	F	1.293725	1.114937	0.370448
	F	1.474030	-0.640516	-0.912543
1-TS3(^{1}A′)	C	-0.069844	0.553500	0.000000
	C	0.165883	-1.054452	0.000000
	N	1.424834	-1.274790	0.000000
	O	-0.774957	-1.847519	0.000000
	F	1.066534	1.263842	0.000000
	F	-0.774957	0.851934	1.085123
	F	-0.774957	0.851934	-1.085123
1-TS4(^{1}A)	C	0.750137	0.117219	-0.126501
	C	-0.693557	-0.046229	-0.079741
	N	-1.505331	-0.358153	-1.045837
	O	-1.601319	0.872920	0.130817
	F	1.526484	-0.744400	-0.646449
	F	-0.315572	-0.969675	1.214827
	F	1.345577	1.169384	0.266262
1-TS5(^{1}A′)	C	-0.537689	0.137490	0.000000
	C	1.556167	1.076559	0.000000
	N	1.120070	-0.103728	0.000000
	O	1.451741	-1.310589	0.000000
	F	-0.946862	1.396238	0.000000
	F	-0.946862	-0.479979	1.081778
	F	-0.946862	-0.479979	-1.081778
1-TS6(^{1}A)	C	-0.586041	-0.008632	-0.012100
	C	1.928635	-0.626800	0.180431
	N	0.458870	-0.811781	-0.545887
	O	1.938643	0.486410	-0.153086
	F	-1.657595	-0.792854	-0.257368
	F	-0.794150	1.179251	-0.608637
	F	-0.523454	0.236245	1.314440
1-TS7(^{1}A)	C	0.585893	-0.006019	-0.004421
	O	-0.572638	0.084954	0.780887
	C	-1.855719	0.675007	-0.024811

	N	-2.002489	-0.540959	-0.011429
	F	0.765340	1.081202	-0.748051
	F	0.574949	-1.071940	-0.795515
	F	1.572765	-0.110023	0.877821
1-TS8(^{1}A)	C	0.670275	-0.046107	0.074463
	C	-0.814983	-0.036049	-0.188089
	N	0.052540	-0.583808	1.192785
	O	-1.368191	-1.132682	-0.090535
	F	1.208802	1.183318	0.231990
	F	-1.461250	1.101881	-0.319813
	F	1.524226	-0.769527	-0.683672
1-TS9(^{1}A)	C	1.202882	-0.360306	-0.029561
	C	-1.034692	-0.036032	-0.113273
	N	0.361203	-1.189069	-0.050977
	O	-1.657493	-0.038472	-1.096636
	F	2.364457	0.116985	-0.011282
	F	-1.430594	-0.065242	1.137127
	F	0.146402	1.171511	-0.016185
1-TS10(^{1}A)	C	0.970595	0.109044	-0.299799
	C	-1.004542	0.069727	0.036672
	N	-0.910686	-0.356095	1.251630
	O	-1.384296	-1.101795	-0.310558
	F	1.732529	0.950379	0.337742
	F	-1.364799	1.208741	-0.509721
	F	1.593699	-1.021965	-0.350041

Table S3: The harmonic vibrational frequencies of all species found on PESs at the B3LYP/6-311+G(d) level. The values in parentheses and *italics* are experimental data. ″*i*″ stands for imaginary frequency.

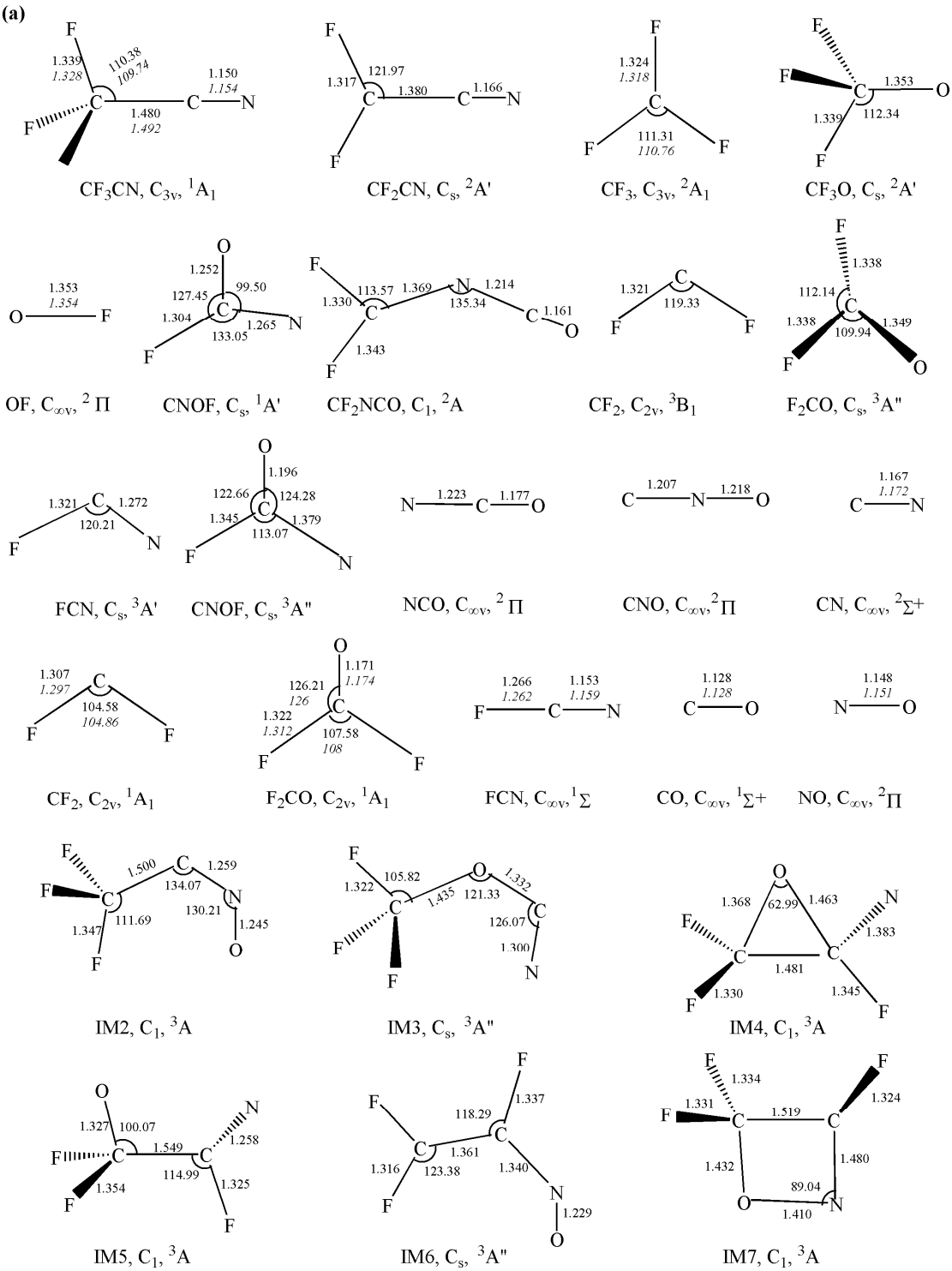
Species	Frequencies(cm^{-1})
$CF_3CN(^1A_1)$	193(*196*), 462(*463*), 518(*522*), 622(*618*), 802(*802*), 1167(*1214*), 1219(*1227*), 2385(*2275*)
$CF_2CN(^2A')$	151, 196, 384, 485, 595, 786, 1296, 1408, 2189
$OF(^2\Pi)$	1092(*1029*)
$CF_3(^2A_1)$	503(*509*), 691(*701*), 1062(*1089*), 1222(*1260*)
$NCO(^2\Pi)$	502, 585, 1297, 1996
$CNO(^2\Pi)$	315, 401, 1196, 1935
$CF_3O(^2A')$	259, 403, 569, 586, 609, 883, 1135, 1174, 1238
$CN(^2\Sigma^+)$	2147(*2069*)
$CF_2NCO(^2A)$	75, 139, 448, 488, 557, 604, 663, 864, 1154, 1207, 1517, 2367
$CF_2(^3B_1)$	509(*667*), 1119(*1114*), 1279(*1225*)
$CNOF(^3A'')$	430, 586, 654, 880, 1182, 1686
$F_2CO(^3A'')$	339, 463, 668, 1036, 1127, 1206
$FCN(^3A')$	559, 1081, 1606
$CF_3C(^2A'')$	262, 294, 519, 520, 573, 820, 1089, 1120, 1252
$NO(^2\Pi)$	1980(*1904*)
$CF_3N(^1A')$	269, 319, 533, 563, 593, 875, 970, 1134, 1347
$CO(^1\Sigma^+)$	2213(*2170*)
$CF_2(^1A_1)$	667, 1087, 1210
$CNOF(^1A')$	375, 525, 646, 960, 1479, 1748
$F_2CO(^1A_1)$	576(*584*), 615(*626*), 772(*774*), 956(*965*), 1202(*1249*), 1974(*1928*)
$FCN(^1\Sigma)$	486(*451*), 1086(*1060*), 2413(*2317*)
IM1($CF_3C(O)N$)($^3A''$)	25, 220, 229, 353, 419, 502, 560, 605, 688, 771, 1094, 1143, 1188, 1269, 1546
IM2(CF_3CNO)(^3A)	3, 152, 226, 325, 444, 526, 539, 585, 728, 814, 1135, 1140, 1147, 1274, 1693
IM3 (CF_3OCN)($^3A''$)	79, 184, 330, 359, 512, 529, 554, 685, 745, 815, 1004, 1130, 1252, 1266, 1399
IM4($F_2C(O)CNF$)(^3A)	188, 211, 300, 426, 488, 514, 545, 653, 667, 786, 1014, 1054, 1208, 1223, 1418
IM5(F_2COCNF)(^3A)	51, 214, 225, 347, 379, 496, 559, 602, 660, 791, 1019, 1110, 1149, 1239, 1635
IM6($F_2CC(F)NO$)($^3A''$)	103, 166, 274, 289, 330, 427, 488, 527, 613, 765, 1107, 1262, 1329, 1535, 1636

IM7(F_2CONCF)(^3A)	124, 200, 330, 420, 473, 545, 620, 736, 877, 937, 998, 1098, 1190, 1220, 1365
1-IM1($CF_3C(O)N$)($^1A'$)	42, 191, 206, 347, 434, 487, 551, 588, 667, 784, 1172, 1191, 1209, 1335, 1815
1-IM2($FOCF_2CN$)($^1A'$)	127, 154, 196, 278, 464, 482, 513, 608, 611, 842, 932, 1115, 1137, 1219, 2381
1-IM3(CF_3OCN) ($^1A'$)	63, 154, 395, 402, 485, 501, 571, 603, 707, 851, 1110, 1150, 1218, 1282, 2383
1-IM4(CF_3CNO)(^1A)	6, 25, 398, 400, 454, 534, 536, 581, 583, 770, 1128, 1130, 1132, 1509, 2456
1-IM5(CF_3NCO)($^1A'$)	30, 124, 405, 414, 531, 581, 585, 617, 695, 825, 1133, 1141, 1194, 1506, 2369
1-IM6($F_2C(N)COF$)(^1A)	211, 238, 344, 447, 477, 576, 611, 656, 685, 802, 1000, 1119, 1257, 1361, 1578
1-IM7($CF_3NC(O)$)(^1A)	56, 244, 264, 389, 436, 531, 587, 645, 721, 781, 891, 1159, 1197, 1214, 1505
1-IM8(CF_3ONC)($^1A'$)	82, 125, 265, 319, 427, 429, 566, 597, 691, 854, 1021, 1129, 1220, 1282, 2189
1-IM9(F_2CNCOF)(^1A)	44, 146, 147, 436, 551, 593, 655, 718, 779, 880, 1002, 1232, 1292, 1866, 1903
TS1($^3A''$)	682*i*, 66, 94, 151, 182, 228, 233, 375, 494, 571, 591, 793, 1306, 1352, 2274
TS1′($^3A'$)	681*i*, 68, 69, 118, 168, 201, 238, 377, 494, 572, 589, 793, 1297, 1352, 2276
TS2($^3A''$)	374*i*, 57, 155, 199, 269, 410, 473, 529, 579, 628, 801, 1169, 1178, 1200, 2200
TS3($^3A''$)	353*i*, 10, 164, 165, 292, 362, 500, 528, 529, 698, 1006, 1211, 1245, 1263, 1754
TS4(^3A)	686*i*, 10, 96, 214, 298, 466, 495, 520, 621, 634, 794, 1142, 1163, 1192, 2019
TS5(^3A)	233*i*, 10, 70, 130, 154, 307, 503, 508, 667, 791, 991, 1172, 1190, 1208, 1808
TS6(^3A)	1596*i*, 89, 91, 138, 149, 255, 352, 378, 446, 472, 512, 834, 1372, 1385, 2159
TS7($^3A'$)	710*i*, 86, 205, 225, 313, 340, 392, 455, 624, 641, 791, 1133, 1327, 1362, 1793
TS8 ($^3A''$)	634*i*, 41, 139, 226, 269, 509, 521, 547, 729, 863, 981, 1095, 1283, 1298, 1633
TS9(^3A)	266*i*, 90, 196, 254, 317, 376, 462, 568, 634, 684, 732, 1037, 1339, 1425, 1469
TS10(^3A)	377*i*, 84, 156, 195, 281, 357, 441, 562, 638, 680, 814, 1089, 1267, 1278, 1546
TS11(^3A)	445*i*, 174, 206, 329, 410, 460, 523, 556, 644, 798, 1013, 1131, 1173, 1284, 1382

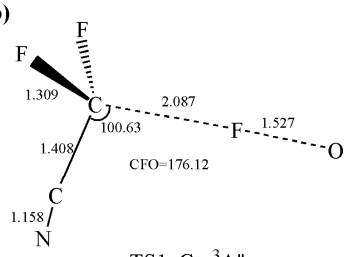
TS12(^{3}A′)	337*i*, 32, 120, 127, 236, 364, 471, 564, 585, 591, 899, 1073, 1161, 1639, 1734
TS13(^{3}A′)	313*i*, 21, 108, 153, 258, 339, 354, 464, 517, 567, 787, 1228, 1298, 1562, 2017
TS14(^{3}A)	595*i*, 150, 216, 272, 380, 483, 547, 580, 727, 781, 1029, 1104, 1195, 1308, 1447
TS15(^{3}A)	1002*i*, 165, 208, 346, 412, 498, 561, 605, 712, 845, 1022, 1083, 1145, 1207, 1337
1-TS1(^{1}A′)	980*i*, 122, 123, 218, 234, 274, 370, 439, 521, 557, 583, 946, 1380, 1582, 2192
1-TS2(^{1}A)	714*i*, 71, 144, 227, 352, 431, 536, 566, 582, 795, 1101, 1134, 1176, 1201, 1466
1-TS3(^{1}A′)	1067*i*, 21, 186, 242, 332, 430, 505, 577, 693, 745, 1038, 1185, 1196, 1276, 1546
1-TS4(^{1}A)	485*i*, 138, 197, 282, 303, 398, 444, 554, 594, 655, 808, 1245, 1380, 1439, 1602
1-TS5(^{1}A′)	378*i*, 40, 252, 279, 318, 466, 516, 612, 618, 737, 997, 1089, 1267, 1272, 1679
1-TS6(^{1}A)	405*i*, 76, 164, 204, 372, 396, 455, 564, 588, 635, 856, 1119, 1128, 1203, 1865
1-TS7(^{1}A)	453*i*, 56, 208, 248, 404, 421, 536, 603, 656, 711, 884, 1121, 1220, 1244, 1778
1-TS8(^{1}A)	452*i*, 107, 223, 333, 373, 507, 526, 585, 652, 773, 884, 1094, 1156, 1375, 1576
1-TS9(^{1}A)	671*i*, 108, 242, 307, 327, 442, 471, 545, 561, 665, 697, 1042, 1110, 1984, 2190
1-TS10(^{1}A)	394*i*, 80, 132, 164, 293, 353, 430, 522, 578, 664, 918, 1190, 1241, 1337, 1658

Fig. S1: The B3LYP/6-311+G(d) optimized geometries (length in Å and angle in degree) for other species on triplet and singlet PESs. (a). Geometries of reactant, products and minima; (b). Geometries of the transition states on triplet PES; (c). Geometries of the transition states on singlet PES. The values in *italics* are experimental data.

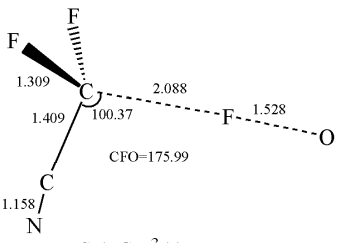
(a)



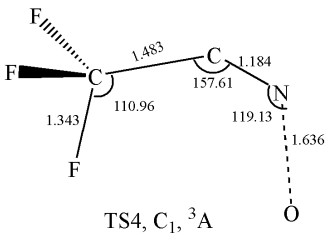
(b)



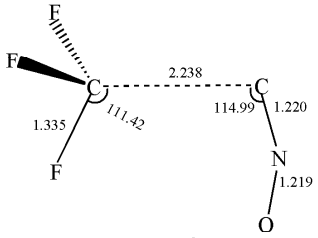
TS1, C_s, ^{3}A"



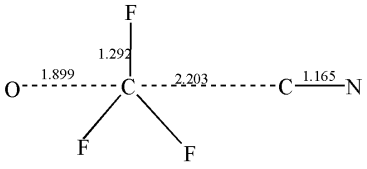
TS1', C_s, ^{3}A'



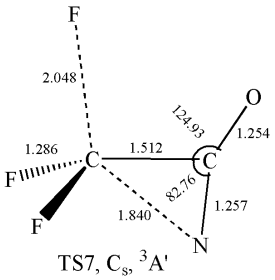
TS4, C_1, ^{3}A



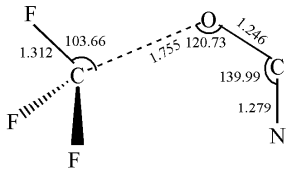
TS5, C_1, ^{3}A



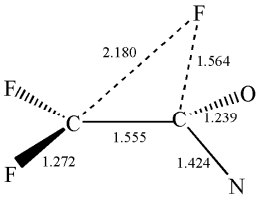
TS6, C_1, ^{3}A



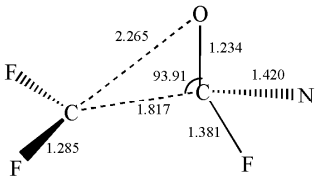
TS7, C_s, ^{3}A'



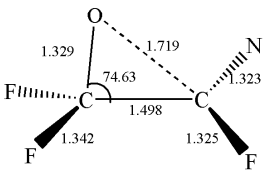
TS8, C_s, ^{3}A"



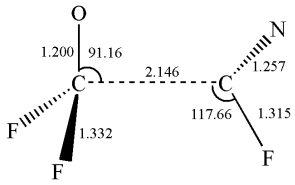
TS9, C_1, ^{3}A



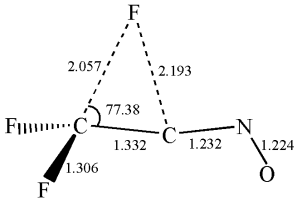
TS10, C_1, ^{3}A



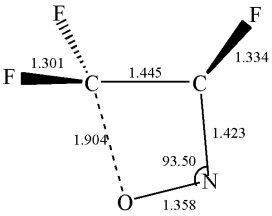
TS11 C_1, ^{3}A



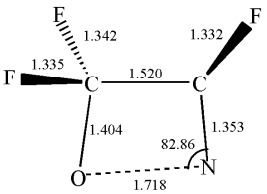
TS12, C_s, ^{3}A'



TS13, C_s, ^{3}A'

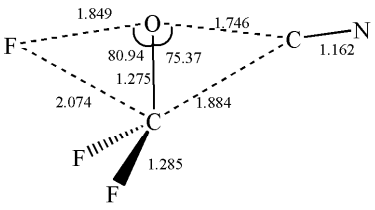


TS14, C_1, ^{3}A

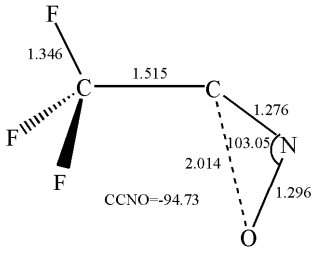


TS15, C_1, ^{3}A

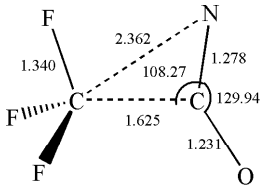
(c)



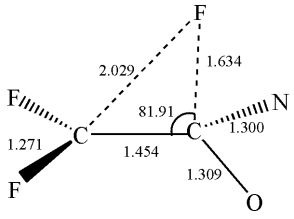
1-TS1, C_s, $^1A'$



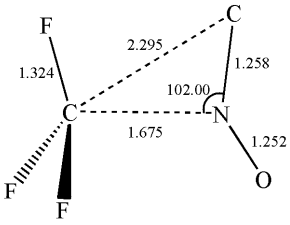
1-TS2, C_1, ^1A



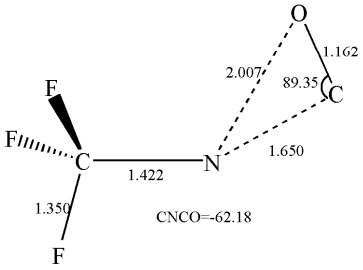
1-TS3, C_s, $^1A'$



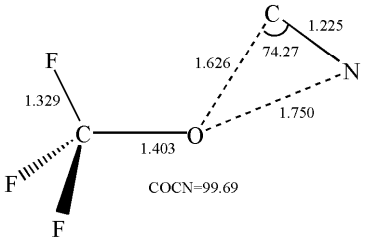
1-TS4, C_1, ^1A



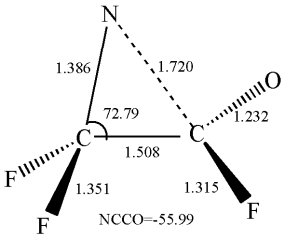
1-TS5, C_s, $^1A'$



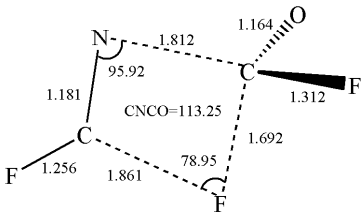
1-TS6, C_1, ^1A



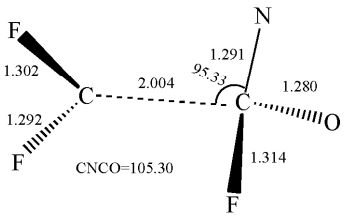
1-TS7, C_1, ^1A



1-TS8, C_1, ^1A



1-TS9, C_1, ^1A



1-TS10, C_1, ^1A