

Removal of the potent greenhouse gas NF_3 by reactions with the atmospheric oxidants $\text{O}(^1\text{D})$, OH and O_3 .

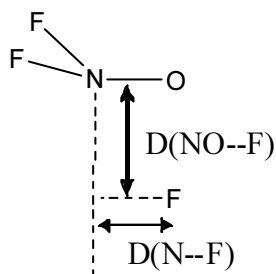
- Supporting Information -

T. J. Dillon, Luc Vereecken, A. Horowitz, V. Khamaganov and J. N. Crowley

A. TS12 : $\text{ONF}_3 \leftrightarrow \text{FONF}_2$ isomerisation

A key isomerisation on the $[\text{ONF}_3]$ potential energy surface (PES) is the 1,2-F-migration, connecting the ONF_3 and FONF_2 isomers. It was proposed by Antoniotti and Grandinetti (2002) as the source of the OF radicals observed earlier by Sorokin (1998). However, as discussed in the main paper, the transition state they proposed was characterized by us as the umbrella inversion of the nitrogen centre in FONF_2 , and hence does not connect to the ONF_3 global energetic minimum. Despite numerous attempts at finding the true isomerisation transition state, however, we were likewise unable to locate a saddle point corresponding to the 1,2-F-shift.

To elucidate the matter, we characterized the relevant section of the PES, i.e. the migration pathways of a F atom between the nitrogen and oxygen centre. To this end, we performed a large set of constrained geometry optimizations, fixing the position of the F atom relative to the O–N atom bond, but leaving all other degrees of freedom unconstrained. The resulting two-dimensional section of the PES yields the minimum-energy PES for F-migration between the ONF_3 and FONF_2 energetic minima. The constrained coordinates are the perpendicular distance of the F atom from the N–O bond axis, $y = D(\text{NO--F})$, and the position of the F-atom along that axis, $x = D(\text{N--F})$, where we set N equal to position 0.0, and O along the positive side of the axis.



In this coordinate system, the F_3NO minimum is located approximately at $x = -0.6 \text{ \AA}$, $y = 1.1 \text{ \AA}$; while *trans*- F_2NOF is located at $x = 1.7 \text{ \AA}$, $y = 1.4 \text{ \AA}$. At small y values, i.e. with small $D(\text{NO--F})$, the F-atom is forced into the electron cloud along the N–O bond, causing high

potential energy values. At large separation, i.e. at large negative or positive x-values and/or at large y values, the geometries essentially correspond to the $F_2NO + F$ dissociation limit. We found that the energetically most favourable F-migration always involved a symmetric position of the two non-migrating F-atoms on the N-atom, one on each side of the N–O–F plane, such that an F-migration would preserve the plane of symmetry. Figure SI-1 shows the resulting potential energy surface cross-section (without ZPE-corrections), with energies in kcal mol^{-1} relative to the F_3NO energetic minimum.

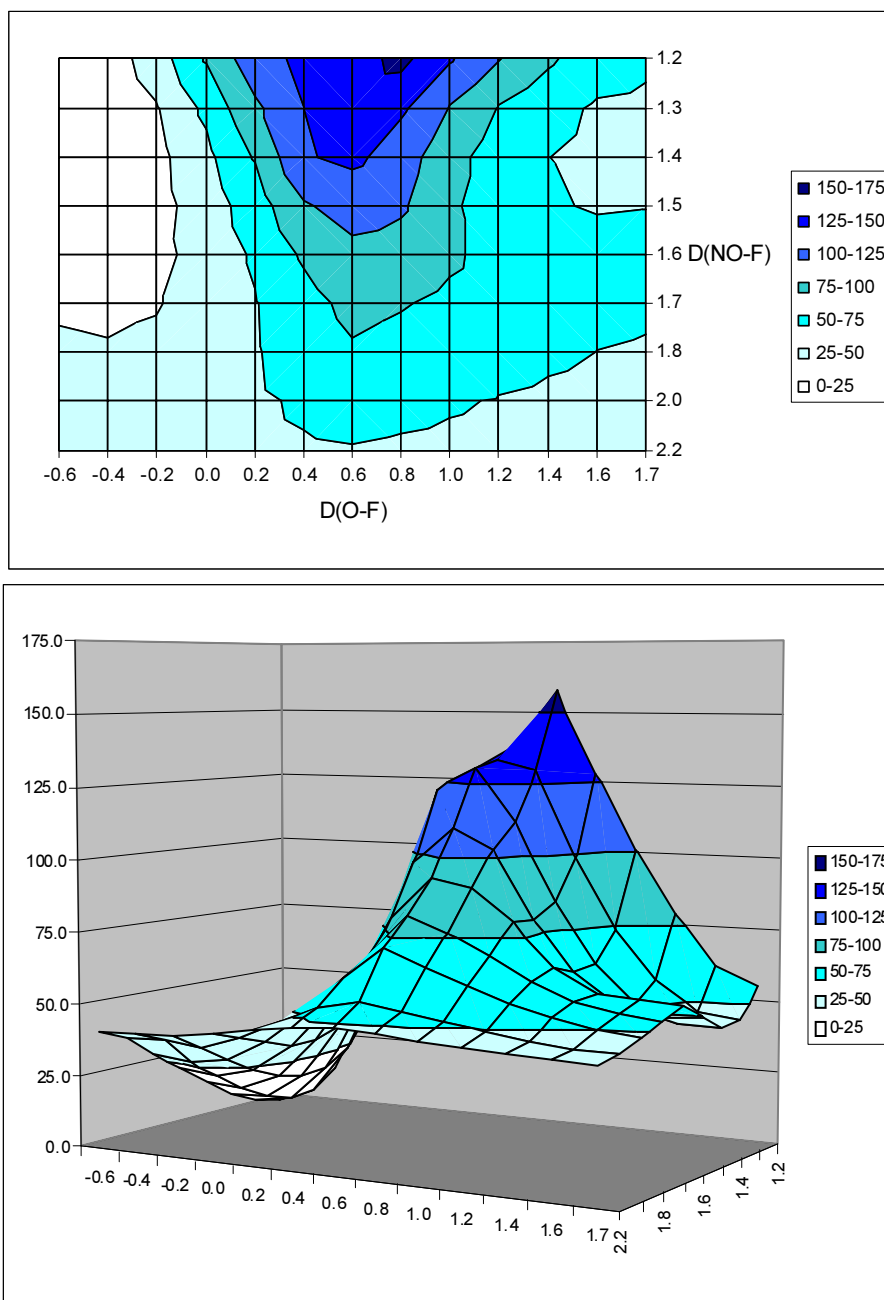


Fig. SI-1: Potential energy surface for the migration of an F-atom (kcal/mol)

This potential energy surface differs strongly from the shape one expects to see for a regular isomerisation (an example of which is shown in Fig SI-2 for a 1,2-H-migration) At the position where one would expect to see a saddle point, roughly at $D(\text{NO-F}) \sim 1.6 \text{ \AA}$ and $D(\text{O-F}) \sim 0.6 \text{ \AA}$, the very low dissociation energy to $\text{F}_2\text{NO} + \text{F}$ lowers the energy at larger F-separation, to the point that the PES shows two convex energy cross-sections: one along the traditional reaction coordinate for F-migration, and another dissociative energy profile perpendicular to it. Hence, no traditional saddle point exists. F-atoms migrating between the N and O centres, then, are energetically and entropically guided towards dissociation. While this does not strictly preclude isomerisation, such a 1-2-F-shift would require a dynamical trajectory that does not follow the lowest-energy path, and hence has a negligible probability compared to the much more favourable dissociation. From this, we conclude that the $\text{ONF}_3 \leftrightarrow \text{FONF}_2$ isomerisation can not carry a significant reaction flux.

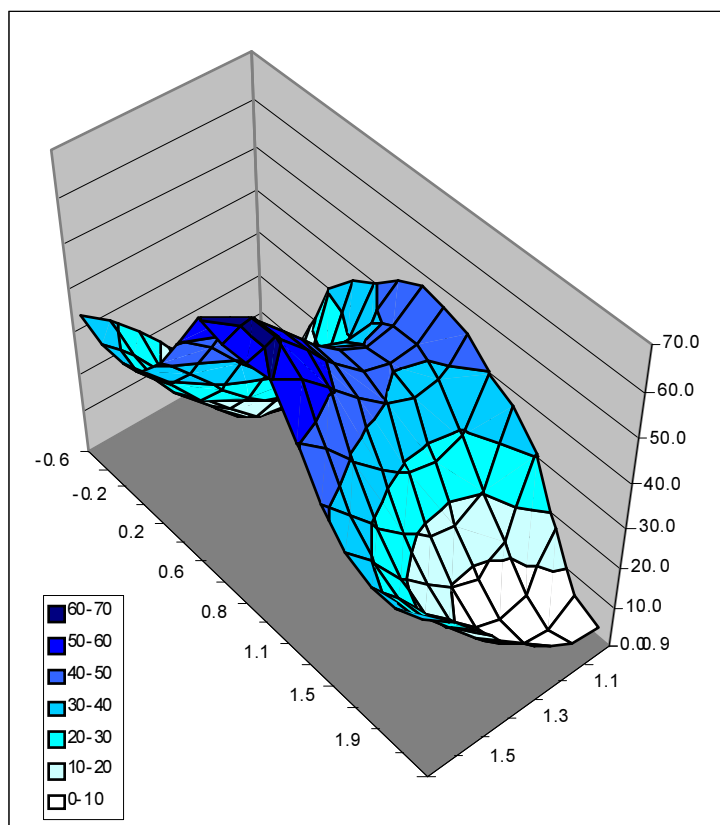


Fig. SI-2: Traditional 1,2-migration showing a saddle point on the PES.

B. Quantum chemical data : [NF3O] PES

F2

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E(RM052X+HF-M052X/6-311G(d)) (Hartree): -199.52871051
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -199.31211286
E(CCSD/Aug-CC-pVTZ) (Hartree): -199.29331651
E(MP2/Aug-CC-pVTZ) (Hartree): -199.29013258
E(MP3/Aug-CC-pVTZ) (Hartree): -199.28824501
E(RHF/Aug-CC-pVTZ) (Hartree): -198.75941981
Point group : D*H
Electronic state : 1-SGG
Cartesian coordinates (Angs):
F 0.000000 0.000000 0.683995
F 0.000000 0.000000 -0.683995
Rotational constants (GHz): 0.0000000 28.4292083 28.4292083
Vibrational harmonic frequencies (cm-1):
1142.1988 (SGG)
Zero-point correction (Hartree): 0.002602

F2NOF.cis

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -429.25864308
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.74253268
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.69061181
E(MP2/Aug-CC-pVTZ) (Hartree): -428.69050821
E(MP3/Aug-CC-pVTZ) (Hartree): -428.67887550
E(RHF/Aug-CC-pVTZ) (Hartree): -427.45565269
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.541889 0.000124 0.525015
F 0.843563 -1.060528 -0.276818
F 0.841210 1.061979 -0.275516
O -0.750719 -0.001642 0.737549
F -1.438937 -0.000088 -0.511610
Rotational constants (GHz): 7.9950600 5.0616800 4.1349500
Vibrational harmonic frequencies (cm-1):
215.1369 304.9891 559.8684
594.4158 814.6842 855.9949
987.4420 1032.6566 1119.4640
Zero-point correction (Hartree): 0.014773

F2NOF.trans

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -429.24814561
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.73364673
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.68305320
E(MP2/Aug-CC-pVTZ) (Hartree): -428.68110123
E(MP3/Aug-CC-pVTZ) (Hartree): -428.67179830
E(RHF/Aug-CC-pVTZ) (Hartree): -427.45077203
Electronic state : 1-A
Cartesian coordinates (Angs):
N -0.325478 0.000185 -0.372684
F -1.098709 -1.056755 0.009645
F -1.096490 1.057891 0.010246
O 0.684998 -0.001271 0.554595
F 1.839461 -0.000151 -0.222999
Rotational constants (GHz): 10.0495400 3.9837900 3.1287800
Vibrational harmonic frequencies (cm-1):
93.4142 431.3536 515.0344
519.2761 663.7778 900.7150
1019.8733 1078.6624 1140.8483
Zero-point correction (Hartree): 0.014496

F

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -99.74403582
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -99.62782704
E(CCSD/Aug-CC-pVTZ) (Hartree): -99.62345241
E(MP2/Aug-CC-pVTZ) (Hartree): -99.61210618
E(MP3/Aug-CC-pVTZ) (Hartree): -99.62216846
E(PMP2/Aug-CC-pVTZ) (Hartree): -99.61371825
E(PMP3/Aug-CC-pVTZ) (Hartree): -99.62300590

E(PUHF/Aug-CC-pVTZ) (Hartree): -99.41002320
E(UHF/Aug-CC-pVTZ) (Hartree): -99.40687935
Point group : OH
Cartesian coordinates (Angs):
F 0.000000 0.000000 0.000000
Zero-point correction (Hartree): 0.000000

FNOF

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -329.41791481
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -329.01444620
E(CCSD/Aug-CC-pVTZ) (Hartree): -328.97517376
E(MP2/Aug-CC-pVTZ) (Hartree): -328.96460312
E(MP3/Aug-CC-pVTZ) (Hartree): -328.96274797
E(PMP2/Aug-CC-pVTZ) (Hartree): -328.96769265
E(PMP3/Aug-CC-pVTZ) (Hartree): -328.96459244
E(PUHF/Aug-CC-pVTZ) (Hartree): -328.03592873
E(UHF/Aug-CC-pVTZ) (Hartree): -328.03112862
Electronic state : 2-A
Cartesian coordinates (Angs):
N -0.467393 0.557214 0.000388
F -1.630590 -0.111666 -0.000321
O 0.400058 -0.497461 0.000375
F 1.638511 0.120465 -0.000314
Rotational constants (GHz): 57.3177400 4.7170300 4.3583500
Vibrational harmonic frequencies (cm-1):
100.8132 394.0223 579.5963
1041.9431 1116.7994 1194.4603
Zero-point correction (Hartree): 0.010087

FNO

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -229.73628257
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -229.44932036
E(CCSD/Aug-CC-pVTZ) (Hartree): -229.41522649
E(MP2/Aug-CC-pVTZ) (Hartree): -229.42354957
E(MP3/Aug-CC-pVTZ) (Hartree): -229.40460930
E(RHF/Aug-CC-pVTZ) (Hartree): -228.71458404
Point group : CS
Electronic state : 1-A'
Cartesian coordinates (Angs):
N 0.000000 0.548617 0.000000
F -0.941653 -0.572852 0.000000
O 1.059359 0.164418 0.000000
Rotational constants (GHz): 98.1245100 12.4777200 11.0700300
Vibrational harmonic frequencies (cm-1):
602.7788 (A') 867.0224 (A') 2019.9976 (A')
Zero-point correction (Hartree): 0.007950

NF2F--O

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -429.12903856
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.61887100
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.56851243
E(MP2/Aug-CC-pVTZ) (Hartree): -428.54690333
E(MP3/Aug-CC-pVTZ) (Hartree): -428.54954872
E(RHF/Aug-CC-pVTZ) (Hartree): -427.36254426
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.725577 0.000000 0.469905
F -0.652636 -0.000005 0.815728
F 0.804192 -1.045380 -0.348569
F 0.804187 1.045384 -0.348564
O -1.710092 0.000001 -0.544586
Rotational constants (GHz): 7.5884800 4.5164900 3.9376400
Vibrational harmonic frequencies (cm-1):
114.6648 211.3510 320.6803
507.1244 540.5630 713.5456
841.6801 1080.2493 1153.4139
Zero-point correction (Hartree): 0.012492

NF2F--O triplet, single point calculation on singlet geometry

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.16867180
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.64772753
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.60347858
E(MP2/Aug-CC-pVTZ) (Hartree): -428.58717908
E(MP3/Aug-CC-pVTZ) (Hartree): -428.59111096

E(PMP2/Aug-CC-pVTZ) (Hartree): -428.58940770
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.59250013
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.44169212
E(UHF/Aug-CC-pVTZ) (Hartree): -427.43807729
Electronic state : 3-A
Cartesian coordinates (Angs):
N -0.390943 0.000026 -0.408300
F 0.625873 -0.000491 0.576156
F -1.124866 -1.046551 -0.011671
F -1.124146 1.046994 -0.011381
O 2.168106 0.000031 -0.264981
Rotational constants (GHz): 9.8325200 3.5452300 2.8974500
Vibrational harmonic frequencies (cm-1):
-243.9143 -225.2137 475.8661
507.6272 652.6151 831.6636
895.7663 1066.1087 1147.6096
Zero-point correction (Hartree): 0.012706

NF2F--O triplet

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.21433683
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.69333761
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.65111526
E(MP2/Aug-CC-pVTZ) (Hartree): -428.63427505
E(MP3/Aug-CC-pVTZ) (Hartree): -428.63988876
E(PMP2/Aug-CC-pVTZ) (Hartree): -428.63616385
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.64101401
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.50047052
E(UHF/Aug-CC-pVTZ) (Hartree): -427.49736557
Electronic state : 3-A
Cartesian coordinates (Angs):
N 0.262497 0.000010 -0.244111
F -0.156963 -0.001260 1.046894
F 1.110892 1.055496 -0.268578
F 1.112375 -1.054252 -0.270150
O -2.554278 0.000008 -0.358090
Rotational constants (GHz): 7.3522500 2.8209100 2.5919600
Vibrational harmonic frequencies (cm-1):
47.6395 56.5535 99.3702
534.3438 534.5828 704.9035
1022.1449 1027.7146 1127.6637
Zero-point correction (Hartree): 0.011744

NF2

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -254.30519806
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -253.99247463
E(CCSD/Aug-CC-pVTZ) (Hartree): -253.96548109
E(MP2/Aug-CC-pVTZ) (Hartree): -253.95734430
E(MP3/Aug-CC-pVTZ) (Hartree): -253.95555789
E(PMP2/Aug-CC-pVTZ) (Hartree): -253.96027005
E(PMP3/Aug-CC-pVTZ) (Hartree): -253.95726496
E(PUHF/Aug-CC-pVTZ) (Hartree): -253.27053582
E(UHF/Aug-CC-pVTZ) (Hartree): -253.26591919
Point group : C2V
Electronic state : 2-B1
Cartesian coordinates (Angs):
N 0.000000 0.000000 0.596577
F 0.000000 1.046978 -0.232002
F 0.000000 -1.046978 -0.232002
Rotational constants (GHz): 71.9416600 12.1337500 10.3826100
Vibrational harmonic frequencies (cm-1):
621.2610 1041.9603 1183.0092
Zero-point correction (Hartree): 0.006484

NF2O

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -329.49760098
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -329.08580001
E(CCSD/Aug-CC-pVTZ) (Hartree): -329.04422785
E(MP2/Aug-CC-pVTZ) (Hartree): -329.04101350
E(MP3/Aug-CC-pVTZ) (Hartree): -329.02988785
E(PMP2/Aug-CC-pVTZ) (Hartree): -329.04776967
E(PMP3/Aug-CC-pVTZ) (Hartree): -329.03398296
E(PUHF/Aug-CC-pVTZ) (Hartree): -328.09960008
E(UHF/Aug-CC-pVTZ) (Hartree): -328.09043836
Electronic state : 2-A

Cartesian coordinates (Angs):
N -0.000603 0.170417 0.287812
O -0.003003 1.273956 -0.106060
F -1.088422 -0.634983 -0.064814
F 1.091560 -0.629969 -0.064764
Rotational constants (GHz): 11.7417400 10.8351600 5.8300100
Vibrational harmonic frequencies (cm-1):
490.2780 532.3951 683.5391
837.9813 956.5710 1633.0631
Zero-point correction (Hartree): 0.011696

NF3

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -354.13611028
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -353.71361080
E(CCSD/Aug-CC-pVTZ) (Hartree): -353.67511638
E(MP2/Aug-CC-pVTZ) (Hartree): -353.67451342
E(MP3/Aug-CC-pVTZ) (Hartree): -353.66566844
E(RHF/Aug-CC-pVTZ) (Hartree): -352.68589143
Point group : CS
Electronic state : 1-A'
Cartesian coordinates (Angs):
N 0.338172 0.330159 0.000000
F -0.939368 0.784832 0.000000
F 0.338172 -0.520811 1.055057
F 0.338172 -0.520811 -1.055057
Rotational constants (GHz): 10.9284500 10.9206100 5.9766700
Vibrational harmonic frequencies (cm-1):
535.1475 (A'') 535.8508 (A') 707.2625 (A')
1022.2475 (A'') 1023.3765 (A') 1125.0404 (A')
Zero-point correction (Hartree): 0.011274

NF3O

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -429.31990448
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.79718475
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.74160543
E(MP2/Aug-CC-pVTZ) (Hartree): -428.76102447
E(MP3/Aug-CC-pVTZ) (Hartree): -428.72923863
E(RHF/Aug-CC-pVTZ) (Hartree): -427.49472946
Point group : CS
Electronic state : 1-A'
Cartesian coordinates (Angs):
N 0.063327 0.181075 0.000000
F -1.327271 -0.012220 0.000000
F 0.442390 -0.628579 1.081606
F 0.442390 -0.628579 -1.081606
O 0.442390 1.269611 0.000000
Rotational constants (GHz): 5.9245400 5.9227900 5.6830200
Vibrational harmonic frequencies (cm-1):
440.0665 (A') 441.8249 (A'') 604.0390 (A'')
604.9817 (A') 610.3034 (A') 858.1856 (A')
991.4868 (A'') 994.4938 (A') 1818.5440 (A')
Zero-point correction (Hartree): 0.016776

NO

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -129.90615892
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -129.72549812
E(CCSD/Aug-CC-pVTZ) (Hartree): -129.70650051
E(MP2/Aug-CC-pVTZ) (Hartree): -129.70248692
E(MP3/Aug-CC-pVTZ) (Hartree): -129.69857676
E(PMP2/Aug-CC-pVTZ) (Hartree): -129.70669919
E(PMP3/Aug-CC-pVTZ) (Hartree): -129.70117402
E(PUHF/Aug-CC-pVTZ) (Hartree): -129.30587777
E(UHF/Aug-CC-pVTZ) (Hartree): -129.30009789
Point group : C*v
Cartesian coordinates (Angs):
N 0.000000 0.000000 -0.606204
O 0.000000 0.000000 0.530429
Rotational constants (GHz): 0.0000000 52.3918563 52.3918563
Vibrational harmonic frequencies (cm-1):
2109.9298 (SG)
Zero-point correction (Hartree): 0.004807

Old

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -74.97444856

E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -74.89795002
E(CCSD/Aug-CC-pVTZ) (Hartree): -74.88723748
E(MP2/Aug-CC-pVTZ) (Hartree): -74.85397838
E(MP3/Aug-CC-pVTZ) (Hartree): -74.87273635
E(RHF/Aug-CC-pVTZ) (Hartree): -74.68550330
Point group : OH
Cartesian coordinates (Angs):
O 0.000000 0.000000 0.000000
Zero-point correction (Hartree): 0.000000

O3P

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -75.07642524
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -74.97895232
E(CCSD/Aug-CC-pVTZ) (Hartree): -74.97552237
E(MP2/Aug-CC-pVTZ) (Hartree): -74.95929413
E(MP3/Aug-CC-pVTZ) (Hartree): -74.97376768
E(PMP2/Aug-CC-pVTZ) (Hartree): -74.96116267
E(PMP3/Aug-CC-pVTZ) (Hartree): -74.97487266
E(PUHF/Aug-CC-pVTZ) (Hartree): -74.81606234
E(UHF/Aug-CC-pVTZ) (Hartree): -74.81298221
Point group : OH
Cartesian coordinates (Angs):
O 0.000000 0.000000 0.000000
Zero-point correction (Hartree): 0.000000

OF

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -174.89297393
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -174.68434009
E(CCSD/Aug-CC-pVTZ) (Hartree): -174.66695761
E(MP2/Aug-CC-pVTZ) (Hartree): -174.65341831
E(MP3/Aug-CC-pVTZ) (Hartree): -174.65826525
E(PMP2/Aug-CC-pVTZ) (Hartree): -174.65655860
E(PMP3/Aug-CC-pVTZ) (Hartree): -174.66025146
E(PUHF/Aug-CC-pVTZ) (Hartree): -174.20086459
E(UHF/Aug-CC-pVTZ) (Hartree): -174.19625016
Point group : C*v
Cartesian coordinates (Angs):
O 0.000000 0.000000 -0.703693
F 0.000000 0.000000 0.625505
Rotational constants (GHz): 0.0000000 32.9400145 32.9400145
Vibrational harmonic frequencies (cm-1):
1178.2151 (SG)
Zero-point correction (Hartree): 0.002684

TS_F2NO_F_diss.t

E(UM052X+HF-M/6-311G(d)) (Hartree): -429.22545536
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.70983428
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.65604214
E(MP2/Aug-CC-pVTZ) (Hartree): -428.61713614
E(MP3/Aug-CC-pVTZ) (Hartree): -428.62189987
E(PMP2/Aug-CC-pVTZ) (Hartree): -428.66825916
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.66966972
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.50801487
E(UHF/Aug-CC-pVTZ) (Hartree): -427.45495132
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.308610 0.000000 -0.207700
F 1.137875 1.076831 -0.061630
F 1.137876 -1.076831 -0.061630
O -0.602291 0.000000 0.615626
F -1.980412 0.000000 -0.262418
Rotational constants (GHz): 9.6861300 3.6368400 2.8894500
Vibrational harmonic frequencies (cm-1):
-1025.0691 159.0053 313.1903
527.0594 570.3455 706.8439
926.0522 1064.5954 1208.4926
Zero-point correction (Hartree): 0.012474

TS_F2NOF_inplane

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.21290556
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.69709662
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.64336389
E(MP2/Aug-CC-pVTZ) (Hartree): -428.61775034
E(MP3/Aug-CC-pVTZ) (Hartree): -428.61463721

E(PMP2/Aug-CC-pVTZ) (Hartree): -428.66217422
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.65670240
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.48178562
E(RHF/Aug-CC-pVTZ) (Hartree): -427.38379756
E(UHF/Aug-CC-pVTZ) (Hartree): -427.43611816
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.353190 0.000001 0.058950
F 1.099582 1.088931 -0.148506
F 1.099619 -1.088917 -0.148504
O -0.633141 -0.000001 0.695783
F -1.911112 -0.000013 -0.367315
Rotational constants (GHz): 8.9858200 3.7525200 2.9984700
Vibrational harmonic frequencies (cm-1):
-438.3963 207.3854 331.7575
542.1869 597.1110 615.3021
930.2623 1230.1045 1654.3843
Zero-point correction (Hartree): 0.013916

TS_F2NOF_introt

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -429.23518830
E(CCS(D)T)/Aug-CC-pVTZ) (Hartree): -428.72197987
E(CCS(D)Aug-CC-pVTZ) (Hartree): -428.67010095
E(MP2/Aug-CC-pVTZ) (Hartree): -428.66853323
E(MP3/Aug-CC-pVTZ) (Hartree): -428.65815046
E(PMP2/Aug-CC-pVTZ) (Hartree): -428.66853323
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.65815046
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.43390810
E(RHF/Aug-CC-pVTZ) (Hartree): -427.43362307
E(UHF/Aug-CC-pVTZ) (Hartree): -427.43390810
Electronic state : 1-A
Cartesian coordinates (Angs):
N -0.534947 0.010940 0.516995
F -0.322681 1.218769 -0.040438
F -1.469480 -0.539747 -0.303667
O 0.615737 -0.803624 0.159130
F 1.660909 0.026803 -0.199451
Rotational constants (GHz): 9.9535100 4.5055000 3.3787000
Vibrational harmonic frequencies (cm-1):
-201.6816 363.7440 468.0319
566.5565 707.2629 843.6426
1037.6479 1092.3714 1121.4986
Zero-point correction (Hartree): 0.014126

TS_FNOF_introt

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -329.41677294
E(CCS(D)T)/Aug-CC-pVTZ) (Hartree): -329.01533096
E(CCS(D)Aug-CC-pVTZ) (Hartree): -328.97429047
E(MP2/Aug-CC-pVTZ) (Hartree): -328.94341238
E(MP3/Aug-CC-pVTZ) (Hartree): -328.94733804
E(PMP2/Aug-CC-pVTZ) (Hartree): -328.96184034
E(PMP3/Aug-CC-pVTZ) (Hartree): -328.96083491
E(PUHF/Aug-CC-pVTZ) (Hartree): -328.05065363
E(UHF/Aug-CC-pVTZ) (Hartree): -328.02936777
Electronic state : 2-A
Cartesian coordinates (Angs):
N 0.482380 -0.466465 0.324494
F 1.586545 0.073393 -0.245585
O -0.399936 0.488159 0.239647
F -1.606230 -0.144506 -0.219819
Rotational constants (GHz): 42.7927200 4.7183900 4.5938900
Vibrational harmonic frequencies (cm-1):
-227.8637 319.6645 493.1000
684.3756 998.7852 1129.2547
Zero-point correction (Hartree): 0.008259

TS_Fabstraction

E(UM052X+HF-M/6-311G(d)) (Hartree): -429.12675839
E(CCS(D)T)/Aug-CC-pVTZ) (Hartree): -428.61892664
E(CCS(D)Aug-CC-pVTZ) (Hartree): -428.56024515
E(MP2/Aug-CC-pVTZ) (Hartree): -428.51313407
E(MP3/Aug-CC-pVTZ) (Hartree): -428.51488928
E(PMP2/Aug-CC-pVTZ) (Hartree): -428.57133959
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.56909148

E(PUHF/Aug-CC-pVTZ) (Hartree): -427.39762204
E(RHF/Aug-CC-pVTZ) (Hartree): -427.32857339
E(UHF/Aug-CC-pVTZ) (Hartree): -427.33769088
Electronic state : 1-A
Cartesian coordinates (Angs):
N -0.736285 -0.000001 0.508781
F 0.870336 -0.000010 0.707888
F -0.840052 1.028800 -0.290488
F -0.840064 -1.028792 -0.290500
O 1.555251 0.000003 -0.587945
Rotational constants (GHz): 8.1410000 4.6213400 3.9571500
Vibrational harmonic frequencies (cm-1):
-296.1287 63.6061 264.9961
415.5559 578.0771 720.4859
739.7961 1111.2883 1189.6825
Zero-point correction (Hartree): 0.011581

TS_NF3_O_insertion

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -429.09068333
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.59053519
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.52708267
E(MP2/Aug-CC-pVTZ) (Hartree): -428.52215762
E(MP3/Aug-CC-pVTZ) (Hartree): -428.50142235
E(RHF/Aug-CC-pVTZ) (Hartree): -427.28736495
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.412559 0.157243 -0.478386
F 0.587401 1.127168 0.349956
F 1.354335 -0.703502 -0.117911
O -1.621320 0.292908 -0.313162
F -0.821442 -0.806329 0.418399
Rotational constants (GHz): 8.6700300 4.6227800 3.4556500
Vibrational harmonic frequencies (cm-1):
-926.5791 158.1537 346.8836
383.9122 530.0336 688.3672
791.2940 981.1482 1187.8076
Zero-point correction (Hartree): 0.011545

TS_umbrella

E(UM052X+HF-M/6-311G(d)) (Hartree): -429.22316036
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -428.69600173
E(CCSD/Aug-CC-pVTZ) (Hartree): -428.64477207
E(MP2/Aug-CC-pVTZ) (Hartree): -428.61990337
E(MP3/Aug-CC-pVTZ) (Hartree): -428.62010635
E(PMP2/Aug-CC-pVTZ) (Hartree): -428.65830482
E(PMP3/Aug-CC-pVTZ) (Hartree): -428.65739766
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.49441497
E(RHF/Aug-CC-pVTZ) (Hartree): -427.37189986
E(UHF/Aug-CC-pVTZ) (Hartree): -427.45539515
Point group : CS
Electronic state : 1-A'
Cartesian coordinates (Angs):
N 0.136530 0.433298 0.000000
F -0.285965 1.088317 1.081828
F -0.285965 1.088317 -1.081828
O 0.845668 -0.508636 0.000000
F -0.285965 -2.061523 0.000000
Rotational constants (GHz): 8.3617400 3.3948900 2.8493800
Vibrational harmonic frequencies (cm-1):
-773.4917 (A') 118.3653 (A'') 170.7769 (A')
302.8790 (A') 547.0110 (A') 594.9430 (A'')
920.7337 (A') 1209.5695 (A'') 1708.1735 (A')
Zero-point correction (Hartree): 0.012695

C. Quantum chemical data : [NF3OH] PES

F3N--OH

E(UM052X+HF-M/6-311G(d)) (Hartree): -429.87252631
Electronic state : 2-A
Cartesian coordinates (Angs):
N -0.501085 0.007581 -0.402073
F 0.047032 -0.951948 0.399450
F -1.829007 -0.196509 -0.204750
F -0.277442 1.132540 0.308159
O 2.422782 0.114388 -0.195772
H 2.660100 -0.824922 -0.145039
Rotational constants (GHz): 9.7771400 2.8407000 2.3776600
Vibrational harmonic frequencies (cm-1):
52.0131 79.9141 122.5570
162.3425 232.5491 535.2833
536.1811 703.8598 1006.4474
1026.6220 1125.8084 3760.4740
Zero-point correction (Hartree): 0.021287

NF3--HO

E(UM052X+HF-M/6-311G(d)) (Hartree): -429.87311135
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.36014981
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.31524919
E(MP2/Aug-CC-pVTZ) (Hartree): -429.30125427
E(MP3/Aug-CC-pVTZ) (Hartree): -429.30399811
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.30325238
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.30514567
E(PUHF/Aug-CC-pVTZ) (Hartree): -428.10841423
E(UHF/Aug-CC-pVTZ) (Hartree): -428.10504057
Electronic state : 2-A
Cartesian coordinates (Angs):
N 1.025840 0.020471 0.158629
F 0.447090 1.205650 -0.190767
F 0.187303 -0.423637 1.127856
F 0.714115 -0.770981 -0.885233
H -1.985239 0.801919 -0.000991
O -2.166528 -0.130563 -0.197015
Rotational constants (GHz): 6.0222900 3.4016800 3.3456800
Vibrational harmonic frequencies (cm-1):
72.6390 83.9613 111.8139
159.2218 274.6754 532.8466
535.0427 704.0463 1007.4535
1034.1954 1125.3231 3760.0587
Zero-point correction (Hartree): 0.021418

F

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -99.74403582
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -99.62782704
E(CCSD/Aug-CC-pVTZ) (Hartree): -99.62345241
E(MP2/Aug-CC-pVTZ) (Hartree): -99.61210618
E(MP3/Aug-CC-pVTZ) (Hartree): -99.62216846
E(PMP2/Aug-CC-pVTZ) (Hartree): -99.61371825
E(PMP3/Aug-CC-pVTZ) (Hartree): -99.62300590
E(PUHF/Aug-CC-pVTZ) (Hartree): -99.41002320
E(UHF/Aug-CC-pVTZ) (Hartree): -99.40687935
Point group : OH
Cartesian coordinates (Angs):
F 0.000000 0.000000 0.000000
Zero-point correction (Hartree): 0.000000

HF

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E(RM052X+HF-M052X/6-311G(d)) (Hartree): -100.44761114
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -100.34957663
E(CCSD/Aug-CC-pVTZ) (Hartree): -100.34203864
E(MP2/Aug-CC-pVTZ) (Hartree): -100.34088926
E(MP3/Aug-CC-pVTZ) (Hartree): -100.33968904
E(RHF/Aug-CC-pVTZ) (Hartree): -100.06089639
Point group : C_v

Electronic state : 1-SG
Cartesian coordinates (Angs):
F 0.000000 0.000000 0.092065
H 0.000000 0.000000 -0.828581
Rotational constants (GHz): 0.0000000 623.0096811 623.0096811
Vibrational harmonic frequencies (cm-1):
4092.4976 (SG)
Zero-point correction (Hartree): 0.009323

HNF2O

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -330.12011859
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -329.71712267
E(CCSD/Aug-CC-pVTZ) (Hartree): -329.67132597
E(MP2/Aug-CC-pVTZ) (Hartree): -329.68521128
E(MP3/Aug-CC-pVTZ) (Hartree): -329.65985002
E(RHF/Aug-CC-pVTZ) (Hartree): -328.67003081
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.003930 0.205835 0.294535
F -1.115667 -0.632817 -0.109869
F 1.092574 -0.670233 -0.109806
O 0.022551 1.278988 -0.174373
H -0.000083 0.054709 1.310315
Rotational constants (GHz): 10.8142300 10.0690600 5.6649800
Vibrational harmonic frequencies (cm-1):
455.5595 467.1756 675.5838
818.5889 940.3641 1348.2524
1502.6878 1716.1228 3378.6038
Zero-point correction (Hartree): 0.025750

HOF

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -175.54764683
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -175.35031507
E(CCSD/Aug-CC-pVTZ) (Hartree): -175.33122445
E(MP2/Aug-CC-pVTZ) (Hartree): -175.32616108
E(MP3/Aug-CC-pVTZ) (Hartree): -175.32620468
E(RHF/Aug-CC-pVTZ) (Hartree): -174.80996464
Point group : CS
Electronic state : 1-A'
Cartesian coordinates (Angs):
O 0.052899 0.690550 0.000000
F 0.052899 -0.708591 0.000000
H -0.899285 0.852919 0.000000
Rotational constants (GHz): 598.3419200 28.2717300 26.9961600
Vibrational harmonic frequencies (cm-1):
1084.8722 (A') 1493.4869 (A') 3809.6024 (A')
Zero-point correction (Hartree): 0.014553

NF2H

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -254.92847340
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -254.62083502
E(CCSD/Aug-CC-pVTZ) (Hartree): -254.59327666
E(MP2/Aug-CC-pVTZ) (Hartree): -254.58732715
E(MP3/Aug-CC-pVTZ) (Hartree): -254.58648411
E(RHF/Aug-CC-pVTZ) (Hartree): -253.85251731
Electronic state : 1-A
Cartesian coordinates (Angs):
N -0.000242 0.556774 -0.164948
F 1.080922 -0.276065 0.024497
F -1.080785 -0.276146 0.024563
H 0.000462 1.072472 0.713102
Rotational constants (GHz): 54.6013700 11.1774400 9.5678200
Vibrational harmonic frequencies (cm-1):
544.4043 1005.2252 1084.6903
1391.1035 1544.7614 3461.7860
Zero-point correction (Hartree): 0.020576

NF2

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -254.30519806
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -253.99247463
E(CCSD/Aug-CC-pVTZ) (Hartree): -253.96548109
E(MP2/Aug-CC-pVTZ) (Hartree): -253.95734430
E(MP3/Aug-CC-pVTZ) (Hartree): -253.95555789
E(PMP2/Aug-CC-pVTZ) (Hartree): -253.96027005

E(PMP3/Aug-CC-pVTZ) (Hartree): -253.95726496
E(PUHF/Aug-CC-pVTZ) (Hartree): -253.27053582
E(UHF/Aug-CC-pVTZ) (Hartree): -253.26591919 Point group : C2V
Electronic state : 2-B1
Cartesian coordinates (Angs):
N 0.000000 0.000000 0.596577
F 0.000000 1.046978 -0.232002
F 0.000000 -1.046978 -0.232002
Rotational constants (GHz): 71.9416600 12.1337500 10.3826100
Vibrational harmonic frequencies (cm-1):
621.2610 1041.9603 1183.0092
Zero-point correction (Hartree): 0.006484

NF2OH.c

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -330.12975859
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -329.72813040
E(CCSD/Aug-CC-pVTZ) (Hartree): -329.68843133
E(MP2/Aug-CC-pVTZ) (Hartree): -329.68622080
E(MP3/Aug-CC-pVTZ) (Hartree): -329.67975483
E(RHF/Aug-CC-pVTZ) (Hartree): -328.70664964
Electronic state : 1-A
Cartesian coordinates (Angs):
N -0.025767 -0.000039 -0.491773
F 0.628657 1.063887 0.122038
F 0.631032 -1.062518 0.122053
O -1.248900 -0.001363 0.030707
H -1.165633 -0.001154 0.999934
Rotational constants (GHz): 10.9194600 10.5574000 5.9938700
Vibrational harmonic frequencies (cm-1):
441.5311 538.7836 635.4263
679.2653 937.8124 964.3002
1122.6532 1505.3349 3680.7316
Zero-point correction (Hartree): 0.023934

NF2OH.t

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -330.12595839
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -329.72564793
E(CCSD/Aug-CC-pVTZ) (Hartree): -329.68664466
E(MP2/Aug-CC-pVTZ) (Hartree): -329.68366569
E(MP3/Aug-CC-pVTZ) (Hartree): -329.67821587
E(RHF/Aug-CC-pVTZ) (Hartree): -328.70626499
Electronic state : 1-A
Cartesian coordinates (Angs):
N 0.031417 -0.000003 0.445166
F -0.653705 1.058481 -0.100072
F -0.653987 -1.058333 -0.100082
O 1.208987 -0.000119 -0.223032
H 1.877415 -0.000353 0.469480
Rotational constants (GHz): 10.8179700 10.7048700 5.9023400
Vibrational harmonic frequencies (cm-1):
334.5987 544.7165 561.4028
692.3850 991.5110 1005.6389
1085.5472 1477.2542 3848.7441
Zero-point correction (Hartree): 0.024016

NF2O

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -329.49760098
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -329.08580001
E(CCSD/Aug-CC-pVTZ) (Hartree): -329.04422785
E(MP2/Aug-CC-pVTZ) (Hartree): -329.04101350
E(MP3/Aug-CC-pVTZ) (Hartree): -329.02988785
E(PMP2/Aug-CC-pVTZ) (Hartree): -329.04776967
E(PMP3/Aug-CC-pVTZ) (Hartree): -329.03398296
E(PUHF/Aug-CC-pVTZ) (Hartree): -328.09960008
E(UHF/Aug-CC-pVTZ) (Hartree): -328.09043836 Electronic state : 2-A
Cartesian coordinates (Angs):
N -0.000603 0.170417 0.287812
O -0.003003 1.273956 -0.106060
F -1.088422 -0.634983 -0.064814
F 1.091560 -0.629969 -0.064764
Rotational constants (GHz): 11.7417400 10.8351600 5.8300100
Vibrational harmonic frequencies (cm-1):
490.2780 532.3951 683.5391
837.9813 956.5710 1633.0631
Zero-point correction (Hartree): 0.011696

NF3

E(RM052X+HF-M052X/6-311G(d)) (Hartree): -354.13611028
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -353.71361080
E(CCSD/Aug-CC-pVTZ) (Hartree): -353.67511638
E(MP2/Aug-CC-pVTZ) (Hartree): -353.67451342
E(MP3/Aug-CC-pVTZ) (Hartree): -353.66566844
E(RHF/Aug-CC-pVTZ) (Hartree): -352.68589143 Point group : CS
Electronic state : 1-A'
Cartesian coordinates (Angs):
N 0.338172 0.330159 0.000000
F -0.939368 0.784832 0.000000
F 0.338172 -0.520811 1.055057
F 0.338172 -0.520811 -1.055057
Rotational constants (GHz): 10.9284500 10.9206100 5.9766700
Vibrational harmonic frequencies (cm-1):
535.1475 (A'') 535.8508 (A') 707.2625 (A')
1022.2475 (A'') 1023.3765 (A') 1125.0404 (A')
Zero-point correction (Hartree): 0.011274

OF

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -174.89297393
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -174.68434088
E(CCSD/Aug-CC-pVTZ) (Hartree): -174.66695811
E(MP2/Aug-CC-pVTZ) (Hartree): -174.65341848
E(MP3/Aug-CC-pVTZ) (Hartree): -174.65826542
E(PMP2/Aug-CC-pVTZ) (Hartree): -174.65655913
E(PMP3/Aug-CC-pVTZ) (Hartree): -174.66025192
E(PUHF/Aug-CC-pVTZ) (Hartree): -174.20086437
E(UHF/Aug-CC-pVTZ) (Hartree): -174.19624969
Point group : C*v
Cartesian coordinates (Angs):
O 0.000000 0.000000 -0.703703
F 0.000000 0.000000 0.625513
Rotational constants (GHz): 0.0000000 32.9391391 32.9391391
Vibrational harmonic frequencies (cm-1):
1178.1511 (SG)
Zero-point correction (Hartree): 0.002684

OH

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -75.73281510
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -75.64557729
E(CCSD/Aug-CC-pVTZ) (Hartree): -75.63969723
E(MP2/Aug-CC-pVTZ) (Hartree): -75.62633692
E(MP3/Aug-CC-pVTZ) (Hartree): -75.63790561
E(PMP2/Aug-CC-pVTZ) (Hartree): -75.62832298
E(PMP3/Aug-CC-pVTZ) (Hartree): -75.63904465
E(PUHF/Aug-CC-pVTZ) (Hartree): -75.42497835
E(UHF/Aug-CC-pVTZ) (Hartree): -75.42162889
Point group : C*v
Cartesian coordinates (Angs):
O 0.000000 0.000000 0.107791
H 0.000000 0.000000 -0.862324
Rotational constants (GHz): 0.0000000 566.3995836 566.3995836
Vibrational harmonic frequencies (cm-1):
3747.9405 (SG)
Zero-point correction (Hartree): 0.008538

TS_F2NOH_F_F2NO_HF

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.87101498
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.35169816
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.29931521
E(MP2/Aug-CC-pVTZ) (Hartree): -429.27122990
E(MP3/Aug-CC-pVTZ) (Hartree): -429.26878067
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.27520679
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.27134988
E(PUHF/Aug-CC-pVTZ) (Hartree): -428.06018236
E(UHF/Aug-CC-pVTZ) (Hartree): -428.05388399
Electronic state : 2-A
Cartesian coordinates (Angs):
N 0.211134 -0.000081 -0.031017
F -1.756827 0.000444 -0.535311
F 0.999128 -1.061767 -0.269015
F 0.996971 1.063896 -0.265656

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O      -0.290183      -0.002566      1.137942
H      -1.309918      -0.002055      0.743426
Rotational constants (GHz):   6.9901400   3.9005900   3.5314200
Vibrational harmonic frequencies (cm-1):
-1572.1812                    62.6270                    267.6356
 550.4722                     551.9530                    625.7727
 819.7488                      895.9514                   1080.8382
1151.5418                     1344.6437                   2211.9294
Zero-point correction (Hartree): 0.021786
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TS_F_NF2OH_SN2

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E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.85546486
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.34221416
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.28975396
E(MP2/Aug-CC-pVTZ) (Hartree): -429.26412915
E(MP3/Aug-CC-pVTZ) (Hartree): -429.26297364
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.28648730
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.27922906
E(PUHF/Aug-CC-pVTZ) (Hartree): -428.07533431
E(UHF/Aug-CC-pVTZ) (Hartree): -428.04897510
Electronic state : 2-A
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Cartesian coordinates (Angs):
N      -0.017132      0.002461      -0.133133
F      -0.018494     -1.042136      0.712521
F       1.458115     -0.112673     -0.652554
F      -1.564544      0.015230     -0.549574
O       0.034400      1.123706      0.567798
H       0.969037      1.249339      0.796017
Rotational constants (GHz):   7.0164700   4.3129900   3.8673000
Vibrational harmonic frequencies (cm-1):
-906.6083                    274.3502                    355.2952
 384.8621                     452.5228                    500.9832
 613.9474                     680.7635                   1042.1504
1143.9324                     1478.0477                   3735.5817
Zero-point correction (Hartree): 0.024291
```

TS_F_ONF2H_SN2

```
-----
E(UM052X+HF-M/6-311G(d)) (Hartree): -429.79937083
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.29124875
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.23041135
E(MP2/Aug-CC-pVTZ) (Hartree): -429.23287845
E(MP3/Aug-CC-pVTZ) (Hartree): -429.20914226
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.24057606
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.21437743
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.98400134
E(UHF/Aug-CC-pVTZ) (Hartree): -427.97419424
Point group : CS
```

```
Electronic state : 2-A''
Cartesian coordinates (Angs):
N       0.166455      0.117334      0.000000
F       0.285698      0.094433      1.675657
F       0.285698      0.094433     -1.675657
H       0.929752      0.788536      0.000000
F      -1.058120      0.648738      0.000000
O       0.285698     -1.143538      0.000000
Rotational constants (GHz):   8.8686700   4.2513200   3.3361500
Vibrational harmonic frequencies (cm-1):
-1164.9906 ( A'')           276.6178 ( A')           374.2060 ( A')
 410.6644 ( A')           499.7467 ( A'')           516.5802 ( A'')
 650.1352 ( A')           1074.7802 ( A')           1189.5188 ( A')
1235.1593 ( A'')           1424.2229 ( A')           3515.4574 ( A')
Zero-point correction (Hartree): 0.025441
```

TS_HNF2O_F_NF2O_HF

```
-----
E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.86207452
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.34181279
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.28931373
E(MP2/Aug-CC-pVTZ) (Hartree): -429.28672203
E(MP3/Aug-CC-pVTZ) (Hartree): -429.27214648
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.28898590
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.27370696
E(PUHF/Aug-CC-pVTZ) (Hartree): -428.06511683
E(UHF/Aug-CC-pVTZ) (Hartree): -428.06143393
Electronic state : 2-A
Cartesian coordinates (Angs):
```

N	-0.374895	-0.005649	0.217123
F	-0.472959	-1.079673	-0.733127
F	-0.510095	1.115166	-0.672825
O	-1.136868	-0.042513	1.106634
H	0.665670	0.006997	0.399823
F	2.211225	0.005912	0.208980

Rotational constants (GHz): 5.8891900 3.0593600 2.9557300
Vibrational harmonic frequencies (cm-1):
-271.1465 21.1438 66.6452
468.3943 488.6090 655.6259
856.1235 935.5989 1287.7532
1419.8302 1690.3067 2500.8820
Zero-point correction (Hartree): 0.023672

TS_NF2_HOF

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.81258934
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.30522407
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.25469792
E(MP2/Aug-CC-pVTZ) (Hartree): -429.20520664
E(MP3/Aug-CC-pVTZ) (Hartree): -429.21988850
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.24077288
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.25164911
E(PUHF/Aug-CC-pVTZ) (Hartree): -428.09748993
E(UHF/Aug-CC-pVTZ) (Hartree): -428.05971477
Electronic state : 2-A
Cartesian coordinates (Angs):
N -0.975724 0.007783 0.519763
F -1.313253 1.044981 -0.232865
F -1.331312 -1.036553 -0.212140
F 0.845819 -0.016523 0.187646
O 2.528343 -0.027866 -0.245956
H 2.792032 0.241298 0.645540
Rotational constants (GHz): 10.3261300 2.3958000 2.0672500
Vibrational harmonic frequencies (cm-1):
-831.1030 115.2118 137.1432
193.9710 236.5942 291.4151
461.8312 637.4653 949.1030
1069.5808 1167.1336 3797.9310
Zero-point correction (Hartree): 0.020634

TS_NF2_HOF_NF2H_OF

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.80974943
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.29254266
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.24217965
E(MP2/Aug-CC-pVTZ) (Hartree): -429.21994398
E(MP3/Aug-CC-pVTZ) (Hartree): -429.22117151
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.22668634
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.22563457
E(PUHF/Aug-CC-pVTZ) (Hartree): -428.01566172
E(UHF/Aug-CC-pVTZ) (Hartree): -428.00664489
Electronic state : 2-A
Cartesian coordinates (Angs):
N -0.985703 -0.061996 0.568059
F -0.969329 1.120974 -0.083920
F -1.168692 -0.969182 -0.417446
H 0.096858 -0.202257 0.819600
O 1.448875 -0.277852 0.657838
F 1.606029 0.165879 -0.616270
Rotational constants (GHz): 7.6226500 3.1058300 2.7530900
Vibrational harmonic frequencies (cm-1):
-1554.3146 46.1631 119.2449
148.9786 356.6287 588.8794
835.8940 1052.0414 1107.3703
1183.6253 1394.8232 1557.4654
Zero-point correction (Hartree): 0.019116

TS_NF2OH_F

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.83721464
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.32733992
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.27514491
E(MP2/Aug-CC-pVTZ) (Hartree): -429.24550740
E(MP3/Aug-CC-pVTZ) (Hartree): -429.24703521
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.27085484
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.26616957

E(PUHF/Aug-CC-pVTZ) (Hartree): -428.06826334
E(UHF/Aug-CC-pVTZ) (Hartree): -428.03897128
Electronic state : 2-A
Cartesian coordinates (Angs):
N 0.009083 -0.007055 0.133646
F 0.090323 -1.012034 -0.735158
F 1.480106 -0.030376 0.691103
F 0.072459 1.082623 -0.612564
O -1.648373 0.018770 0.459419
H -1.662586 -0.462697 1.298702
Rotational constants (GHz): 6.8732100 4.2214400 3.8820500
Vibrational harmonic frequencies (cm-1):
-972.3880 232.0371 270.5670
358.8975 413.5046 455.4055
614.7887 656.0926 1050.3536
1088.9267 1191.7182 3796.4563
Zero-point correction (Hartree): 0.023075

TS_NF3O_H_NF2_HF

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.79865165
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.28325212
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.22485139
E(MP2/Aug-CC-pVTZ) (Hartree): -429.22409215
E(MP3/Aug-CC-pVTZ) (Hartree): -429.19805622
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.24232949
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.21185937
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.98818208
E(UHF/Aug-CC-pVTZ) (Hartree): -427.96754590
Electronic state : 2-A
Cartesian coordinates (Angs):
N 0.197339 -0.000001 0.173461
F 0.484391 -1.082385 -0.653121
F 0.484393 1.082388 -0.653114
F -1.367060 0.000006 0.076989
O 0.642473 -0.000006 1.233725
H -2.936670 -0.000024 -0.020808
Rotational constants (GHz): 5.9069900 4.9909500 4.8253500
Vibrational harmonic frequencies (cm-1):
-1345.7890 270.5865 284.7026
414.2378 414.7659 556.2369
565.2149 585.5773 817.5070
934.0660 1004.9440 1838.7949
Zero-point correction (Hartree): 0.017511

TS_NF3O_H_NF2OHc_F

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.78274132
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.26712493
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.20990223
E(MP2/Aug-CC-pVTZ) (Hartree): -429.19709065
E(MP3/Aug-CC-pVTZ) (Hartree): -429.18070738
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.22038060
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.19893285
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.98198220
E(UHF/Aug-CC-pVTZ) (Hartree): -427.95597309
Electronic state : 2-A
Cartesian coordinates (Angs):
N -0.106182 -0.000100 0.097632
F -0.137262 1.068920 -0.742209
F 1.432116 -0.001087 0.500342
O -0.914098 -0.001224 0.962434
F -0.138047 -1.066656 -0.745289
H -2.355210 -0.000105 0.501504
Rotational constants (GHz): 6.0152300 5.0735000 4.9430300
Vibrational harmonic frequencies (cm-1):
-1732.8639 251.9571 338.3179
366.6925 489.4827 577.9480
630.1111 647.5869 873.9063
962.2332 1065.2496 1630.5395
Zero-point correction (Hartree): 0.017847

TS_NF3O_H_NF2O_HF

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.79865165
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.28325212
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.22485139
E(MP2/Aug-CC-pVTZ) (Hartree): -429.22409215

E(MP3/Aug-CC-pVTZ) (Hartree): -429.19805622
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.24232949
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.21185937
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.98818208
E(UHF/Aug-CC-pVTZ) (Hartree): -427.96754590
Electronic state : 2-A
Cartesian coordinates (Angs):
N 0.197339 -0.000001 0.173461
F 0.484391 -1.082385 -0.653121
F 0.484393 1.082388 -0.653114
F -1.367060 0.000006 0.076989
O 0.642473 -0.000006 1.233725
H -2.936670 -0.000024 -0.020808
Rotational constants (GHz): 5.9069900 4.9909500 4.8253500
Vibrational harmonic frequencies (cm-1):
-1345.7890 270.5865 284.7026
414.2378 414.7659 556.2369
565.2149 585.5773 817.5070
934.0660 1004.9440 1838.7949
Zero-point correction (Hartree): 0.017511

TS_NF3O_H_NF2Oht_F

E(UM052X+HF-M052X/6-311G(d)) (Hartree): -429.78081258
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.28325212
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.22485139
E(MP2/Aug-CC-pVTZ) (Hartree): -429.22409215
E(MP3/Aug-CC-pVTZ) (Hartree): -429.19805622
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.24232949
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.21185937
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.98818208
E(UHF/Aug-CC-pVTZ) (Hartree): -427.96754590
Electronic state : 2-A
Cartesian coordinates (Angs):
N 0.074591 0.169496 0.000001
F 0.761648 -0.283420 -1.075066
F 0.761644 -0.283429 1.075067
O -0.268730 1.296601 0.000004
F -1.145821 -0.862650 -0.000005
H -1.769532 1.306204 0.000002
Rotational constants (GHz): 5.6959400 5.2346700 5.1865700
Vibrational harmonic frequencies (cm-1):
-1781.1211 332.9265 378.7060
411.6675 501.0510 570.6919
627.6190 663.4499 827.1432
1047.5860 1100.7017 1691.2109
Zero-point correction (Hartree): 0.018573

TS_ONF2H_F

E(UM052X+HF-M/6-311G(d)) (Hartree): -429.75060897
E(CCSD(T)/Aug-CC-pVTZ) (Hartree): -429.23290301
E(CCSD/Aug-CC-pVTZ) (Hartree): -429.16185385
E(MP2/Aug-CC-pVTZ) (Hartree): -429.16386900
E(MP3/Aug-CC-pVTZ) (Hartree): -429.14100391
E(PMP2/Aug-CC-pVTZ) (Hartree): -429.16746234
E(PMP3/Aug-CC-pVTZ) (Hartree): -429.14383014
E(PUHF/Aug-CC-pVTZ) (Hartree): -427.88640680
E(UHF/Aug-CC-pVTZ) (Hartree): -427.88242605
Point group : CS
Electronic state : 2-A"
Cartesian coordinates (Angs):
N 0.160659 0.051128 0.000000
F -0.568051 0.394717 1.063320
F -0.568051 0.394717 -1.063320
H 0.189673 -1.037741 0.000000
F 1.495005 1.323120 0.000000
O -0.568051 -2.291642 0.000000
Rotational constants (GHz): 6.6468900 2.7396300 2.6002300
Vibrational harmonic frequencies (cm-1):
-1103.2694 (A') 90.8067 (A') 109.4204 (A")
200.2473 (A") 215.6277 (A') 344.3402 (A')
589.4694 (A') 908.3473 (A') 1120.2912 (A")
1142.1046 (A') 1515.7815 (A") 1721.0820 (A')
Zero-point correction (Hartree): 0.018129

Removal of the potent greenhouse gas NF_3 by reactions with the atmospheric oxidants $\text{O}(^1\text{D})$, OH and O_3 .

Supplemental info. #2 – correlation of $\text{O}(^1\text{D})$ rate constants with ionisation energy.

Terry J. Dillon^{*}, Luc Vereecken, Abraham Horowitz, Victor Khamaganov, John N. Crowley and Jos Lelieveld

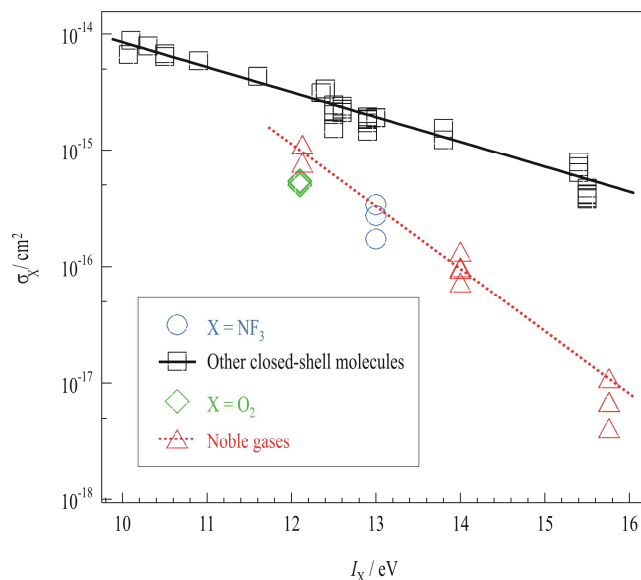


Figure 1 supplemental.

Displays plots of per-collision rate constants against ionisation potential I_X of collider X for reactions of the type $\text{O}(^1\text{D}) + \text{X} \rightarrow (\text{products})$. To compare the $\text{O}(^1\text{D})$ destruction efficiency of various collision partners, thermally averaged reaction cross-sections, σ_X , were calculated using expression (S1)

$$\sigma_X = k_X(298 \text{ K}) / \langle c \rangle \quad (\text{S1})$$

where $\langle c \rangle$ is the mean velocity of the $\text{O}(^1\text{D}) - \text{X}$ collision (from collision theory). The black squares depict literature data for closed-shell molecules (not atoms), with the values already used in ¹⁻² augmented by subsequently published rate coefficient data for $\text{X} = \text{CH}_4$;³ N_2O ;^{4,5} N_2 from this work and ⁵; H_2O and H_2 ;⁶ SO_2F_2 ;^{5,7} and CS_2 and SO_2 .⁷ The solid black line describes an unweighted fit to yield $\sigma_X = 1.20 \times 10^{-12} \exp\{-0.50 I_X\} \text{ cm}^2$. This empirical relationship may be used in conjunction with a literature value for $I_{\text{NF}_3} = 13.0 \text{ eV}$ ⁸ to calculate a predicted $k_2 \approx 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a factor of 5 or so larger than the measurements from ⁷ and in this work. Experimentally derived data for NF_3 (the blue circles) however lies on the correlation line derived from $\text{O}(^1\text{D}) + \text{noble gas}$ data (red triangles, *nb.* $\text{X} = \text{Ne}$ off-scale at $I = 21.56 \text{ eV}$, $\sigma = 5.97 \times 10^{-20} \text{ cm}^2$). An unweighted fit yields $\sigma_X = 3.05 \times 10^{-9} \exp\{-1.23 I_X\} \text{ cm}^2$ (the red dotted line). Note this relationship may be skewed by experimentally derived rate coefficients that were essentially upper-limit values, for this reason no $\text{X} = \text{He}$ data was used.

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