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

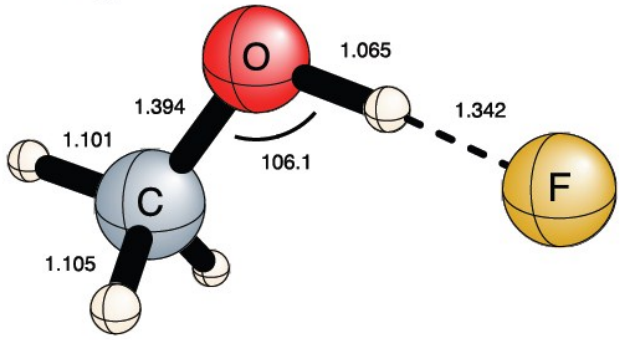

# Supplementary Materials for Transition-State Dynamics of the $F + HOCH_3 \rightarrow HF + OCH_3$ Reaction

**Table S1.** HF product vibrational population distributions. Populations determined by fitting $E_{TOT}$ spectrum with Gaussians centered over each shelf like peak (see Figure 4).

| Energetic Pathway | Energetic Range (eV) | Fraction |
|---|---|---|
| $HF(v=0) + OCH_3 + e^-$ | 1.48 – 1.01 | 16 % |
| $HF(v=1) + OCH_3 + e^-$ | 1.01 – 0.55 | 33% |
| $HF(v=2) + OCH_3 + e^-$ | 0.55 – 0.12 | 37% |
| $HF(v=3) + OCH_3 + e^-$ | 0.12 – 0.00 | 14% |

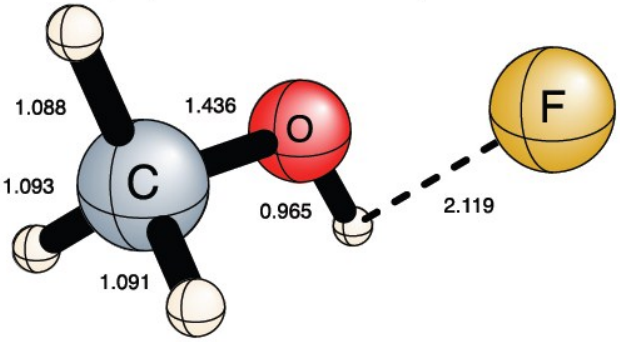
**Figures S1.** Optimized geometries, frequencies and complete basis set extrapolated energetics for the $FHOCH_3^-$ anion, neutral stationary points and fragments. As supported in literature, the methoxy radical has a $C_S$ symmetry as expected from Jahn-Teller effects.(*1*)

$[F\text{-}HOCH_3]^-$



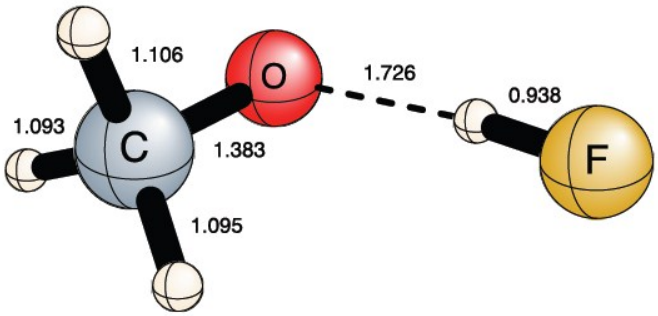

```
Symmetry: Cs
Multiplicity: 1
Charge: -1
Reference: RHF
Theory: CCSD(T)/aug-cc-pVTZ
Geometry (Angstroms):
    H    -2.4647567198  -0.2118348704  -0.0000000000
    C    -1.3967367626  -0.4805422825  -0.0000000000
    O    -0.6171933427   0.6753384974   0.0000000000
    H     0.3958138769   0.3472605467   0.0000000000
    F     1.6407838745  -0.1537544394  -0.0000000000
    H    -1.2176445280  -1.1166972155   0.8852937091
    H    -1.2176445280  -1.1166972155  -0.8852937091
Frequencies (Harmonic, cm-1):
      65.5860
     165.6900
     406.8881
    1119.6254
    1151.6290
    1168.7870
    1223.9246
    1451.9802
    1487.5865
    1510.3612
    1641.4504
    2065.3915
    2913.1364
    2928.3139
    2970.6270
Zero-Point Vibrational Energy: 11135.489 cm-1
Focal-Point Extrapolation (Hartrees):
              HF              MP2             CCSD          CCSD(T)          CCSDT          CCSDT(Q)
DZ    -214.528818304008  -215.134240441367  -215.153478490614  -215.171385493782  -215.172132014215  -215.173053015990
TZ    -214.582538712364  -215.322783808309  -215.332862241548  -215.360403529232  -215.361150049665* -215.362071051440*
QZ    -214.596510026014  -215.385157717157  -215.388666644793  -215.418383812629  -215.419130333062* -215.420051334837*
5Z    -214.600130770769  -215.408132539130  -215.406515404155  -215.437042877529  -215.437789397962* -215.438710399737*
CBS   -214.601397347778  -215.429705033219  -215.422709734193  -215.454087364197  -215.454833884630  -215.455754886405
CBS[CCSDT(Q)] = -215.455754886405
Notes: * = Additive; XZ = aug-cc-pVXZ
```

## $[F\text{-}HOCH_3]^\bullet$ (Entrance Complex)



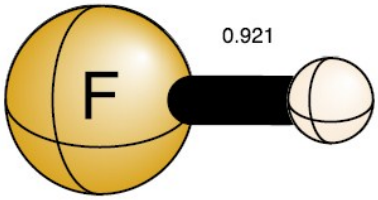

```
Symmetry: C1
Multiplicity: 2
Charge: 0
Reference: UHF
Theory: CCSD(T)/aug-cc-pVTZ
Geometry (Angstroms):
O    -0.4199777929  -0.6802073674   0.0641361132
C    -1.2587027875   0.4823405114  -0.0134355405
H    -1.3308708483   0.8752604344   0.9981086628
H    -0.8171698749   1.2356230446  -0.6668517538
H    -2.2516092782   0.1979151751  -0.3716138658
H    -0.1836185310  -0.9503173902  -0.8319669937
F     1.3917524950   0.1959460060   0.0007645288
Frequencies (Harmonic, cm-1):
     116.6274
     186.6914
     349.4645
     468.3833
    1028.5867
    1066.7706
    1165.7133
    1355.9393
    1465.1192
    1503.8684
    1511.4339
    3036.5505
    3116.7783
    3159.3996
    3797.9918
Zero-Point Vibrational Energy: 11664.659 cm-1
Focal-Point Extrapolation (Hartrees):
            HF              MP2              CCSD           CCSD(T)           CCSDT            CCSDT(Q)
DZ    -214.424724455647  -214.958457387933  -215.000499392410  -215.016498241167  -215.017834246235  -215.018718564177
TZ    -214.479190268640  -215.142141044872  -215.176495296530  -215.200584766612  -215.201920771680* -215.202805089622*
QZ    -214.493584278040  -215.202183779485  -215.230427963283  -215.256505578315  -215.257841583383* -215.258725901325*
5Z    -214.497307231537  -215.224372184546  -215.247858204833  -215.274678061346  -215.276014066414* -215.276898384356*
CBS   -214.498606107943  -215.245044649479  -215.263538498212  -215.291137099886  -215.292473104954  -215.293357422896
CBS[CCSDT(Q)] = -215.293357422896
Notes: * = Additive; XZ = aug-cc-pVXZ
```

## $[FH\text{-}OCH_3]^\bullet$ (Exit Complex)



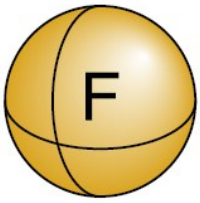

```
Symmetry: C1
Multiplicity: 2
Charge: 0
Reference: UHF
Theory: CCSD(T)/aug-cc-pVTZ
Geometry (Angstroms):
O     0.7471955025  -0.6716662508   0.0033854591
C     1.4803063123   0.5014271410   0.0080598458
H     2.4834837470   0.3552522450   0.4173463214
H     1.5846008667   0.7683203853  -1.0596938507
H     0.9406431622   1.3214318767   0.4932909297
H    -0.9280909032  -0.2574876955  -0.0054424187
F    -1.7805481639   0.1327208608   0.0002547406
Frequencies (Harmonic, cm-1):
      71.9009
      83.9551
     241.2792
     602.5135
     751.1805
     939.9783
    1059.2103
    1108.1638
    1382.5050
    1398.9144
    1517.4867
    2931.7169
    3036.0868
    3095.6729
    3751.2820
Zero-Point Vibrational Energy: 10985.923 cm-1
Focal-Point Extrapolation (Hartrees):
              HF              MP2             CCSD          CCSD(T)          CCSDT          CCSDT(Q)
DZ    -214.475573326999  -215.012504745392  -215.047546209600  -215.061645523621  -215.062667018114  -215.063456149631
TZ    -214.531192125908  -215.197899131230  -215.225557768438  -215.247752033330  -215.248773527823* -215.249562659340*
QZ    -214.545646653089  -215.258462789392  -215.280061175398  -215.304174890157  -215.305196384650* -215.305985516167*
5Z    -214.549352682666  -215.280634666356  -215.297481046509  -215.322312441734  -215.323333936227* -215.324123067744*
CBS   -214.550630503598  -215.301286491104  -215.313147160198  -215.338731531650  -215.339753026143  -215.340542157660
CBS[CCSDT(Q)] = -215.340542157660
Notes: * = Additive; XZ = aug-cc-pVXZ
```

## HF



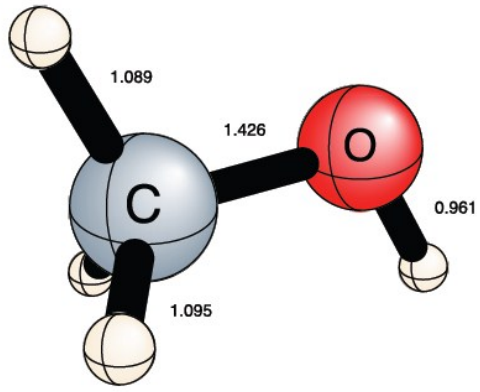

```
Symmetry: CXv
Multiplicity: 1
Charge: 0
Reference: RHF
Theory: CCSD(T)/aug-cc-pVTZ
Geometry (Angstroms):
H    -0.0000000000   0.0000000000   0.8745636244
F     0.0000000000   0.0000000000  -0.0463937473
Frequencies (Harmonic, cm-1):
    4124.7472
Zero-Point Vibrational Energy: 2062.374 cm-1
Focal-Point Extrapolation (Hartrees):
              HF                MP2              CCSD           CCSD(T)           CCSDT            CCSDT(Q)
DZ    -100.033287053413  -100.255788305249  -100.259474686961  -100.263630442566  -100.263830428628  -100.264137163873
TZ    -100.060880269470  -100.340889967261  -100.342036759143  -100.349576765218  -100.349776751280* -100.350083486525*
QZ    -100.068353271317  -100.369755134558  -100.369064955507  -100.377372356504  -100.377572342566* -100.377879077811*
5Z    -100.070365351721  -100.380551635374  -100.377999965242  -100.386617173132  -100.386817159194* -100.387123894439*
CBS   -100.071106704182  -100.390509428923  -100.386004718968  -100.394946970157  -100.395146956219  -100.395453691464
CBS[CCSDT(Q)] = -100.395453691464
Notes: * = Additive; XZ = aug-cc-pVXZ
```

## F



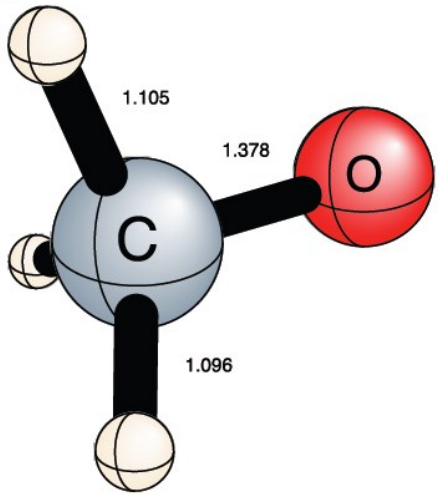

```
Symmetry: N/A
Multiplicity: 2
Charge: 0
Reference: N/A
Theory: N/A
Geometry (Angstroms):
F     0.0000000000   0.0000000000  0.0000000000
Frequencies (Harmonic, cm-1): N/A
Zero-Point Vibrational Energy: 0.000 cm-1
Focal-Point Extrapolation (Hartrees):
              HF                MP2              CCSD           CCSD(T)           CCSDT            CCSDT(Q)
DZ     -99.377068840441  -99.535819217185  -99.547684437107  -99.550034466009  -99.550257301114  -99.550306424593
TZ     -99.402083121383  -99.612395455677  -99.623349655754  -99.627771310919  -99.627994146024* -99.628043269503*
QZ     -99.409209020633  -99.638366845418  -99.647865823443  -99.652845103801  -99.653067938907* -99.653117062386*
5Z     -99.411197055579  -99.648484015450  -99.656371164198  -99.661598289020  -99.661821124125* -99.661870247604*
CBS    -99.411966301848  -99.657782190334  -99.663978239511  -99.669465397870  -99.669688232975  -99.669737356454
CBS[CCSDT(Q)] = -99.669737356454
Notes: * = Additive; XZ = aug-cc-pVXZ
```

$CH_3OH$




```
Symmetry: Cs
Multiplicity: 1
Charge: 0
Reference: RHF
Theory: CCSD(T)/aug-cc-pVTZ
Geometry (Angstroms):
H    -1.0996475426   1.0120821384  -0.0000000000
C    -0.7311839008  -0.0131018148  -0.0000000000
O     0.6924885394   0.0641652550  -0.0000000000
H     1.0384884430  -0.8324625523   0.0000000000
H    -1.1115275507  -0.5209838335   0.8921594664
H    -1.1115275507  -0.5209838335  -0.8921594664
Frequencies (Harmonic, cm-1):
     286.3098
    1053.6102
    1082.3107
    1175.8976
    1379.1734
    1484.0511
    1512.3468
    1522.8069
    3010.8930
    3069.2137
    3128.3213
    3843.6384
Zero-Point Vibrational Energy: 11274.286 cm-1
Focal-Point Extrapolation (Hartrees):
              HF              MP2             CCSD          CCSD(T)          CCSDT          CCSDT(Q)
DZ    -115.061422396222  -115.421725085753  -115.445030408706  -115.455506518321  -115.456019241274  -115.456666120204
TZ    -115.091859989843  -115.528980458176  -115.546474699481  -115.562384200492  -115.562896923445* -115.563543802375*
QZ    -115.099343567672  -115.563036674836  -115.576018231604  -115.593165648254  -115.593678371206* -115.594325250136*
5Z    -115.101211146891  -115.575260055851  -115.585154987102  -115.602736972637  -115.603249695590* -115.603896574520*
CBS   -115.101832203338  -115.586746215820  -115.593402720301  -115.611440646961  -115.611953369914  -115.612600248844
CBS[CCSDT(Q)] = -115.612600248844
Notes: * = Additive; XZ = aug-cc-pVXZ
```

$CH_3O$




```
Symmetry: Cs
Multiplicity: 2
Charge: 0
Reference: UHF
Theory: CCSD(T)/aug-cc-pVTZ
Geometry (Angstroms):
H     1.0589098640  -0.9626481038   0.0000000000
C    -0.0072949200  -0.6740554807   0.0000000000
O    -0.0035957065   0.7042224416   0.0000000000
H    -0.4574919989  -1.0940049732  -0.9069787207
H    -0.4574919989  -1.0940049732   0.9069787207
Frequencies (Harmonic, cm-1):
     760.1169
     960.6815
    1106.6601
    1390.6514
    1393.4597
    1521.8374
    2936.1158
    3017.5659
    3060.8824
Zero-Point Vibrational Energy: 8073.986 cm-1
Focal-Point Extrapolation (Hartrees):
               HF                MP2              CCSD            CCSD(T)            CCSDT             CCSDT(Q)
DZ    -114.433894085706  -114.743505444305  -114.775351745145  -114.784455336522  -114.785266592797  -114.785716951955
TZ    -114.462520855853  -114.844067954478  -114.871086983345  -114.884876470341  -114.885687726616* -114.886138085774*
QZ    -114.469626817458  -114.875907721423  -114.898771603962  -114.913696358191  -114.914507614467* -114.914957973625*
5Z    -114.471416567147  -114.887448562581  -114.907449431160  -114.922777604705  -114.923588860980* -114.924039220138*
CBS   -114.472019102185  -114.898281750964  -114.915278801617  -114.931030234773  -114.931841491048  -114.932291850206
CBS[CCSDT(Q)] = -114.932291850206
Notes: * = Additive; XZ = aug-cc-pVXZ
```

1. N. D. K. Petraco, W. D. Allen, H. F. Schaefer, Fragmentation path for hydrogen atom dissociation from methoxy radical. *J. Chem. Phys.* **116**, 10229-10237 (2002).