Supplementary Material

High-Accuracy First-Principles-based Rate Coefficients for the Reaction of OH and CH_3OOH

Thanh Lam Nguyen,[1] and Ajith Perera,[1]
[1]*Quantum Theory Project, Departments of Chemistry and Physics, University of Florida, Gainesville, FL. 32611, USA.*

Jozef Peeters[2,*]
[2]*Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.*

Corresponding authors: jozef.peeters@kuleuven.be; tlam.nguyen@chem.ufl.edu

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Figures 1-3 and Table 1 can be found in the main text.

Geometries of various species optimized at fc-CCSD(T)/aVTZ level of theory

$CH_3OOH(C_1, {}^1A)$

CH3OOH
C
H 1 B1*
H 1 B2* 2 A1*
H 1 B3* 2 A2* 3 D1*
O 1 B4* 2 A3* 4 D2*
O 5 B5* 1 A4* 2 D3*
H 6 B6* 5 A5* 1 D4*

B1 = 1.091645197619005
B2 = 1.093522963757435
A1 = 110.132565261864912
B3 = 1.092355356550471
A2 = 110.013076468606712
D1 = -121.508894255252287
B4 = 1.420215165057833
A3 = 104.643188247094528
D2 = -118.924646619023164
B5 = 1.460965686633438
A4 = 105.263175973693833
D3 = 177.113911395724614
B6 = 0.967173702517603
A5 = 99.773803333695767
D4 = 116.580447413081416

$CH_3OO(C_s, {}^2A')$

CH3OO
O
O 1 R1*
C 2 R2* 1 A1*
H 3 R3* 2 A2* 1 T180
H 3 R4* 2 A3* 4 T2*
H 3 R4* 2 A3* 4 T3*

R1 = 1.325044184105788
R2 = 1.447180813090181
A1 = 109.899561667711836
R3 = 1.088914231377361
A2 = 105.474592243366061
T180 = 180.000000000000000
R4 = 1.089117305766924
A3 = 108.868966685897945
T2 = 119.459327100774644

T3 = -119.459327100774644

OH($C_{\infty v}$, $X^2\Pi$)

OH: Optimized at CCSD(T)/AUG-PVTZ level
O
H 1 B1*

B1 = 0.973275224901106

CH_2O (C_{2v}, X^1A_1)

CH2O
O
C 1 R1*
H 2 R2* 1 A1*
H 2 R2* 1 A1* 3 T180

R1 = 1.211515087382290
R2 = 1.103061904375071
A1 = 121.714028216910862
T180 = 180.000000000000000

H_2O (C_{2v},X^1A_1)

H2O
O
H 1 R1*
H 1 R1* 2 A1*

R1 = 0.961579640410436
A1 = 104.179636130297880

PRC-1(C_1, ^2A)

OH--CH3OOH
C
H 1 B1*
O 1 B2* 2 A1*
O 3 B3* 1 A2* 2 D1*
H 4 B4* 3 A3* 1 D2*
O 3 B5* 1 A4* 4 D3*
H 6 B6* 3 A5* 1 D4*
H 1 B7* 3 A6* 4 D5*
H 1 B8* 3 A7* 4 D6*

B1 = 1.091588727025372
B2 = 1.424786496164878
A1 = 104.809690296401882
B3 = 1.460594085866826
A2 = 105.550813493638614
D1 = -177.194367084823654
B4 = 0.972909743620295
A3 = 99.864318044119159
D2 = -114.214612072144945
B5 = 2.805190587575620
A4 = 121.181632132720864
D3 = -88.028323497980665
B6 = 0.980871267585947
A5 = 27.475348465952969
D4 = -92.817898790759102
B7 = 1.091149139435444
A6 = 110.184559758062875
D5 = -58.692161211568447
B8 = 1.093004827987438
A7 = 110.966291912426527
D6 = 63.624666037144401

PRC-2(C_1, ^2A)

OH--CH3OOH
C
H 1 B1*
O 1 B2* 2 A1*
O 3 B3* 1 A2* 2 D1*
H 4 B4* 3 A3* 1 D2*
O 4 B5* 3 A4* 1 D3*
H 6 B6* 4 A5* 3 D4*
H 1 B7* 3 A6* 4 D5*
H 1 B8* 3 A7* 4 D6*

B1 = 1.0911074377
B2 = 1.4249914953
A1 = 104.1626488153
B3 = 1.4587377444
A2 = 106.1446377267
D1 = 178.4357943291
B4 = 0.9673745276
A3 = 100.5661486211
D2 = 110.8790351554
B5 = 2.9328001571
A4 = 119.7573105098
D3 = -32.3232584276
B6 = 0.9777384088
A5 = 1.9429392061
D4 = -144.3656268727

B7 = 1.0930696423
A6 = 111.0617388840
D5 = -62.9977002740
B8 = 1.0917306290
A7 = 110.9710521597
D6 = 60.0002821117

TS1a(C_1, ^2A)

TS1a
C
H 1 B1*
O 1 B2* 2 A1*
O 3 B3* 1 A2* 2 D1*
H 4 B4* 3 A3* 1 D2*
O 4 B5* 3 A4* 1 D3*
H 6 B6* 4 A5* 3 D4*
H 1 B7* 3 A6* 4 D5*
H 1 B8* 3 A7* 4 D6*

B1 = 1.090759695296664
B2 = 1.427588668816066
A1 = 104.831836223227569
B3 = 1.421110557342773
A2 = 107.176996020398533
D1 = -177.729609865989403
B4 = 1.037542852595872
A3 = 103.561565707204338
D2 = -72.067395452404725
B5 = 2.366197147918492
A4 = 100.931958300649313
D3 = -87.099694549202340
B6 = 0.972425005941957
A5 = 91.434449456041904
D4 = -73.655255437308369
B7 = 1.091437510895782
A6 = 110.377613261548504
D5 = -58.584158466653982
B8 = 1.094387416103645
A7 = 110.220232774968679
D6 = 63.848121425168053

TS1b(C_1, ^2A)

TS1b
C
H 1 B1*
O 1 B2* 2 A1*
O 3 B3* 1 A2* 2 D1*

H 4 B4* 3 A3* 1 D2*
O 4 B5* 3 A4* 1 D3*
H 6 B6* 4 A5* 3 D4*
H 1 B7* 3 A6* 4 D5*
H 1 B8* 3 A7* 4 D6*

B1 = 1.090760744297297
B2 = 1.425782321874379
A1 = 104.818210873633745
B3 = 1.419301882709666
A2 = 106.616913772766480
D1 = 176.920868744479009
B4 = 1.046791597000261
A3 = 102.892293677782206
D2 = 102.374250889587628
B5 = 2.294592489421196
A4 = 102.674523897511037
D3 = 80.854848582945166
B6 = 0.971823001651056
A5 = 94.185549088020949
D4 = -137.584651793234116
B7 = 1.094128086603258
A6 = 109.666175451931096
D5 = -64.442850351650577
B8 = 1.091734145654033
A7 = 110.471570752421897
D6 = 57.782623025712390

TS2a(C_1, ^2A)

TS2
C
H 1 B1*
O 1 B2* 2 A1*
O 3 B3* 1 A2* 2 D1*
H 4 B4* 3 A3* 1 D2*
O 1 B5* 3 A4* 4 D3*
H 6 B6* 1 A5* 3 D4*
H 1 B7* 3 A6* 4 D5*
H 1 B8* 3 A7* 4 D6*

B1 = 1.090556226079533
B2 = 1.392877437764292
A1 = 107.310149375369889
B3 = 1.453894719002093
A2 = 105.957934156330126
D1 = 179.403959922730792
B4 = 0.977568422200095
A3 = 99.847753100889292

D2 = 67.257672151334788
B5 = 2.562625242008479
A4 = 92.241076556335969
D3 = -59.687011094884589
B6 = 0.973805408679551
A5 = 92.849404617052684
D4 = -74.344602695792204
B7 = 1.170528880361910
A6 = 108.327256364727546
D5 = -62.765258443787481
B8 = 1.092690561652747
A7 = 112.848555772302234
D6 = 53.578284972300807

TS2b(C_1, ^2A)

TS2b
C
H 1 B1*
O 1 B2* 2 A1*
O 3 B3* 1 A2* 2 D1*
H 4 B4* 3 A3* 1 D2*
O 1 B5* 3 A4* 4 D3*
H 6 B6* 1 A5* 3 D4*
H 1 B7* 3 A6* 4 D5*
H 1 B8* 3 A7* 4 D6*

B1 = 1.090849359532236
B2 = 1.392529794755667
A1 = 107.199172091191528
B3 = 1.453249053853418
A2 = 106.094734756239987
D1 = 179.081795611584823
B4 = 0.976799991099919
A3 = 99.632113259533966
D2 = 70.508021140371014
B5 = 2.569720062525119
A4 = 93.906487589899044
D3 = -56.818096505047023
B6 = 0.973409249110573
A5 = 98.078140440412085
D4 = 130.005358661229167
B7 = 1.169102238917989
A6 = 107.503224941745927
D5 = -65.242892398731286
B8 = 1.092312930043115
A7 = 112.748971347270853
D6 = 53.530146374382383

Ro-vibrational parameters and anharmonic constants for relevant species

CH_3OOH

Har. vib. frequencies	CCSD(T)/aVTZ
Vib (1DHR)	185.2673
Vib (1DHR)	252.7168
vib	444.0688
vib	848.9585
vib	1048.3839
vib	1173.5470
vib	1206.8179
vib	1359.9221
vib	1456.3420
vib	1479.1789
vib	1520.2682
vib	3022.3930
vib	3099.9745
vib	3126.9426
vib	3769.7714
Rotational constants (cm^{-1})	
A=	1.41209
B=	0.35026
C=	0.30388

Anharmonic constants (cm^{-1})

7 7	-27.5146
7 8	-4.2606
7 9	-1.1840
7 10	-1.4782
7 11	6.0200
7 12	1.2585
7 13	4.9029
7 14	5.1206
7 15	-0.0456
7 16	-1.0156
7 17	1.0797
7 18	0.2089
7 19	-1.9400
7 20	1.7036
7 21	1.7391
8 8	-5.5353
8 9	-1.5882

```
 8 10      -1.3973
 8 11       0.3471
 8 12      -1.6770
 8 13      -5.6941
 8 14      -0.3632
 8 15       2.0285
 8 16       3.0763
 8 17      -1.9972
 8 18       0.7098
 8 19       1.9303
 8 20      -1.4129
 8 21       0.1646
 9  9       0.2516
 9 10      -4.8359
 9 11      -4.7736
 9 12       0.4703
 9 13      -1.7467
 9 14      -1.6290
 9 15      -0.4766
 9 16      -0.8040
 9 17       0.2419
 9 18       0.1704
 9 19       0.5264
 9 20      -0.7403
 9 21       0.5482
10 10      -6.1248
10 11      -5.5537
10 12      -0.3760
10 13      -3.0002
10 14     -14.3598
10 15      -1.2432
10 16      -1.0516
10 17      -0.4461
10 18      -0.1246
10 19       0.3898
10 20      -1.5278
10 21      -1.7237
11 11      -7.4284
11 12      -8.7352
11 13      -8.9616
11 14      -3.9528
11 15      -6.9938
11 16      -2.6074
11 17      -2.9272
11 18       1.3104
11 19       4.0600
11 20      -0.6316
11 21      -1.7847
12 12      -1.7468
12 13      -0.2984
12 14      -1.1009
```

12 15	-2.2776
12 16	-6.0474
12 17	-10.1011
12 18	-4.4654
12 19	-4.0118
12 20	-3.4025
12 21	-0.4574
13 13	-2.4341
13 14	-15.5536
13 15	-8.3404
13 16	-2.4139
13 17	-3.2340
13 18	-3.4301
13 19	-3.6347
13 20	-5.7550
13 21	0.1504
14 14	-10.4267
14 15	-1.0994
14 16	-0.7334
14 17	-0.8862
14 18	0.1606
14 19	0.7995
14 20	-0.6376
14 21	-28.3700
15 15	-7.9130
15 16	-3.5589
15 17	-3.3054
15 18	12.9828
15 19	-7.7323
15 20	-14.4466
15 21	-0.1412
16 16	-5.8894
16 17	-3.8691
16 18	-6.9340
16 19	-12.0813
16 20	-19.4613
16 21	0.0292
17 17	-15.1221
17 18	31.1447
17 19	-18.9250
17 20	-5.6942
17 21	-0.4367
18 18	-21.5691
18 19	-97.7506
18 20	-61.3893
18 21	-0.8875
19 19	-33.7076
19 20	-38.7018
19 21	-0.9452
20 20	-39.8475
20 21	-0.4482

21 21 -93.4546

PRC-1

Rotationally projected vibrational frequencies (cm^{-1}, at CCSD(T)/aVTZ)

7	49.0456
8	129.9006
9	182.4594
10	251.5371
11	273.1338
12	383.2561
13	443.4460
14	588.6770
15	850.0265
16	1045.2506
17	1177.6138
18	1208.9177
19	1438.0952
20	1457.4721
21	1479.7800
22	1521.0606
23	3028.8062
24	3112.5723
25	3132.6765
26	3591.3432
27	3683.9091

Zero-point energy: 41.4990 kcal/mol = 173.6319 kJ/mol = 14514.490 cm-1

Rotational constants (in cm-1):

0.1049922518	0.1283707650	0.3780107547

PRC-2

Rotationally projected vibrational frequencies (cm^{-1}, at fc-CCSD(T)/aVDZ)

7	50.3588
8	68.3616
9	143.1047
10	233.2623
11	280.2010
12	398.7313
13	436.2215
14	548.1124
15	800.3864
16	1010.1470
17	1153.6695
18	1189.7119
19	1341.6668
20	1431.7529

21	1453.3737
22	1479.4348
23	3016.6121
24	3108.8258
25	3131.5503
26	3601.1681
27	3739.1493

Zero-point energy: 40.9083 kcal/mol = 171.1606 kJ/mol = 14307.901 cm-1

Rotational constants (in cm-1):
0.0880044941 0.1098088404 0.3703350008

TS1a

As shown below in Fig. S7 transition state TS1 has two minima, with distinct vibrational frequencies. The lower minimum is designated here as TS1b, while the higher, secondary minimum as TS1a. Similar for transition state TS2.

Har. vib. frequencies	CCSD(T)/aVTZ
IMAG	1196.1286i
Vib (1DHR)	86.3854
vib	123.9071
vib	228.6799
vib	284.0348
vib	369.3336
vib	468.8965
vib	686.3552
vib	894.1869
vib	1043.6341
vib	1170.0918
vib	1205.8553
vib	1449.6554
vib	1453.7220
vib	1483.5884
vib	1511.1097
vib	1752.3858
vib	3022.7578
vib	3106.5456
vib	3138.6764
vib	3738.4171

Rotational constants (cm^{-1})	
A=	0.4419
B=	0.1342
C=	0.1165

TS1b

As shown below in Fig. S7 transition state TS1 has two minima, with distinct vibrational frequencies. The lower minimum is designated here as TS1b, while the higher, secondary minimum as TS1a. Similar for transition state TS2.

Har. vib. frequencies	CCSD(T)/aVTZ
IMAG	1503.0361i
Vib (1DHR)	89.1983
vib	169.9031
vib	222.7990
vib	268.2715
vib	358.5662
vib	467.4197
vib	738.7049
vib	899.7550
vib	1043.1380
vib	1168.5814
vib	1209.6346
vib	1346.5379
vib	1449.2306
vib	1478.8460
vib	1512.3987
Vib (a)	1869.5046
vib	3021.9190
vib	3105.8661
vib	3138.1008
vib	3742.8003
Rotational constants (cm^{-1})	
A=	0.43499
B=	0.14131
C=	0.11986

[a)] This mode, corresponding to the CH_3OO–H stretch in TS1, has unreliable anharmonic constants and is therefore treated separately as a harmonic oscillator.

Anharmonic constants (cm^{-1})

7 7	-570.1225
7 8	9.7698i
7 9	19.4326i
7 10	-9.2519i
7 11	12.7818i
7 12	113.9518i
7 13	10.8067i
7 14	168.8305i
7 15	30.3857i
7 16	0.4130i
7 17	-2.4092i
7 18	-0.2580i
7 19	-117.5624i
7 20	-2.5453i
7 21	0.0912i
7 22	-3.8227i
7 23	-1184.9443i
7 24	4.8709i
7 25	9.1645i
7 26	9.3313i
7 27	24.7372i
8 8	-1.8165
8 9	-1.7176
8 10	-5.6368
8 11	-2.4430
8 12	2.4375
8 13	-2.1515
8 14	-0.0093
8 15	0.3469
8 16	0.2795
8 17	-0.1687
8 18	-0.5624
8 19	-10.9554
8 20	0.5510
8 21	0.1381
8 22	0.1270
8 23	3.6183
8 24	1.3033
8 25	1.1405
8 26	0.2003
8 27	0.6190
9 9	-0.8859
9 10	-4.2470
9 11	-3.9573
9 12	-1.4109
9 13	0.9837
9 14	-0.7164

9 15	-0.9294
9 16	-0.4100
9 17	-0.2925
9 18	-0.3987
9 19	-15.0926
9 20	0.1494
9 21	0.1047
9 22	-1.1069
9 23	-2.4241
9 24	0.1727
9 25	0.2351
9 26	-0.2938
9 27	-0.1152
10 10	-11.7133
10 11	-2.2284
10 12	-1.1155
10 13	-1.8630
10 14	-1.8181
10 15	-0.4834
10 16	0.0116
10 17	-1.4742
10 18	-0.4533
10 19	-44.9791
10 20	-0.0190
10 21	0.1010
10 22	-1.2129
10 23	9.0203
10 24	-0.0264
10 25	-0.6332
10 26	0.3926
10 27	-2.3939
11 11	-3.8993
11 12	0.3076
11 13	3.4202
11 14	-0.0644
11 15	-0.9776
11 16	0.0186
11 17	-0.6925
11 18	-2.9179
11 19	-19.7509
11 20	1.3259
11 21	0.5207
11 22	-2.2407
11 23	19.8953
11 24	1.0872
11 25	1.9520
11 26	-1.2036
11 27	0.1179
12 12	11.3101
12 13	1.6483
12 14	12.0614

12 15	9.7524
12 16	1.7196
12 17	-0.3754
12 18	-0.2534
12 19	-11.5401
12 20	-0.8229
12 21	-0.2381
12 22	-0.3095
12 23	-20.0553
12 24	0.4049
12 25	0.9562
12 26	0.9253
12 27	3.3708
13 13	-0.0112
13 14	-0.0997
13 15	-4.0572
13 16	-4.4280
13 17	0.2847
13 18	-1.3829
13 19	-4.3711
13 20	0.0446
13 21	-0.6977
13 22	-0.9120
13 23	-2.2510
13 24	0.4812
13 25	0.7566
13 26	-0.6182
13 27	0.3371
14 14	4.7790
14 15	3.2058
14 16	-0.4887
14 17	-0.5212
14 18	-0.3660
14 19	-8.5956
14 20	-0.1703
14 21	-0.0704
14 22	-0.5247
14 23	-42.0855
14 24	0.6145
14 25	1.1496
14 26	1.0032
14 27	-8.8035
15 15	-6.2709
15 16	-9.9544
15 17	-1.2828
15 18	-2.6372
15 19	-8.2207
15 20	-1.6843
15 21	-0.9571
15 22	-0.4690
15 23	3.6707

15 24	0.4022
15 25	0.8436
15 26	-1.2800
15 27	0.5077
16 16	-7.5521
16 17	-7.9619
16 18	-8.3802
16 19	-4.8230
16 20	-6.8087
16 21	-2.6072
16 22	-3.0377
16 23	0.6861
16 24	1.4808
16 25	3.7261
16 26	-0.3958
16 27	0.1934
17 17	-1.8068
17 18	-0.5992
17 19	-1.5894
17 20	-4.0449
17 21	-5.9478
17 22	-8.6379
17 23	1.2745
17 24	-5.5353
17 25	-4.8065
17 26	-3.1508
17 27	0.1333
18 18	-2.1673
18 19	-1.5387
18 20	-7.0431
18 21	-4.8550
18 22	-4.6911
18 23	1.3110
18 24	-3.4039
18 25	-4.4436
18 26	-6.5041
18 27	-0.0071
19 19	-46.6985
19 20	-0.6814
19 21	-0.3094
19 22	-0.3282
19 23	101.6839
19 24	-0.8405
19 25	-1.5146
19 26	-1.4352
19 27	2.2920
20 20	-7.1007
20 21	-2.9562
20 22	-2.7450
20 23	-0.2684
20 24	9.7178

20 25	-8.2793
20 26	-12.7625
20 27	-0.0594
21 21	-5.7537
21 22	-4.3842
21 23	-0.8912
21 24	-6.9629
21 25	-11.9005
21 26	-20.1433
21 27	-0.0406
22 22	-1.7677
22 23	1.1069
22 24	-22.6399
22 25	-19.4397
22 26	-7.7786
22 27	0.0245
23 23	56.9173
23 24	-5.9523
23 25	-7.5890
23 26	-5.9791
23 27	-23.3399
24 24	-22.6566
24 25	-97.5543
24 26	-55.3814
24 27	0.0096
25 25	-32.4463
25 26	-40.1600
25 27	0.1041
26 26	-40.4974
26 27	0.0253
27 27	-86.6730

TS2b

Har. Vib. frequencies	CCSD(T)/aVTZ
IMAG	779.4271i
vib	143.3570
vib	166.8299
vib (1DHR)	261.1231
vib	382.3244
vib	446.5961
vib	546.0607
vib	753.2441
vib	852.4799
vib	910.3131
vib	1092.3906
vib	1196.4375

vib	1335.4111
vib	1427.4584
vib	1438.2994
vib	1469.7532
Vib (a)	1740.3137
vib	3055.3688
vib	3148.3688
vib	3597.6155
vib	3713.4027
Rotational constants (cm^{-1})	
A	0.3326
B	0.1684
C	0.1252

[a)] This mode, corresponding to the H–CH_2OOH stretch in TS2, has unreliable anharmonic constants and is therefore treated separately as a harmonic oscillator.

Anharmonic constants (cm^{-1})

7 7	-94.7788
7 8	-13.9486i
7 9	42.4687i
7 10	5.9780i
7 11	64.9522i
7 12	26.0258i
7 13	20.6090i
7 14	120.5213i
7 15	2.4061i
7 16	-6.1086i
7 17	19.5110i
7 18	-3.0600i
7 19	-64.1188i
7 20	-30.2283i
7 21	-23.3003i
7 22	4.7870i
7 23	-912.4041i
7 24	-5.2155i
7 25	12.1373i
7 26	-41.3338i
7 27	14.2133i
8 8	-6.7390
8 9	-4.7613
8 10	-10.8462
8 11	-4.1404
8 12	1.1381
8 13	-34.8326
8 14	9.9308

8 15	-0.0121
8 16	9.7180
8 17	-1.1459
8 18	1.7272
8 19	6.4450
8 20	-6.2482
8 21	-0.9057
8 22	-5.9426
8 23	-34.7591
8 24	0.5065
8 25	-0.3579
8 26	15.9899
8 27	1.4197
9 9	-0.5678
9 10	-0.4194
9 11	0.7416
9 12	2.0899
9 13	-9.8603
9 14	-0.4962
9 15	-0.4400
9 16	-1.8225
9 17	-0.1902
9 18	-3.4956
9 19	-7.3298
9 20	-1.3519
9 21	-27.4528
9 22	-1.8078
9 23	2.2824
9 24	0.8359
9 25	1.2731
9 26	4.5793
9 27	0.3041
10 10	-5.5602
10 11	-11.4443
10 12	-0.6030
10 13	-27.4167
10 14	7.5084
10 15	-0.1855
10 16	-0.0825
10 17	0.1592
10 18	-0.2638
10 19	-0.4222
10 20	-2.3008
10 21	-3.4866
10 22	-5.4819
10 23	-11.1577
10 24	-0.1716
10 25	-0.1404
10 26	19.2618
10 27	-2.3412
11 11	-6.4162

11 12	-3.3241
11 13	-9.3061
11 14	0.8697
11 15	-0.2178
11 16	14.9055
11 17	0.6169
11 18	-4.1770
11 19	2.0721
11 20	-0.6449
11 21	-0.4161
11 22	3.7537
11 23	-35.9420
11 24	-0.6410
11 25	-1.3083
11 26	7.2358
11 27	1.1760
12 12	-0.9331
12 13	-1.1087
12 14	-8.5477
12 15	-3.5209
12 16	-11.8785
12 17	-1.5872
12 18	-1.1819
12 19	-2.9675
12 20	5.5959
12 21	0.7867
12 22	0.0078
12 23	16.9015
12 24	0.2800
12 25	-0.2568
12 26	-0.9344
12 27	-0.3665
13 13	-56.4295
13 14	7.0189
13 15	-0.5472
13 16	2.0276
13 17	-2.3868
13 18	2.7876
13 19	1.6762
13 20	-4.6478
13 21	-0.3688
13 22	-13.8226
13 23	-65.9856
13 24	0.1716
13 25	-0.5484
13 26	66.3777
13 27	2.4171
14 14	-7.3504
14 15	-1.2013
14 16	58.5501
14 17	-0.0149

14 18	-1.0566
14 19	0.0611
14 20	3.0081
14 21	4.7765
14 22	2.5277
14 23	91.8977
14 24	0.7325
14 25	0.3061
14 26	-7.1997
14 27	-8.3925
15 15	-1.6351
15 16	-1.5746
15 17	-2.3663
15 18	-1.5804
15 19	-1.2882
15 20	-4.6473
15 21	-1.6975
15 22	-7.7210
15 23	-1.4131
15 24	-0.5582
15 25	-1.3577
15 26	-2.3000
15 27	-0.1789
16 16	4.2842
16 17	-3.1544
16 18	7.7929
16 19	34.5367
16 20	6.8147
16 21	-2.9188
16 22	-5.4602
16 23	212.3493
16 24	1.0750
16 25	-3.1449
16 26	5.2637
16 27	-7.0885
17 17	-7.0063
17 18	-6.4639
17 19	-7.1673
17 20	-4.9494
17 21	-4.4582
17 22	-4.2835
17 23	-21.6471
17 24	-0.7548
17 25	-2.9984
17 26	3.0048
17 27	0.3126
18 18	-1.8372
18 19	-5.6001
18 20	-5.6103
18 21	-4.2722
18 22	-1.4792

18 23	5.5112
18 24	-8.9323
18 25	-5.7519
18 26	-2.0020
18 27	-0.4197
19 19	-1.5336
19 20	1.0106
19 21	-3.8097
19 22	0.8647
19 23	78.0773
19 24	-2.2474
19 25	-15.1003
19 26	-0.3758
19 27	-2.2201
20 20	-4.0740
20 21	-7.6242
20 22	-16.9571
20 23	18.1432
20 24	-5.8399
20 25	-13.1709
20 26	-0.6608
20 27	-0.1611
21 21	-4.1068
21 22	-6.4353
21 23	-0.2539
21 24	-3.7394
21 25	-5.3497
21 26	-1.5261
21 27	-1.1605
22 22	-6.7022
22 23	-25.5345
22 24	-4.2758
22 25	-8.2389
22 26	0.5963
22 27	0.0808
23 23	171.9785
23 24	-0.0040
23 25	-8.6426
23 26	61.6485
23 27	-12.6893
24 24	-35.3712
24 25	-110.6131
24 26	-0.9934
24 27	0.0779
25 25	-38.2354
25 26	-0.6131
25 27	0.2471
26 26	-118.0476
26 27	-3.4634
27 27	-87.3595

TS2a

Har. Vib. frequencies	CCSD(T)/aVTZ
IMAG	756.2618i
vib	140.5286
vib	173.9947
vib (1DHR)	250.5207
vib	358.9616
vib	439.6146
vib	510.0320
vib	757.1732
vib	853.1157
vib	907.7255
vib	1090.9565
vib	1196.7926
vib	1344.2711
vib	1415.6175
vib	1440.8948
vib	1460.6680
vib (a)	1750.8745
vib	3055.9441
vib	3146.6559
vib	3612.5218
vib	3718.0126
Rotational constants (cm^{-1})	
A	0.33588
B	0.16571
C	0.12273

[a)] This mode, corresponding to the H–CH_2OOH stretch in TS2, has unreliable anharmonic constants and is therefore treated separately as a harmonic oscillator

Anharmonic constants (cm-1)

7 7	-118.5688
7 8	-10.6667i
7 9	46.2924i
7 10	24.8250i
7 11	96.4394i
7 12	17.3963i
7 13	23.3338i
7 14	163.2716i

7 15 -1.6721i
7 16 -90.6746i
7 17 17.6839i
7 18 5.4862i
7 19 -54.1304i
7 20 -25.8624i
7 21 -21.8643i
7 22 11.3981i
7 23 -978.9088i
7 24 -1.1128i
7 25 14.5294i
7 26 -45.3860i
7 27 14.6210i
8 8 -6.3258
8 9 -6.0077
8 10 -15.5903
8 11 0.2450
8 12 -2.8258
8 13 -28.1368
8 14 2.5601
8 15 0.0845
8 16 18.1713
8 17 -1.5333
8 18 1.0745
8 19 2.9623
8 20 -2.4111
8 21 -2.9063
8 22 -9.2077
8 23 -46.5938
8 24 0.4761
8 25 -0.0372
8 26 16.6243
8 27 1.0896
9 9 -1.0011
9 10 -4.6755
9 11 1.8601
9 12 -3.2615
9 13 -12.1529
9 14 2.4448
9 15 -0.6732
9 16 -16.6442
9 17 -0.3377
9 18 -1.4271
9 19 -6.7896
9 20 -24.5451
9 21 -4.3104
9 22 -4.5809
9 23 1.3897
9 24 0.2255
9 25 0.8876
9 26 10.3532

9 27	0.5439
10 10	-8.6192
10 11	-1.0864
10 12	-2.2171
10 13	-35.3643
10 14	6.9842
10 15	-0.8451
10 16	-3.6697
10 17	-0.4825
10 18	0.5786
10 19	-0.9316
10 20	-1.3107
10 21	-1.7927
10 22	-9.0452
10 23	-38.8414
10 24	0.3780
10 25	0.6099
10 26	24.9036
10 27	-1.7204
11 11	-5.6923
11 12	-1.0481
11 13	-1.0434
11 14	10.5857
11 15	-0.3656
11 16	-14.4767
11 17	1.2107
11 18	-3.2108
11 19	-4.3721
11 20	1.1734
11 21	5.1531
11 22	1.7865
11 23	-21.4175
11 24	-0.5014
11 25	-0.7960
11 26	2.1839
11 27	1.4546
12 12	-0.2524
12 13	-10.5780
12 14	-0.8409
12 15	-2.9730
12 16	-12.3212
12 17	-1.9104
12 18	-0.9133
12 19	-1.1099
12 20	3.2221
12 21	-0.8695
12 22	-2.4397
12 23	-1.9738
12 24	-0.5430
12 25	-0.9320
12 26	3.6576

12 27 -0.1102
13 13 -42.0564
13 14 0.2069
13 15 -1.4200
13 16 4.0181
13 17 -2.7039
13 18 2.1689
13 19 -2.4230
13 20 0.5877
13 21 -3.5943
13 22 -19.9993
13 23 -68.8371
13 24 0.2769
13 25 -0.2291
13 26 54.7839
13 27 1.5721
14 14 3.1341
14 15 -1.2335
14 16 -33.8255
14 17 2.7331
14 18 5.5299
14 19 -6.0680
14 20 3.4650
14 21 -4.5053
14 22 1.8209
14 23 -62.0245
14 24 -0.5028
14 25 1.4081
14 26 -9.2741
14 27 -8.7522
15 15 -1.7033
15 16 1.9844
15 17 -2.3706
15 18 -1.6469
15 19 -0.3474
15 20 -1.9441
15 21 -2.5809
15 22 -9.7563
15 23 4.3355
15 24 -0.5045
15 25 -1.4262
15 26 -1.7111
15 27 -0.2050
16 16 46.8462
16 17 -5.3615
16 18 -4.5381
16 19 34.8593
16 20 -4.8562
16 21 11.9813
16 22 -1.9806
16 23 436.4961

16 24	1.5012
16 25	-5.8731
16 26	6.8134
16 27	-7.0636
17 17	-7.1708
17 18	-6.4800
17 19	-7.7857
17 20	-3.8845
17 21	-4.7416
17 22	-4.2229
17 23	-24.8984
17 24	-0.7672
17 25	-2.7720
17 26	3.2746
17 27	0.3920
18 18	-1.1974
18 19	-4.6334
18 20	-0.0085
18 21	-7.7125
18 22	-1.9594
18 23	-8.1665
18 24	-8.8120
18 25	-5.5705
18 26	-1.9045
18 27	-0.2390
19 19	-3.2567
19 20	-2.9418
19 21	-0.0597
19 22	0.0860
19 23	48.6586
19 24	-0.9721
19 25	-14.2872
19 26	1.4655
19 27	-2.1222
20 20	-1.1388
20 21	-4.2493
20 22	-7.3199
20 23	-6.8701
20 24	-5.1487
20 25	-5.3264
20 26	-2.9232
20 27	-0.9406
21 21	-5.0816
21 22	-12.8228
21 23	22.7741
21 24	-7.3463
21 25	-14.8108
21 26	1.2269
21 27	-0.6833
22 22	-10.1845
22 23	-23.1598

22 24	-2.7012
22 25	-6.7736
22 26	2.8074
22 27	0.3280
23 23	169.8470
23 24	-2.3764
23 25	-9.2299
23 26	72.4547
23 27	-14.6926
24 24	-34.7513
24 25	-112.8755
24 26	-1.2113
24 27	-0.2295
25 25	-37.6713
25 26	-0.9077
25 27	0.1788
26 26	-118.8690
26 27	-2.3147
27 27	-87.3310

Table S1: Relative energies (ΔE, kcal mol^{-1}) and rovibrational parameters of grid points along the (variational) reaction coordinate: OH + $CH_3OOH \rightarrow$ PRC1*

	RC = 3.25 Å	3.5	3.75	4	4.25	4.5	4.75	5	5.25	5.5
vib	53.9899	48.3897	43.8391	30.1214	21.2453	18.6635	30.2263	26.7869	23.7657	21.4999
vib	134.9467	97.8482	79.8115	38.6061	40.2460	85.6252	61.3893	49.9414	42.3061	47.1363
vib	157.3351	139.3960	128.6913	110.5311	83.6964	243.1684	220.4599	207.4286	189.8928	181.8112
vib	248.1631	241.0567	198.7739	209.6619	217.1599	257.5112	254.6957	253.8230	235.0774	190.8880
vib	315.0733	274.0600	258.4927	258.4857	258.8320	342.7006	313.1105	256.2177	249.1297	244.3112
vib	427.8135	432.7611	436.4409	434.4561	372.5554	376.8555	323.1292	309.9147	269.3689	255.1805
vib	449.4792	468.6694	516.5371	465.3288	441.2517	438.0764	437.1502	436.9296	436.8987	437.9123
vib	804.3184	805.5602	806.3876	807.3827	804.2420	796.9900	796.0434	795.6324	797.1777	798.7796
vib	1020.2037	1022.9688	1023.1897	1022.8602	1020.9930	1011.2900	1012.2112	1013.4666	1014.5430	1015.2135
vib	1157.3479	1156.7774	1156.3569	1155.9013	1155.6342	1155.8447	1155.8393	1155.5032	1155.4819	1155.5817
vib	1190.1260	1190.4461	1190.6876	1190.5885	1189.7858	1187.7888	1188.1252	1188.1606	1188.2936	1188.5756
vib	1416.2404	1409.9689	1384.2698	1369.7169	1350.4884	1342.5095	1343.9245	1342.9526	1343.2636	1343.8466
vib	1428.0353	1427.4975	1427.1068	1426.6938	1426.7861	1428.0609	1427.9069	1427.6946	1427.6581	1427.7684
vib	1446.7202	1446.2115	1446.0938	1446.1745	1446.1332	1446.0294	1445.8934	1445.9372	1446.0150	1446.1069
vib	1489.2959	1488.8470	1488.4921	1487.9617	1487.9901	1488.3485	1488.0919	1488.1006	1488.0404	1488.0273
vib	3015.1971	3013.1557	3012.4614	3012.2500	3013.1306	3019.1285	3018.4043	3017.6809	3017.1885	3016.8911
vib	3102.2490	3098.4670	3097.1994	3096.6584	3097.9171	3107.5859	3106.4569	3105.2141	3104.2815	3103.8250
vib	3123.0766	3120.7695	3120.4291	3121.1640	3122.4524	3129.9198	3128.8948	3128.0430	3127.6404	3127.4623
vib	3642.9064	3660.6441	3669.6211	3672.8738	3672.5236	3627.2652	3635.6673	3644.6892	3653.6526	3661.3795
vib	3669.0679	3674.4726	3683.6216	3699.7968	3716.2562	3742.3613	3742.8057	3742.6380	3742.0372	3741.5466
A	0.4257	0.4848	0.5600	0.6527	0.7619	0.6838	0.6753	0.6905	0.6792	0.6274
B	0.1009	0.0888	0.0792	0.0727	0.0670	0.0638	0.0593	0.0548	0.0500	0.0455
C	0.0894	0.0822	0.0760	0.0707	0.0656	0.0616	0.0568	0.0524	0.0479	0.0438
ΔE	0.0915	0.5360	0.8820	1.0778	1.3480	1.5695	1.7911	2.3247	2.7699	3.1282

Table S1: (Continued)

RC = 5.75 Å	6	6.25	6.5	6.75	7	7.25	7.5	7.75	8
20.2831	18.6319	17.0818	15.6864	14.4275	13.3819	12.2217	11.0109	10.5118	9.8251
31.7351	27.5767	26.3200	22.4472	20.7798	18.5365	15.7556	13.9126	12.6567	11.4878
153.7343	138.4774	132.4768	120.0161	108.9703	96.7236	88.0959	80.7824	74.5983	69.2271
191.3966	170.0738	139.3157	127.0739	116.4693	113.7687	103.7073	95.3464	88.1355	81.7631
229.5432	226.3661	225.0253	222.2366	221.1204	219.4534	217.7338	216.7737	215.9748	215.3335
256.1800	255.5043	254.9328	254.7538	254.6247	254.5786	254.4901	254.4054	254.3559	254.3112
437.3670	437.4823	437.6164	437.6506	437.7107	437.7155	437.7330	437.7641	437.7685	437.7840
799.9114	800.7511	801.4502	801.8327	802.1180	802.2575	802.4833	802.6439	802.7817	802.8867
1015.9699	1016.4273	1016.6651	1016.9651	1017.2139	1017.4690	1017.6437	1017.7789	1017.8913	1017.9907
1155.5694	1155.6221	1155.6845	1155.7192	1155.7513	1155.7770	1155.8106	1155.8312	1155.8460	1155.8610
1188.6523	1188.7230	1188.7864	1188.7870	1188.7891	1188.7483	1188.7448	1188.7395	1188.7332	1188.7274
1343.6289	1343.7742	1343.9227	1343.9548	1344.0457	1344.0759	1344.1204	1344.1690	1344.2032	1344.2470
1427.7064	1427.7434	1427.8145	1427.8179	1427.8218	1427.8002	1427.8119	1427.8153	1427.7978	1427.8428
1446.1542	1446.1883	1446.2058	1446.2142	1446.2230	1446.2259	1446.2313	1446.2339	1446.2354	1446.2363
1488.0726	1488.1174	1488.1627	1488.1963	1488.2264	1488.2461	1488.2638	1488.2810	1488.2977	1488.3138
3016.5617	3016.3729	3016.2669	3016.1382	3016.0241	3015.9220	3015.8407	3015.7787	3015.7272	3015.6911
3103.1325	3102.7883	3102.6144	3102.3887	3102.1968	3102.0170	3101.8877	3101.7924	3101.7183	3101.6571
3127.1022	3126.8982	3126.7789	3126.6142	3126.4687	3126.3277	3126.2220	3126.1347	3126.0610	3125.9973
3667.0929	3671.0822	3673.9526	3676.0973	3677.7459	3678.8053	3679.9366	3680.7031	3681.2483	3681.6588
3741.4226	3741.4019	3741.3923	3741.4150	3741.4122	3741.5074	3741.5565	3741.6078	3741.6585	3741.7253
0.6663	0.6570	0.5902	0.5786	0.5673	0.6023	0.5885	0.5745	0.5591	0.5472
0.0417	0.0383	0.0354	0.0328	0.0304	0.0282	0.0262	0.0244	0.0228	0.0213
0.0403	0.0372	0.0344	0.0319	0.0296	0.0276	0.0257	0.0240	0.0224	0.0209
3.3639	3.5413	3.6653	3.7552	3.8253	3.8813	3.9151	3.9430	3.9665	3.9848

Table S2: Relative energies (ΔE, kcal mol^{-1}) and rovibrational parameters of grid points along the (variational) reaction coordinate: OH + $CH_3OOH \rightarrow$ PRC2*

	RC = 3.0 Å	3.2	3.4	3.6	3.8
vib	31.6779	53.2711	32.3123	55.3550	47.4821
vib	92.4535	77.3989	59.2364	83.5554	86.3226
vib	261.1210	247.2116	241.6330	227.7970	226.6496
vib	279.4924	280.1503	273.1638	276.9271	256.1631
vib	436.9019	395.4549	362.6588	315.9241	288.1478
vib	483.2664	429.4635	384.9325	345.5111	314.6925
vib	511.8196	450.3226	441.0910	442.7155	441.6694
vib	800.7182	801.2398	800.9711	802.0377	801.9177
vib	1009.5514	1013.2682	1015.3547	1016.4990	1018.1279
vib	1167.5699	1153.2300	1153.4991	1150.5032	1131.5124
vib	1188.4929	1190.1671	1188.0147	1190.8653	1190.7739
vib	1341.7861	1343.0928	1344.1985	1344.8795	1345.0105
vib	1432.9870	1431.2634	1428.4565	1429.5016	1427.3548
vib	1484.5049	1453.6454	1454.3106	1451.0882	1443.9511
vib	1496.9421	1499.1054	1503.7589	1508.0253	1504.5041
vib	3022.1841	3018.2694	3017.3911	3017.6607	3014.9295
vib	3124.8758	3104.2273	3099.5656	3094.9880	3082.7543
vib	3136.6102	3131.5662	3131.9415	3129.7635	3130.6510
vib	3602.2265	3613.6463	3623.8742	3633.7280	3644.2483
vib	3738.4601	3739.7978	3740.6608	3741.2802	3741.8580
A (cm^{-1})	0.3505	0.3467	0.3437	0.3423	0.3434
B	0.1172	0.1075	0.0998	0.0931	0.0873
C	0.0901	0.0840	0.0790	0.0747	0.0710
ΔE (kcal mol^{-1})	0.0000	0.1200	0.4947	0.9908	1.3329

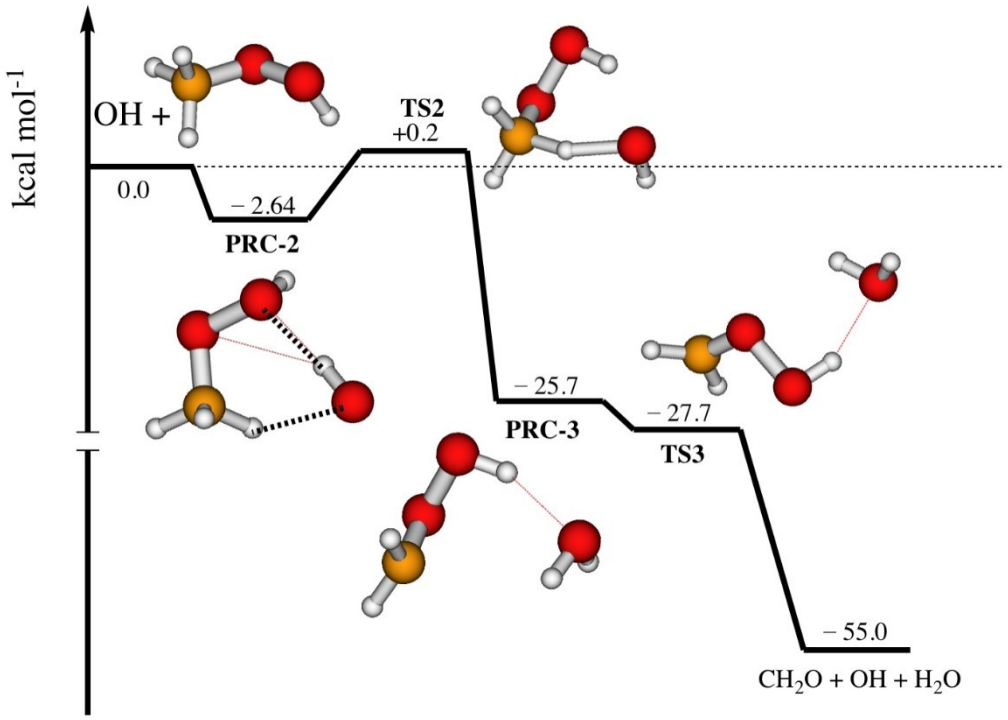

Fig. S1: Unscaled potential energy surface for the H-abstraction pathway at a αH-atom of the CH_3 group of CH_3OOH, constructed using the amHEAT-345(Q) method.

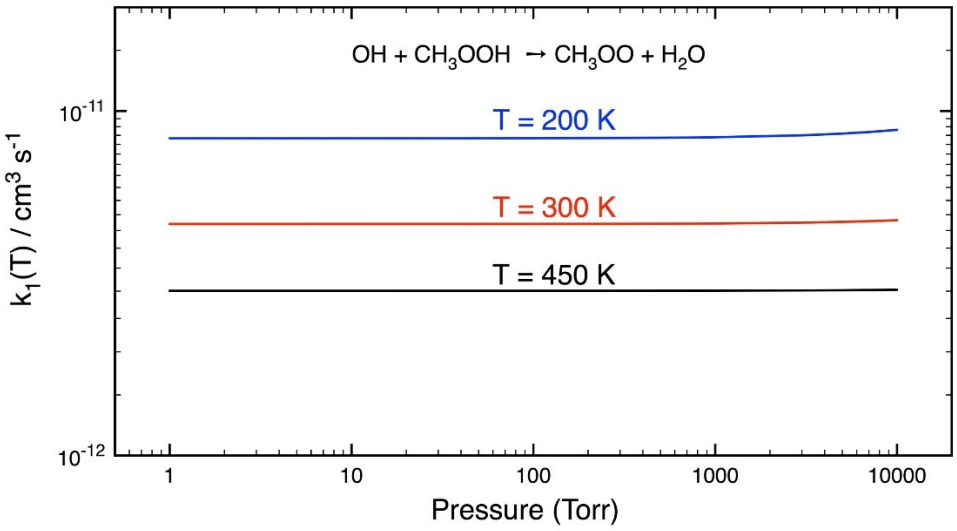

Fig. S2: Fall-off curves for the OH + $CH_3OOH \rightarrow CH_3OO + H_2O$ pathway, calculated as functions of temperature and pressure.

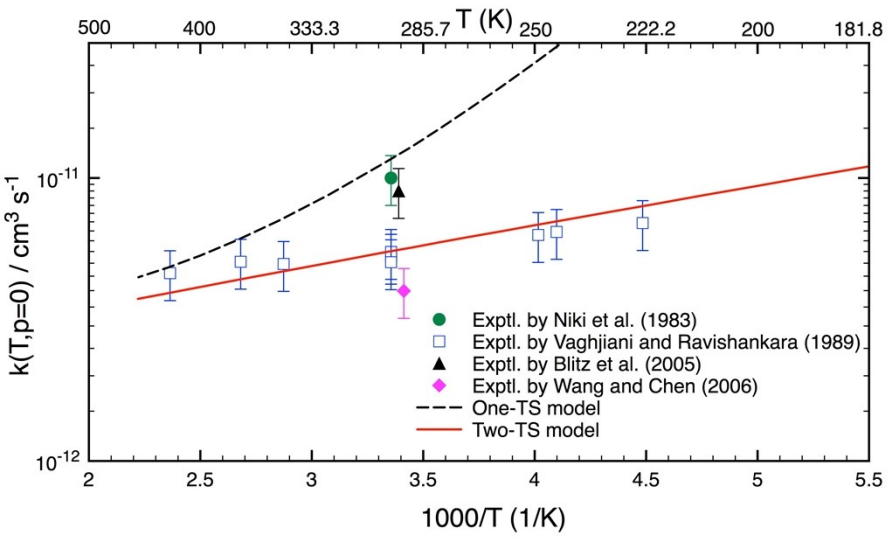

Figure S3: A comparison of the one-TS kinetic model and the two-TS kinetic model.

Table S3: Collisional parameters and energies are used in the E,J-resolved 2DME model.

Parameters	Values
N_2	Mass = 28.01 g/mol, σ = 3.7047 Å, ε/k_B = 84.942 K
CH_5O_3	Mass = 65.0 g/mol, σ = 5.46 Å, ε/k_B = 401 K
E_{max}	30,000 cm^{-1} above CH_5O_3 when $T \leq 500; 0\ K$
ΔE_{grain}	10 cm^{-1} when $T \leq 500\ K$
$\langle \Delta E_d \rangle$	$20\left(\frac{T}{300}\right)^{0.9}\ cm^{-1}$, for the fixed-J ME model $18\left(\frac{T}{300}\right)^{0.9}\ cm^{-1}$, for the E,J-resolved ME model
J_{max}	200 with $T \leq 500\ K$
ΔJ	5

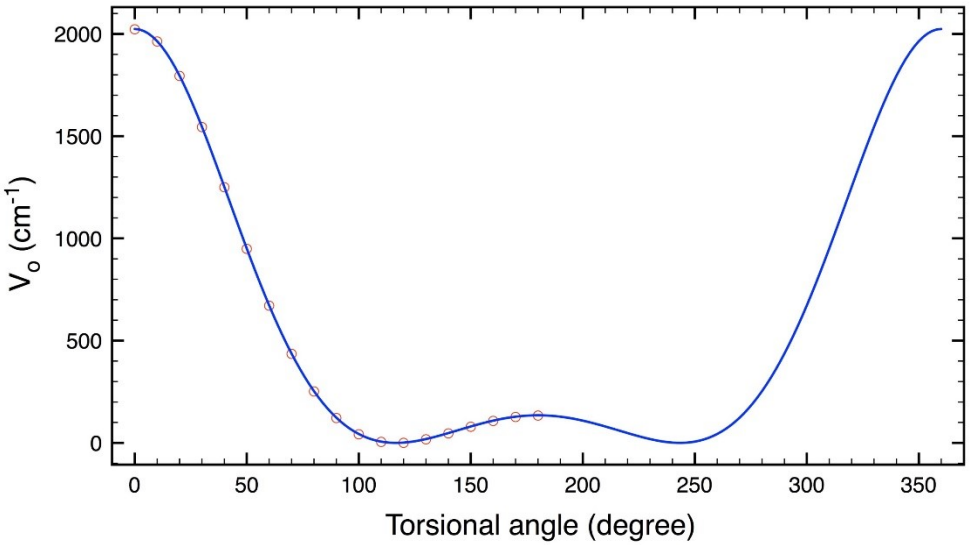

Fig. S4: Torsional potential energy (cm^{-1}),

$$V(\theta) = 583.7 + 849.743\cos(\theta) + 477.487\cos(2\theta) + 91.231\cos(3\theta) + 17.6154\cos(4\theta) + 3.68253\cos(5\theta) + 0.675265\cos(6\theta),\ \theta\ in\ rad$$

, as a function of the torsional dihedral angle, ∠HOOC in CH_3OOH, calculated at fc-CCSD(T)/aug-cc-pVTZ level of theory.

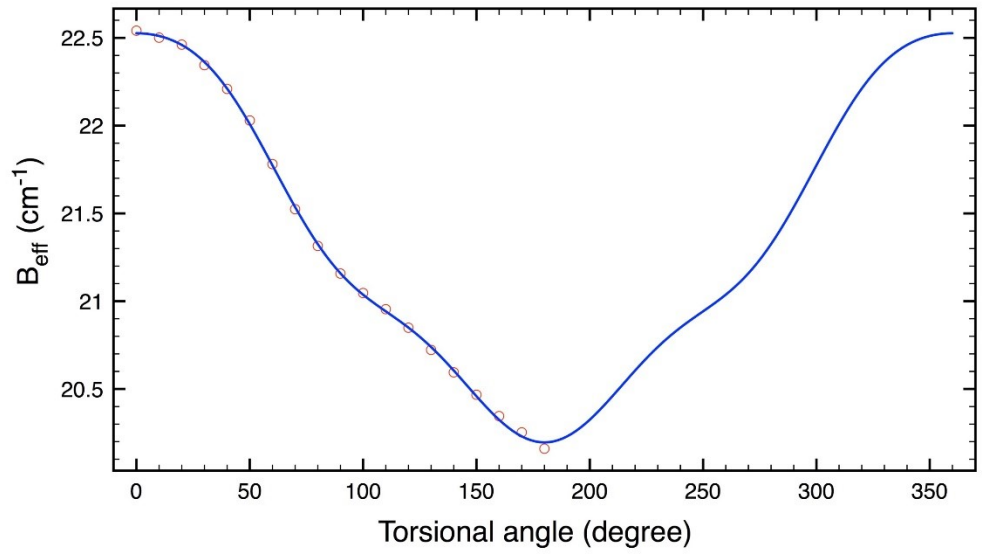

Fig. S5: Effective rotational constant (cm^{-1}),

$$B_{eff}(\theta) = 21.3275 + 1.09194\cos(\theta) + 0.100323\cos(2\theta) + 0.0802694\cos(3\theta) - 0.0675463\cos(4\theta) - 0.0\cos(5\theta) + 0.00071675\cos(6\theta),\ \theta\ in\ rad$$

, as a function of the torsional dihedral angle, ∠HOOC in CH_3OOH, calculated at fc-CCSD(T)/aug-cc-pVTZ level of theory.

List of eigenvalues (cm^{-1}) for 1DHR with the torsional dihedral angle, ∠HOOC in CH_3OOH:

1	75.6270181972906
2	90.3260263764187
3	196.523350235676
4	281.814563346696
5	394.143067260202
6	517.511211000539
7	651.100512938799
8	792.625620557009
9	940.462323131874
10	1093.17355940034
11	1249.13225842406
12	1407.57026932762
13	1563.68228278988
14	1725.55863072864
15	1855.88271315338
16	2045.68207117911
17	2098.83586139822
18	2387.21171350578
19	2394.98402287398
20	2771.77567321435
21	2772.46496197221
22	3204.74384482189
23	3204.79274786983
24	3684.63017631727
25	3684.63315822797
26	4209.86572641677
27	4209.86588789967
28	4779.51189088640
29	4779.51189880768
30	5393.01082747935
31	5393.01082783593
32	6050.01200275167
33	6050.01200276627
34	6750.28386777755
35	6750.28386777793
36	7493.66732958988
37	7493.66732959009
38	8280.04958149238
39	8280.04958149249
40	9109.34853834079
41	9109.34853834103
42	9981.50315442849
43	9981.50315442862
44	10896.4671758169
45	10896.4671758170
46	11854.2049834597

47 11854.2049834600
48 12854.6887543447
49 12854.6887543449
50 13897.8964785363
51 13897.8964785364
52 14983.8105464502
53 14983.8105464503
54 16112.4167246456
55 16112.4167246457
56 17283.7034016201
57 17283.7034016203
58 18497.6610245913
59 18497.6610245913
60 19754.2816735236
61 19754.2816735238
62 21053.5587352217
63 21053.5587352221
64 22395.4866513262
65 22395.4866513263
66 23780.0607215539
67 23780.0607215542
68 25207.2769486920
69 25207.2769486922
70 26677.1319154606
71 26677.1319154606
72 28189.6226859406
73 28189.6226859408
74 29744.7467260930
75 29744.7467260932
76 31342.5018392421
77 31342.5018392422

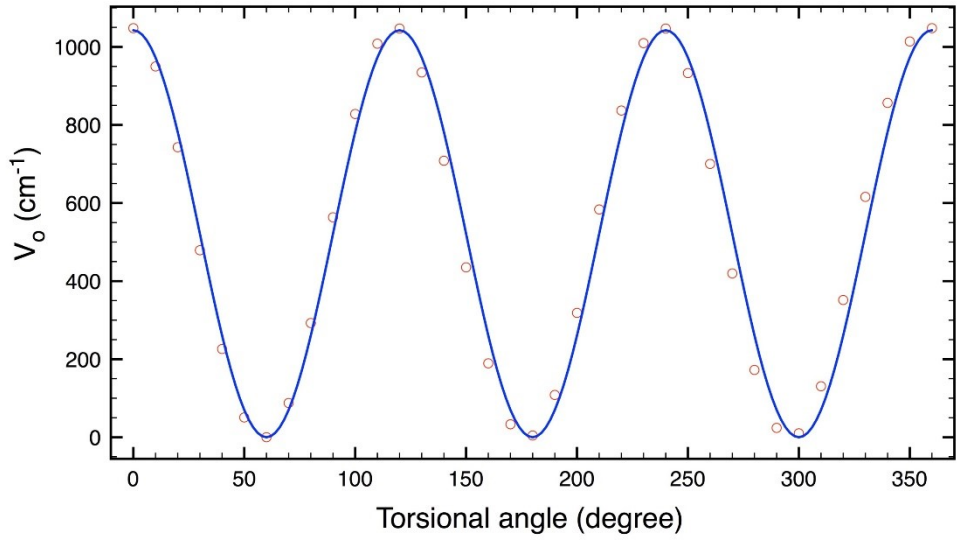

Fig. S6: Torsional potential energy (cm^{-1}), $V(\theta) = 521.287 + 521.287\cos(3\theta), \theta\ in\ rad$, as a function of the torsional dihedral angle, ∠HCOO in CH_3OOH, calculated at fc-CCSD(T)/aug-cc-pVTZ level of theory.

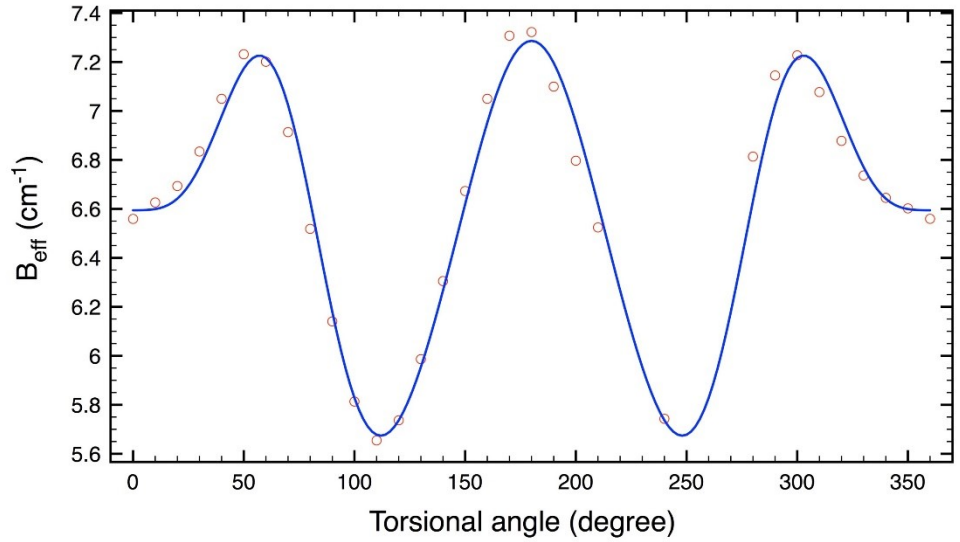

Fig. S7: Effective rotational constant (cm^{-1}),

$$B_{eff}(\theta) = 6.57699 + 0.174864\cos(\theta) + 0.326404\cos(2\theta) - 0.608597\cos(3\theta) - 0.0171895\cos(4\theta) + 0.0\cos(5\theta) + 0.0541331\cos(6\theta), \theta\ in\ rad$$

, as a function of the torsional dihedral angle, ∠HCOO in CH_3OOH, calculated at fc-CCSD(T)/aug-cc-pVTZ level of theory.

List of eigenvalues (cm^{-1}) for 1DHR with the torsional dihedral angle, ∠HCOO in CH_3OOH

1	123.482637004839
2	123.482734765220
3	124.511626231452
4	363.875130141331
5	363.880769426969
6	366.177605443605
7	582.225322245887
8	582.364092700877
9	586.018457048000
10	775.409171692808
11	776.957419646519
12	781.308535949279
13	930.364427525533
14	945.915004530029
15	948.547338258088
16	1053.60088848284
17	1055.23402977935
18	1122.00305434303
19	1148.59876922421
20	1244.01317498870
21	1244.74604156107
22	1370.78221526950
23	1370.88957792553
24	1513.41889381170
25	1513.78833065054
26	1671.43446086360
27	1671.45331110713
28	1843.68861479100
29	1843.69042901685
30	2029.95509156887
31	2029.95628020805
32	2229.99601826858
33	2229.99611195046
34	2443.64404673565
35	2443.64405416696
36	2670.78246137133
37	2670.78246304427
38	2911.32640441287
39	2911.32640458091
40	3165.21289233541
41	3165.21289234888
42	3432.39426701066
43	3432.39426701219
44	3712.83385757639
45	3712.83385757654
46	4006.50303527969
47	4006.50303527974

48 4313.37916299957
49 4313.37916299968
50 4633.44413719022
51 4633.44413719023
52 4966.68333187842
53 4966.68333187848
54 5313.08482141492
55 5313.08482141493
56 5672.63880013518
57 5672.63880013530
58 6045.33714344141
59 6045.33714344144
60 6431.17307196114
61 6431.17307196117
62 6830.14089184269
63 6830.14089184276
64 7242.23579197237
65 7242.23579197239
66 7667.45368421795
67 7667.45368421797
68 8105.79107652899
69 8105.79107652905
70 8557.24497136096
71 8557.24497136100
72 9021.81278378903
73 9021.81278378905
74 9499.49227505382
75 9499.49227505397
76 9990.28149829396
77 9990.28149829400
78 10494.1787539691
79 10494.1787539692
80 11011.1825530425
81 11011.1825530426
82 11541.2915864130
83 11541.2915864131
84 12084.5046994098
85 12084.5046994098
86 12640.8208704136
87 12640.8208704136
88 13210.2391928570
89 13210.2391928571
90 13792.7588600061
91 13792.7588600061
92 14388.3791520415
93 14388.3791520415
94 14997.0994250514
95 14997.0994250515
96 15618.9191016180
97 15618.9191016181
98 16253.8376627393

99	16253.8376627394
100	16901.8546408745
101	16901.8546408746
102	17562.9696139364
103	17562.9696139365
104	18237.1822000876
105	18237.1822000877
106	18924.4920532188
107	18924.4920532189
108	19624.8988590093
109	19624.8988590093
110	20338.4023314849
111	20338.4023314849
112	21065.0022100042
113	21065.0022100042
114	21804.6982566107
115	21804.6982566108
116	22557.4902537045
117	22557.4902537045
118	23323.3780019861
119	23323.3780019861
120	24102.3613186400
121	24102.3613186400
122	24894.4400357247
123	24894.4400357248
124	25699.6139987438
125	25699.6139987439
126	26517.8830653737
127	26517.8830653737
128	27349.2471043307
129	27349.2471043308
130	28193.7059943590
131	28193.7059943591
132	29051.2596233248
133	29051.2596233249
134	29921.9078874052
135	29921.9078874053
136	30805.6506903595
137	30805.6506903596

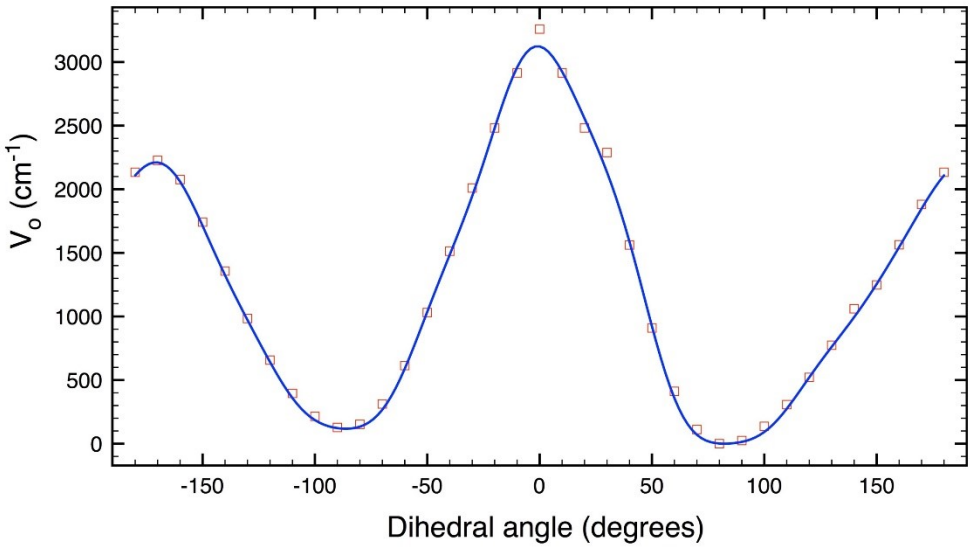

Fig. S8: Torsional potential energy (cm^{-1}),

$$V(\theta) = 1210.366 + 311.712\cos(\theta) + 1260.61\cos(2\theta) + 182.382\cos(3\theta) + 102.931\cos(4\theta) - 17.6955 + 13.2608\cos(6\theta) + 8.15387\cos(7\theta) + 28.487\cos(8\theta) + 22.7053\cos(9\theta) - 91.6507\sin(\theta) + 77.2507\sin(2\theta) - 42.4738\sin(3\theta) + 94.4265\sin(4\theta) - 21.6312\sin(5\theta) + 11.5739\sin(6\theta) - 32.1508\sin(7\theta) - 14.7979\sin(8\theta) - 15.41sin(9\theta),\ \theta\ in\ rad$$

, as a function of the torsional dihedral angle, ∠COOOH in **TS1**, calculated at fc-CCSD(T)/aug-cc-pVTZ level of theory.

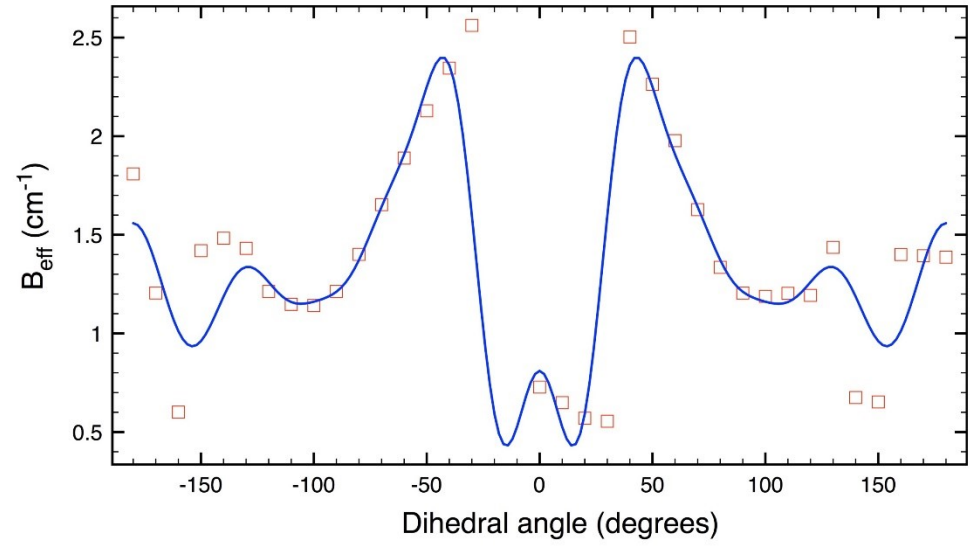

Fig. S9: Effective rotational constant (cm^{-1}),

$$B_{eff}(\theta) = 1.33718 + 0.109138\cos(\theta) - 0.207952\cos(2\theta) - 0.427485\cos(3\theta) - 0.336358\cos(4\theta) - 0.204\cos(5\theta) + 0.0969854\cos(6\theta) + 0.00337438\cos(7\theta) + 0.180567\cos(8\theta) + 0.087079\cos(9\theta) + 0.0974984\cos(10\theta) + 0.0577174\cos(11\theta) + 0.0163259\cos(12\theta),\ \theta\ in\ rad$$

, as a function of the torsional dihedral angle, ∠COOOH in **TS1**, calculated at fc-CCSD(T)/aug-cc-pVTZ level of theory.

List of eigenvalues (cm^{-1}) for 1DHR with the torsional dihedral angle, ∠COOOH in TS1b

1	38.9823524715608
2	120.582291133320
3	159.576697018413
4	213.193742418202
5	246.405063852239
6	310.627601163344
7	341.546290482596
8	410.157749360313
9	441.043960601990
10	510.033589209126
11	542.908113346252
12	609.034033443731
13	645.865623613807
14	706.329554868179
15	749.022786365376
16	801.482278365599
17	851.730072792490
18	894.443367132008
19	953.527246203393
20	985.423113659317
21	1054.11599203890
22	1074.67159822198
23	1153.32996216747
24	1162.34654024570
25	1248.53167060628
26	1251.09128804919
27	1333.31154058940
28	1347.36257861471
29	1416.81767032095
30	1442.11116119841
31	1499.22782010905
32	1535.29219230731
33	1580.73152667071
34	1626.84282086163
35	1661.48332784256
36	1716.67547002296
37	1741.56192197854

38 1804.66342063845
39 1820.94207110391
40 1890.61561281812
41 1899.47361434272
42 1974.22771185175
43 1976.85282137900
44 2052.44478830286
45 2055.05798297731
46 2124.80437110861
47 2132.39734256854
48 2190.21250963565
49 2206.97490214876
50 2252.18754649530
51 2281.65184011514
52 2321.63037960928
53 2357.95910402130
54 2397.19027299877
55 2435.84332539508
56 2475.26115249167
57 2514.60869870603
58 2554.08520398698
59 2593.44882167016
60 2632.67667589097
61 2671.67172254060
62 2710.38996156943
63 2748.78669602013
64 2786.84276999035
65 2824.53025610775
66 2861.88593349962
67 2898.77148750553
68 2935.51923121083
69 2971.12738733133
70 3007.86805054841
71 3039.84710745184
72 3079.52410494734
73 3101.19872462821
74 3152.03994169810
75 3160.47475242286
76 3227.38508164553
77 3229.57078229637
78 3306.69580975201
79 3307.20260717157
80 3390.12027733245
81 3390.23668047368
82 3477.40900244609
83 3477.43619034414
84 3568.27907512625
85 3568.28559024153
86 3662.50539730847
87 3662.50700422561
88 3759.91987376720

89 3759.92028187680
90 3860.39608058286
91 3860.39618723090
92 3963.83665201325
93 3963.83668067287
94 4070.16474414152
95 4070.16475203496
96 4179.31840507375
97 4179.31840730358
98 4291.24679456782
99 4291.24679521290
100 4405.90757086754
101 4405.90757105664
102 4523.26503103371
103 4523.26503109106
104 4643.28875219569
105 4643.28875221325
106 4765.95257573412
107 4765.95257573934
108 4891.23383262591
109 4891.23383262824
110 5019.11274241485
111 5019.11274241883
112 5149.57193982063
113 5149.57193982347
114 5282.59609689157
115 5282.59609690152
116 5418.17161789018
117 5418.17161792167
118 5556.28639031468
119 5556.28639034292
120 5696.92957971881
121 5696.92957977182
122 5840.09145934251
123 5840.09145954251
124 5985.76326766832
125 5985.76326787757
126 6133.93708777526
127 6133.93708805614
128 6284.60574521472
129 6284.60574654481
130 6437.76272251546
131 6437.76272443141
132 6593.40208353755
133 6593.40208370761
134 6751.51840285176
135 6751.51840901375
136 6912.10672492342
137 6912.10673673897
138 7075.16250859892
139 7075.16251346378

140 7240.68155588844
141 7240.68158286813
142 7408.66002561070
143 7408.66009877865
144 7579.09440798617
145 7579.09448592758
146 7751.98143241264
147 7751.98147309989
148 7927.31790597897
149 7927.31819871768
150 8105.10119921305
151 8105.10167374205
152 8285.32891948472
153 8285.32906864706
154 8467.99779044338
155 8467.99881492978
156 8653.10582881230
157 8653.10842711671
158 8840.65200784438
159 8840.65482666729
160 9030.63493313296
161 9030.63559089590
162 9223.04676289534
163 9223.05486756790
164 9417.89104202082
165 9417.90535545563
166 9615.17133826347
167 9615.17966016122
168 9814.87141068108
169 9814.89052219522
170 10016.9831142698
171 10017.0436795582
172 10221.5320915221
173 10221.6126451919
174 10428.5441093437
175 10428.5713950497
176 10637.9083754038
177 10638.0282555720
178 10849.6567833608
179 10849.9433242718
180 11063.9027664233
181 11064.1879180427
182 11280.6529535055
183 11280.7374740268
184 11499.3433641402
185 11500.1531253401
186 11720.4906441500
187 11721.9484534748
188 11944.5046302823
189 11945.7526561288
190 12171.2704178725

191 12171.6774330673
192 12398.7067188831
193 12401.7737259638
194 12628.9933152426
195 12633.7781936170
196 12863.3230839769
197 12866.1069472493
198 13097.8031154748
199 13102.1657261442
200 13330.5977711672
201 13344.5031041021
202 13568.8266338107
203 13587.5065616997
204 13815.6510717911
205 13826.8974594253
206 14060.8235706811
207 14070.6952578222
208 14296.8450276668
209 14330.5128270185
210 14545.6359009634
211 14586.8958936971
212 14808.9009353990
213 14819.3322051958
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