Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Supplementary Material

Ab Initio Rate Coefficients for the Reaction of OH and H_2O_2 under Upper Troposphere and Lower Stratosphere Conditions

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Table S1. A comparison of relative energies (kcal/mol) of various species in the OH + H_2O_2 reaction reported in the literature and obtained with amHEAT-345(Q) level of theory in this work.

Species	amHEAT [a)]	CASPT2 [b)]	CCSD(T)/6-31G* [c)]	MPW1K [d)]	CCSD(T)/CBS [e)]
OH + H_2O_2	0.00	0.0	0.0	0.0	0.0
PRC	-3.60	-3.7	-8.4	-4.4	-3.9
TS1	+0.75	-0.9	+4.9	+0.1	+1.2
PPC	-38.22	n/a	n/a	-38.3	-38.0
H_2O + HO_2	-31.48	-31.4	-34.3	-30.7	-31.4

a) This work.
b) From ref. (Bahri et al., 2003).
c) From ref. (Atadinc et al., 2005).
d) From ref. (Ginovska et al., 2007).
e) From ref. (Buszek et al., 2012).

Bahri, M., Tarchouna, Y., Jaidane, N., Ben Lakhdar, Z., and Flament, J. P.: Ab initio study of the hydrogen abstraction reaction H_2O_2+OH -> HO_2+H_2O, J Mol Struc-Theochem, 664, 229-236, 10.1016/j.theochem.2003.09.007, 2003.

Atadinc, F., Gunaydin, H., Ozen, A. S., and Aviyente, V.: A quantum mechanical approach to the kinetics of the hydrogen abstraction reaction H_2O_2+OH -> HO_2+H_2O, Int J Chem Kinet, 37, 502-514, 10.1002/kin.20102, 2005.

Ginovska, B., Camaioni, D. M., and Dupuis, M.: Reaction pathways and excited states in H_2O_2+OH -> HO_2+H_2O: A new ab initio investigation, J Chem Phys, 127, Artn 084309
10.1063/1.2755765, 2007.

Buszek, R. J., Torrent-Sucarrat, M., Anglada, J. M., and Francisco, J. S.: Effects of a Single Water Molecule on the OH+H_2O_2 Reaction, J Phys Chem A, 116, 5821-5829, 10.1021/jp2077825, 2012.

Table S2. Collisional parameters and energies are used in the E,J-resolved 2DME model.

Parameters	Values
Air (N_2:O_2=4:1)	Mass = 28.8 g/mol, σ = 3.668 Å, ε/k_B = 86.2 K [1-2)]
H_3O_3	Mass = 51 g/mol, σ = 4.08 Å, ε/k_B = 421 K [1-2)]
E_{max}	30,000 cm^{-1} above H_3O_3 when $T \leq 5\ 0\ ;0\ \ K$
ΔE_{grain}	10 cm^{-1} when $T \leq 5\ 0\ 0\ \ K$
$\langle \Delta E_d \rangle$	$2\ \ 2\left(\frac{T}{3\ 0\ 0}\right)^{0\ \cdot}(9\ \ 5\ \bar{l}\ \bar{d}\ \bar{n}\ \bar{m}^{1})$, for the fixed-J ME model $2\ \ 2\left(\frac{T}{3\ 0\ 0}\right)^{0\ \cdot}(9\ \ 5\ \bar{l}\ \bar{d}\ \bar{n}\ \bar{m}^{1})$, for the E,J-resolved ME model
J_{max}	200 with $T \leq 5\ 0\ 0\ \ K$
ΔJ	5 for T ≥ 200 K; and 2 for T < 200 K

1) From Hippler et al.(Hippler et al., 1983)
2) From the Multiwell software package.(Barker et al., Jan. 2022)

Hippler, H., Troe, J., and Wendelken, H. J.: Collisional Deactivation of Vibrationally Highly Excited Polyatomic-Molecules .3. Direct Observations for Substituted Cycloheptatrienes, J Chem Phys, 78, 6718-6724, Doi 10.1063/1.444671, 1983.

Barker, J. R., Nguyen, T. L., Stanton, J. F., Aieta, C., Ceotto, M., Gabas, F., Kumar, T. J. D., Li, C. G. L., Lohr, L. L., Maranzana, A., Ortiz, N. F., Preses, J. M., Simmie, J. M., Sonk, J. A., and Stimac, P. J.: MULTIWELL Program Suite, in, Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI 48109-2143. , Jan. 2022.

Table S3. Calculated relative energies (kcal/mol) and ro-vibrational parameters of grid geometries along the barrier-less association of OH and H_2O_2 leading to PRC.

Type of mode	OH—H_2O_2 = 4.50 Å	4.75 Å	5.00 Å	5.25 Å	5.50 Å
IMAG	40.7714	35.1540i	46.8227i	45.1677i	39.7626i
vib	68.3256	59.0471	54.6751	46.9005	39.5815
vib	80.5695	72.0093	70.4167	61.0524	50.2346
vib	302.9196	267.0282	234.3111	203.8667	178.3994
vib	388.7760	340.1727	289.5646	247.3645	213.7562
vib	408.4206	394.8521	394.1622	392.7085	390.9095
vib	895.1889	892.6494	892.4796	893.3696	894.3325
vib	1324.5713	1324.5855	1324.5817	1324.5931	1324.4141
vib	1426.8430	1425.7949	1425.5042	1425.4838	1425.4149
vib	3695.3271	3703.1851	3711.0959	3718.7860	3724.9716
vib	3798.6746	3799.5596	3800.3774	3800.9773	3801.4422
vib	3802.6842	3803.0334	3803.0387	3803.0328	3803.0625
A (cm^{-1})	2.9948	3.3422	3.3515	3.1892	2.9533
B (cm^{-1})	0.0937	0.0838	0.0750	0.0674	0.0609
C (cm^{-1})	0.0919	0.0825	0.0740	0.0665	0.0600
Rel. E (kcal/mol)	1.1832	1.7161	2.2283	2.6139	2.8913

(**To be continued**)

Table S3. (Continued)

Type of mode	5.75 Å	6.00 Å	6.25 Å	6.50 Å	6.75 Å
IMAG	33.9915i	28.5906i	24.0503i	20.3427i	17.4266i
vib	35.9778	31.8349	26.6077	23.2697	21.8965
vib	54.9320	50.3715	47.1529	43.6634	41.8316
vib	156.9454	139.8368	124.0547	111.3463	98.9606
vib	186.6366	166.0136	147.6793	132.2352	120.2337
vib	391.9473	390.7913	390.2570	389.3720	387.9523
vib	895.1191	895.6271	896.0770	896.4025	896.5556
vib	1324.3946	1324.0853	1323.8613	1323.6207	1323.2317
vib	1425.5515	1425.5354	1425.6229	1425.6999	1425.6933
vib	3729.6539	3732.6606	3735.3416	3737.3534	3738.5638
vib	3801.8545	3802.1335	3802.4333	3802.7048	3802.8695
vib	3803.1738	3803.2250	3803.3684	3803.4888	3803.5553
A (cm^{-1})	2.6970	2.4356	2.2238	2.0377	1.8705
B (cm^{-1})	0.0551	0.0501	0.0457	0.0419	0.0385
C (cm^{-1})	0.0544	0.0494	0.0451	0.0412	0.0379
Rel. E (kcal/mol)	3.1147	3.2602	3.3595	3.4306	3.4832

(To be continued)

Table S3. (Continued)

Type of mode	7.00 Å	7.25 Å	7.50 Å	7.75 Å	8.00 Å
IMAG	14.8451i	12.9891i	11.3910i	10.0293i	8.9579i
vib	19.4098	21.4436	13.1904	13.2439	11.4684
vib	41.3047	37.5877	31.9898	32.9408	30.0673
vib	97.9466	87.1622	73.9034	74.3942	65.7912
vib	114.9041	104.0326	90.7500	87.8867	79.9498
vib	387.7356	387.0591	386.2042	385.6309	385.0783
vib	896.5110	896.6874	896.9430	896.8722	896.9706
vib	1323.0037	1322.8160	1322.6668	1322.4178	1322.2744
vib	1425.8091	1425.9430	1426.0522	1426.1446	1426.2580
vib	3738.3445	3739.5516	3741.1893	3740.9040	3741.5885
vib	3802.9097	3803.1254	3803.4048	3803.4313	3803.5985
vib	3803.4556	3803.6131	3803.7875	3803.7572	3803.8487
A (cm^{-1})	1.6813	1.6216	1.5327	1.4203	1.3573
B (cm^{-1})	0.0354	0.0327	0.0304	0.0282	0.0262
C (cm^{-1})	0.0348	0.0322	0.0299	0.0277	0.0258
Rel. E (kcal/mol)	3.5423	3.5684	3.5605	3.5964	3.6000

(The end of Table S3)

Optimized geometries of various species in the OH + H_2O_2 reaction

H_2O_2 (C_2, $^1A_1$)
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1
O 2 R2 1 A1
H 3 R1 2 A1 1 T1

R1 = 0.960957646491903
R2 = 1.449516137189599
A1 = 99.997368939888048
T1 = 112.439744901600434

OH ($C_{\infty v}$, $^2\Pi$)
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1

R1 = 0.967976529283547

HO_2 (C_s, $^2A''$)
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1
O 2 R2 1 A1

R1 = 0.968666185912004
R2 = 1.327756340067187
A1 = 104.300831099874273

H_2O (C_{2v}, $^1A_1$)
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1
H 2 R1 1 A1

R1 = 0.956232853776853
A1 = 104.245881335704212

PRC (C_1, ^2A): van der Waals complex of OH and H_2O_2
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1
O 2 R2 1 A1
H 3 R3 2 A2 1 T1
O 1 R4 2 A3 3 T2
H 5 R5 1 A4 2 T3

R1 = 0.967288488911262
R2 = 1.451400599408027

A1 = 99.644425751111626
R3 = 0.961214978657093
A2 = 100.185603166143622
T1 = 114.482095120863633
R4 = 2.081487011327985
A3 = 139.855803360315406
T2 = 10.204265266116137
R5 = 0.974441630778625
A4 = 73.562652828307264
T3 = -3.142937680089966

PPC (C_1, ^2A): van der Waals complex of HO_2 and H_2O
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1
O 2 R2 1 A1
H 3 R3 2 A2 1 T0
O 4 R4 3 A3 2 T0
H 5 R5 4 A4 3 T3

R1 = 0.982839113241171
R2 = 1.325760542193833
A1 = 102.663950196043331
R3 = 2.282378287905783
A2 = 88.250222560329703
T0 = 0.000000000000000
R4 = 0.962020260245092
A3 = 113.989460714354848
R5 = 0.956785612050913
A4 = 105.333997355706842
T3 = 121.536830291282101

TS1a (C_1, ^2A): H-abstraction from **PRC** to **PPC**
Optimized at ae-CCSD(T)/cc-pVQZ level of theory
H
O 1 R1
O 2 R2 1 A1
H 3 R3 2 A2 1 T1
O 4 R4 3 A3 1 T2
H 5 R5 4 A4 3 T3

R1 = 0.962935313099540
R2 = 1.411873196416155
A1 = 101.285925123970742
R3 = 1.051487897151125
A2 = 103.407223908589827
T1 = 112.088103952533274
R4 = 1.328997469628874
A3 = 145.344150378921768
T2 = -66.097992882213219
R5 = 0.966090287083184
A4 = 104.270430783681988
T3 = -43.146271540265630

TS1b (C_1, ^2A): H-abstraction from **PRC** to **PPC**
Optimized at ae-CCSD(T)/cc-pVQZ level of theory

```
H
O 1 R1
O 2 R2 1 A1
H 3 R3 2 A2 1 T1
O 4 R4 3 A3 1 T2
H 5 R5 3 A4 2 T3

R1  =      0.962880375755570
R2  =      1.417182996277398
A1  =    100.629878362399964
R3  =      1.059977334526446
A2  =    102.277958066201833
T1  =    126.504218558327906
R4  =      1.308529387445732
A3  =    145.592495763111998
T2  =    -63.478184439443162
R5  =      0.966413789255112
A4  =     92.847603140259054
T3  =    -32.407044533209053
```

TS1c (C_1, ^2A): H-abstraction from **PRC** to **PPC**
Optimized at fc-CCSD(T)/ANO1 level of theory

```
H
O 1 R1
O 2 R2 1 A1
H 3 R3 2 A2 1 T1
X 4 R0 3 A3 2 T2
O 4 R4 5 A3 3 T0
H 6 R5 3 A4 2 T3

R1  =      0.967996359635115
R2  =      1.422799946731776
A1  =    101.703021793412333
R3  =      1.055786637304783
A2  =    103.630891793116433
T1  =     82.336545808511858
R0  =      1.000000818629781
A3  =    101.639984464023570
T2  =    -96.205207262072648
R4  =      1.322662372914322
T0  =   -180.000000000000000
R5  =      0.970913831664662
A4  =     92.256897776352616
T3  =     70.218366072567576
```

Ro-vibrational parameters and anharmonic constants of various species in the $OH + H_2O_2$ reaction

H_2O_2 (C_2, $^1A_1$)

Calculated at ae-CCSD(T)/aug-cc-pCVTZ

Har. vib. frequencies (cm^{-1})

7	382.8277 (1DHR)
8	900.8763
9	1319.6088
10	1426.1990
11	3777.7699
12	3777.8810

Zero-point energy: 16.5618 kcal/mol

Rotational constants (in cm-1):

0.8476795201 0.8746394600 10.0755083013

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

ANHARMONICITY CONSTANTS X(ij)
(cm-1)

(*) Near-zero denominators were removed

I	J	X(IJ)
7	7	-35.1309
7	8	-2.4370
7	9	-12.4320
7	10	24.1197
7	11	1.9399
7	12	3.1720
8	8	-7.8252
8	9	-16.0692
8	10	-18.0315
8	11	-2.4707
8	12	-2.6205
9	9	-10.5113
9	10	-14.8896
9	11	-11.0980
9	12	-9.7829
10	10	-11.0384
10	11	-17.3841
10	12	-18.5014
11	11	-47.1968
11	12	-186.0538
12	12	-46.5443

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

Calculated at ae-CCSD(T)/aug-cc-pCVTZ

Har. vib. frequencies (cm^{-1})

6	3719.5510

Zero-point energy: 5.3174 kcal/mol

Rotational constants (in cm-1):

18.8071967494 18.8071967494

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

ANHARMONICITY CONSTANTS X(ij)
(cm-1)

(*) Near-zero denominators were removed

I	J	X(IJ)
6	6	-88.3986

HO_2 (C_s, $^2A''$)

Calculated at ae-CCSD(T)/aug-cc-pCVTZ

Har. vib. frequencies (cm^{-1})

7	1127.3217
8	1432.4462
9	3643.2952

Zero-point energy: 8.8677 kcal/mol = 37.1026 kJ/mol = 3101.532 cm-1

Rotational constants (in cm-1):

1.0581462078 1.1155847062 20.5515770859

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

ANHARMONICITY CONSTANTS X(ij)
(cm-1)

(*) Near-zero denominators were removed

I	J	X(IJ)
7	7	-8.7277
7	8	-15.2687
7	9	-2.7041
8	8	-12.7652
8	9	-23.6028
9	9	-105.6170

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

Calculated at ae-CCSD(T)/aug-cc-pCVTZ

Har. vib. frequencies (cm^{-1})

7	1645.5174
8	3813.5687
9	3920.9478

Zero-point energy: 13.4094 kcal/mol = 56.1051 kJ/mol = 4690.017 cm-1

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

ANHARMONICITY CONSTANTS X(ij)
(cm-1)

(*) Near-zero denominators were removed

I	J	X(IJ)

7	7 -14.1879
7	8 -18.5582
7	9 -23.1097
8	8 -45.6381
8	9 -175.1331
9	9 -51.0722

PRC (C_1, ^2A): van der Waals complex of OH and H_2O_2

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

Har. vib. frequencies (cm^{-1})

7	56.82
8	126.6678
9	180.7000
10	354.0624
11	420.3868
12	550.8952
13	849.6317
14	1323.7388
15	1407.5215
16	3607.7750
17	3731.4592
18	3748.0254

Zero-point energy: 23.3032 kcal/mol = 97.5008 kJ/mol = 8150.432 cm-1

Rotational constants (in cm-1):

0.1298257433 0.1481115041 0.9684434114

Calculated at fc-CCSD(T)/ANO1

Har. vib. frequencies (cm^{-1})

7	158.4982
8	183.2669
9	251.1837
10	288.9430
11	447.4001
12	572.5988
13	893.7082
14	1330.0903
15	1483.7886
16	3646.9477
17	3716.4272
18	3804.8908

Zero-point energy: 23.9850 kcal/mol = 100.3532 kJ/mol = 8388.872 cm-1

Rotational constants (in cm-1):

0.1617286010 0.1969533703 0.8452127111

PPC (C_1, ^2A): van der Waals complex of HO_2 and H_2O

Calculated at fc-CCSD(T)/ANO1

Har. vib. frequencies (cm^{-1})

7	136.6811
8	215.0644
9	261.6981
10	292.0863
11	490.7935
12	679.6185
13	1155.8707
14	1563.6210

15	1656.3154
16	3447.1263
17	3787.7997
18	3917.6320

Zero-point energy: 25.1666 kcal/mol = 105.2972 kJ/mol = 8802.154 cm-1

Rotational constants (in cm-1):

0.1709881808 0.2012319572 1.0561072100

TS1a (C_1, ^2A): H-abstraction from **PRC** to **PPC**

Calculated at ae-CCSD(T)/aug-cc-pCVTZ

Har. vib. frequencies (cm^{-1})

1	1757.7135i
8	161.3404 (1DHR)
9	184.0366
10	323.1823 (1DHR)
11	400.1764
12	762.7402
13	958.4413
14	1252.7653
15	1413.1269
16	1760.7771
17	3746.4554
18	3751.6825

Zero-point energy: 21.0357 kcal/mol = 88.0136 kJ/mol = 7357.362 cm-1

Rotational constants (in cm-1):

0.1813608324 0.2040482051 1.2715775004

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

ANHARMONICITY CONSTANTS X(ij)

(cm-1)

I J	X(IJ)
7 7	-539.0814
7 8	-71.2132i
7 9	33.3557i
7 10	54.1541i
7 11	96.4597i
7 12	174.1993i
7 13	24.9273i
7 14	-161.3973i
7 15	-17.3343i
7 16	-841.9557i
7 17	-13.5202i
7 18	22.0676i
8 8	-40.0246
8 9	-16.2058
8 10	14.5094
8 11	-10.2028
8 12	-10.8210
8 13	-5.8214
8 14	-94.0916
8 15	-4.7027

```
 8 16      32.7904
 8 17       1.2662
 8 18       3.1463
 9  9       0.0012
 9 10       0.4517
 9 11       1.6166
 9 12      -0.2111
 9 13      -0.8304
 9 14     -29.1941
 9 15      -5.6321
 9 16      10.8915
 9 17      -0.6401
 9 18      -0.9299
10 10      -3.4314
10 11       1.0019
10 12       8.6966
10 13       2.6280
10 14      12.9985
10 15       4.9087
10 16     -23.2394
10 17      -4.1790
10 18      -0.0362
11 11      18.7700
11 12      25.6066
11 13      11.0030
11 14     -21.8928
11 15       1.0162
11 16      49.4698
11 17      -0.6790
11 18       3.8129
12 12       6.6671
12 13       3.8459
12 14     -12.4703
12 15       1.0198
12 16       4.4200
12 17      -2.6568
12 18      -6.2723
13 13     -11.9767
13 14     -11.5791
13 15     -16.4027
13 16      15.0570
13 17      -0.9027
13 18       0.3997
14 14     -81.3129
14 15     -35.1058
14 16      96.2061
14 17       0.1469
14 18       5.6560
15 15     -11.1948
15 16       8.1285
15 17     -21.9590
15 18      -3.8382
16 16     -28.9251
16 17       1.0425
16 18     -17.2646
17 17     -70.5914
```

17 18	-89.1505
18 18	-66.0077

TS1b (C_1, ^2A): H-abstraction from **PRC** to **PPC**

Calculated at ae-CCSD(T)/aug-cc-pCVTZ

	Har. vib. frequencies (cm^{-1})
1	1889.7873i
8	122.6037
9	232.4750
10	367.0679
11	419.9558
12	734.8056
13	950.9419
14	1336.7353
15	1486.5548
16	1596.6677
17	3746.0820
18	3750.5787

Zero-point energy: 21.0782 kcal/mol = 88.1915 kJ/mol = 7372.234 cm-1

Rotational constants (in cm-1):

0.1862130986 0.2145271048 1.1873436974

Calculated at ae-CCSD(T)/aug-cc-pCVDZ

ANHARMONICITY CONSTANTS X(ij) (cm-1)

I J	X(IJ)
7 7	-568.3942
7 8	7.6495i
7 9	-9.4186i
7 10	84.6058i
7 11	51.1025i
7 12	89.7204i
7 13	-39.5788i
7 14	9.3575i
7 15	12.1140i
7 16	-704.9867i
7 17	20.8433i
7 18	-10.2089i
8 8	5.3111
8 9	-32.0001
8 10	8.2912
8 11	5.6914
8 12	9.9433
8 13	26.7212
8 14	-34.0575
8 15	-36.2493
8 16	31.7453
8 17	2.6061
8 18	-0.2960
9 9	-21.3278
9 10	-4.6037
9 11	9.4263

9 12	5.0864
9 13	32.8841
9 14	-25.6263
9 15	-41.9041
9 16	28.3364
9 17	4.5324
9 18	0.3465
10 10	-1.2137
10 11	-13.8940
10 12	4.0570
10 13	20.1045
10 14	4.1159
10 15	5.0521
10 16	-15.0256
10 17	0.1978
10 18	-4.2592
11 11	-15.9287
11 12	-14.0322
11 13	21.2123
11 14	8.7078
11 15	-4.2661
11 16	55.6167
11 17	-0.3551
11 18	-0.9973
12 12	-0.8913
12 13	30.8845
12 14	2.2617
12 15	-2.5026
12 16	-9.1746
12 17	-8.8051
12 18	-3.0916
13 13	-5.8096
13 14	-12.6368
13 15	-11.2837
13 16	15.2525
13 17	-0.6144
13 18	-0.8232
14 14	-11.1154
14 15	-30.2485
14 16	6.5937
14 17	1.0643
14 18	-13.3972
15 15	-23.2641
15 16	-41.3563
15 17	3.6788
15 18	-8.3731
16 16	-49.0294
16 17	-20.0122
16 18	-2.0392
17 17	-62.2520
17 18	-106.8427
18 18	-65.8613

TS1c (C_1, ^2A): H-abstraction from **PRC** to **PPC**

Calculated at fc-CCSD(T)/ANO1

Har. vib. frequencies (cm^{-1})

1	1641.2478i
8	121.8505
9	256.0236
10	318.7858
11	456.2019
12	730.2368
13	954.5131
14	1392.7325
15	1401.7443
16	1492.8503
17	3756.9177
18	3769.6303

Zero-point energy: 20.9453 kcal/mol = 87.6354 kJ/mol = 7325.743 cm-1
Rotational constants (in cm-1):
0.1821171780 0.2067888858 1.1679258717

1DHR treatments for H_2O_2 and TS1

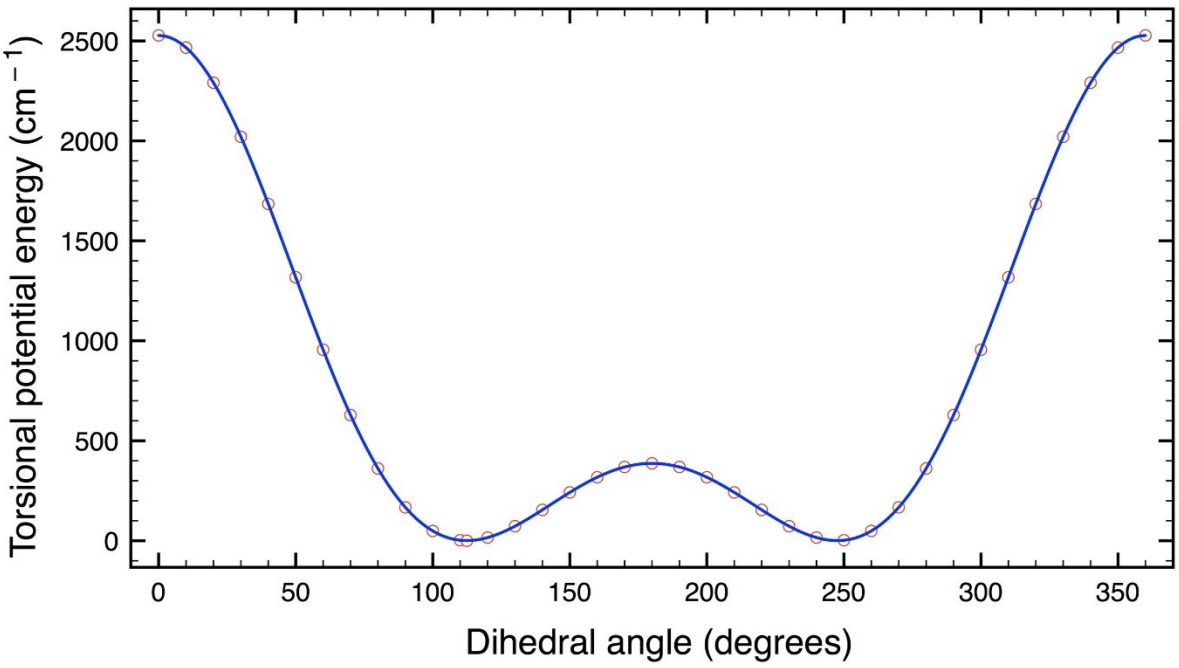

Fig. S1: Torsional potential energy curve (cm-1) for H_2O_2 calculated at ae-CCSD(T)/aug-cc-pCVTZ level of theory.

$$V(\theta\ in\ rad) = 809.601 + 1026.71\cos(\theta) + 645.21\cos(2\theta) + 43.5448\cos(3\theta) + 2.40657\cos(4\theta) - 0.139588\cos(6\theta) + 0.107161\cos(7\theta) + 0.846987\cos(8\theta) + 0.0121486\cos(9\theta)$$

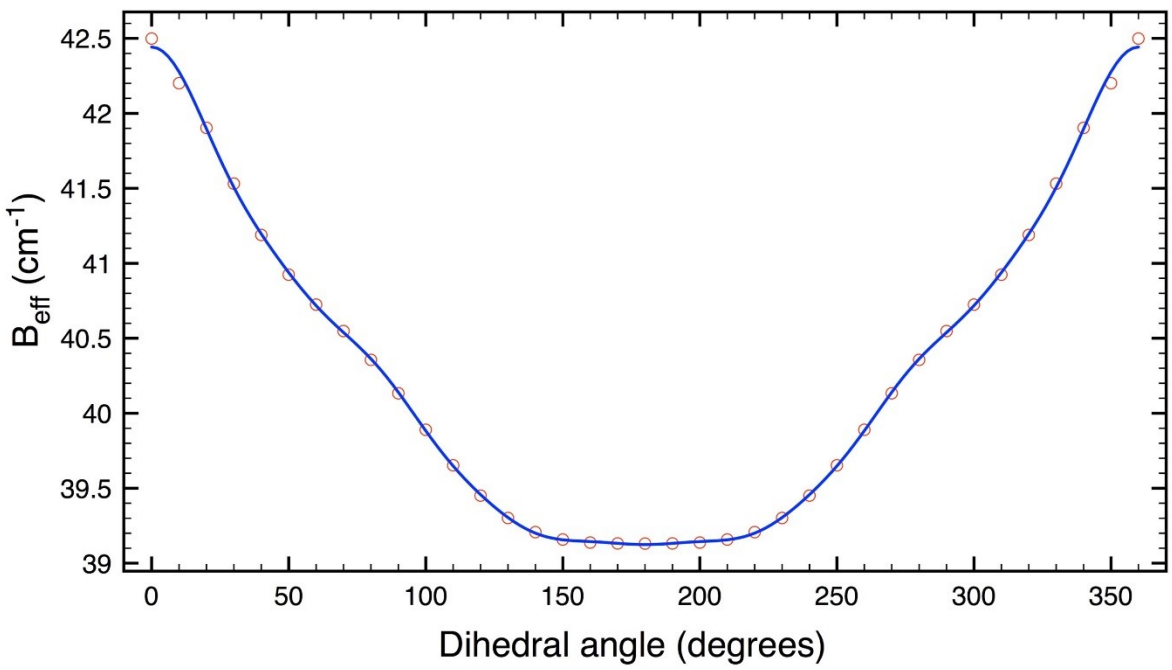

Fig. S2: Effective rotational constant for the torsional vibration in H_2O_2 calculated at ae-CCSD(T)/aug-cc-pCVTZ level of theory.

$$B_{eff}(\theta\ in\ rad) = 40.2935 + 1.44162\cos(\theta) + 0.295664\cos(2\theta) + 0.1194\cos(3\theta) + 0.153894\cos($$
$$\cos(5\theta) + 0.0260459\cos(6\theta) + 0.0170418\cos(7\theta) + 0.0141807\cos(8\theta) + 0.0134$$
$$\cos(9\theta),\ in\ cm^{-1}$$

A list of torsional eigenvalues (in cm^{-1}) calculated for H_2O_2

1 170.880407166364 (torsional ZPE)
2 182.686061772580
3 425.955748655930
4 543.653395632472
5 743.558462138967
6 951.267960499802
7 1177.22306656419
8 1412.60330952693
9 1652.71541039051
10 1897.05031399662
11 2122.97830666411
12 2383.03428446402
13 2509.83123864532
14 2888.76801969643
15 2910.15242745519
16 3463.08632361049
17 3464.57615242976
18 4126.40963507574
19 4126.47629282033
20 4877.48813168047
21 4877.49007677618
22 5713.42726574173
23 5713.42728595436

24 6632.58090159240
25 6632.58090375636
26 7634.03506128665
27 7634.03506157507
28 8717.24529909824
29 8717.24529913342
30 9881.86733807560
31 9881.86733807991
32 11127.6732584044
33 11127.6732584052
34 12454.5065894629
35 12454.5065894635
36 13862.2566717271
37 13862.2566717275
38 15350.8432715670
39 15350.8432715672
40 16920.2069666849
41 16920.2069666855
42 18570.3029310999
43 18570.3029311001
44 20301.0968004641
45 20301.0968004644
46 22112.5618521960
47 22112.5618521963
48 24004.6770401084
49 24004.6770401086
50 25977.4255980460
51 25977.4255980464
52 28030.7940306845
53 28030.7940306847
54 30164.7713728458
55 30164.7713728462
56 32379.3486382846
57 32379.3486382850
58 34674.5184042633
59 34674.5184042635
60 37050.2744948314
61 37050.2744948316
62 39506.6117367889
63 39506.6117367891
64 42043.5257698037
65 42043.5257698042
66 44661.0128973305
67 44661.0128973308
68 47359.0699685765
69 47359.0699685771
70 50137.6942843206
71 50137.6942843212

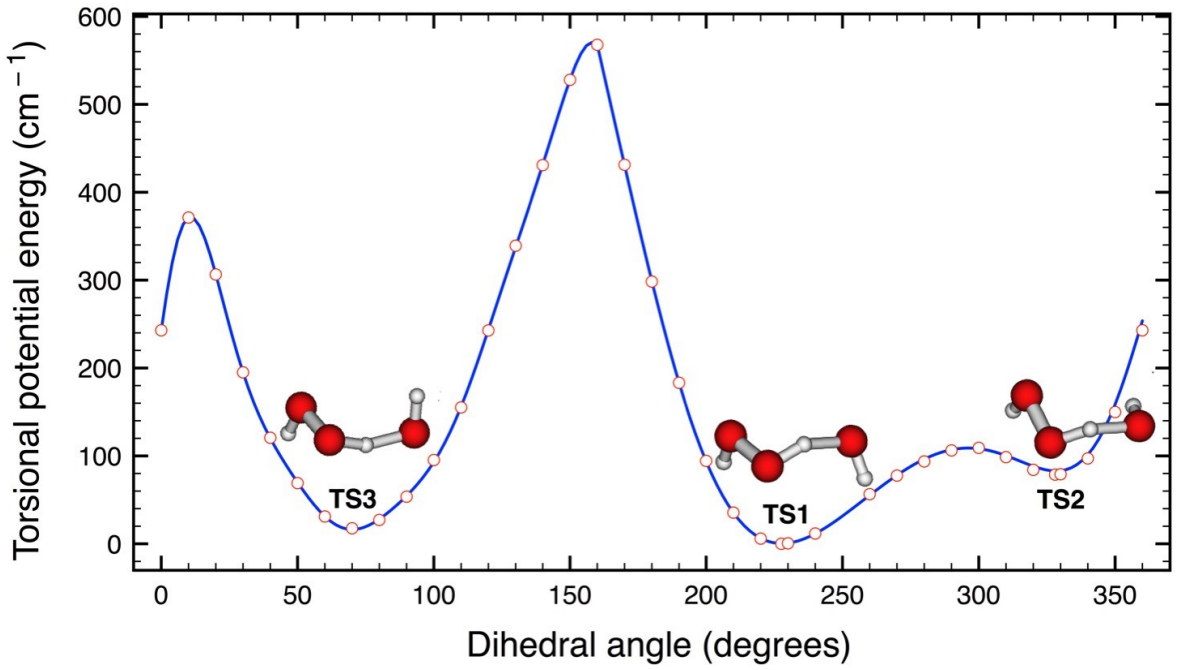

Fig. S3: (First) torsional potential energy curve (cm^{-1}) in TS1 calculated at fc-CCSD(T)/ANO1 level of theory.

$$V(\theta\ in\ rad) = 162.495 - 56.561\cos(\theta) + 112.924\cos(2\theta) + 10.6556\cos(3\theta) + 16.3473\cos(4\theta - 2.40405\cos(6\theta) + 9.40682\cos(7\theta) - 7.0922\cos(8\theta) + 2.93191\cos(9\theta) - 6.3218 - 1.38695\cos(11\theta) - 3.8245\cos(12\theta) - 2.75904\cos(13\theta) - 1.62862\cos(14\theta) - 4.1\cos(15\theta) + 69.681\sin(\theta) - 93.5381\sin(2\theta) + 112.474\sin(3\theta) - 4.41864\sin(4\theta) + \sin(5\theta) + 7.79593\sin(6\theta) + 13.9519\sin(7\theta) + 7.09443\sin(8\theta) + 6.99612\sin(9\theta)\sin(10\theta) - 0.105336\sin(11\theta) + 5.91558\sin(12\theta) - 1.14115\sin(13\theta) + 1.98525\sin - 0.313506\sin(15\theta) + 1.62159\sin(16\theta),\ in\ cm^{-1}$$

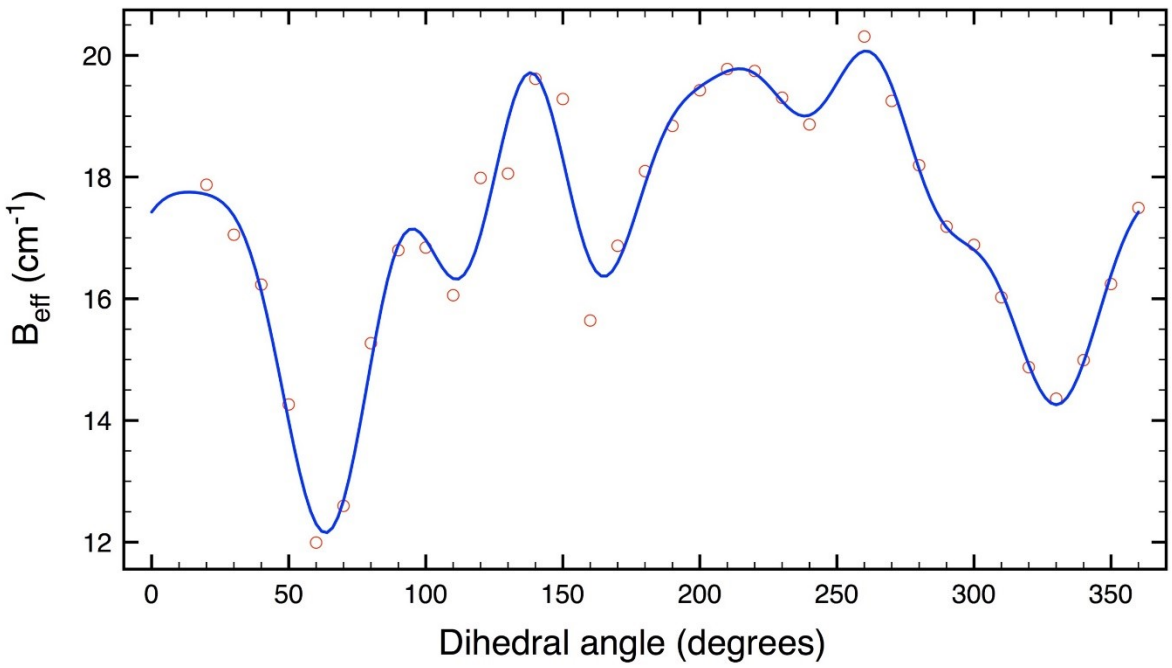

Fig. S4: Effective rotational constant for the (first) torsional vibration in TS1 calculated at fc-CCSD(T)/ANO1 level of theory.

$$B_{eff}(\theta\ in\ rad) = 17.2102 - 1.58256\cos(\theta) + 0.193691\cos(2\theta) + 1.21684\cos(3\theta) + 0.243705\cos(5\theta) - 0.463423\cos(6\theta) + 0.107632\cos(7\theta) + 0.468284\cos(8\theta) - 0.131467\cos - 1.22968\sin(\theta) + 0.288289\sin(2\theta) + 0.709313\sin(3\theta) + 0.913825\sin(4\theta) + 0.1\sin(5\theta) + 0.414191\sin(6\theta) - 0.519961\sin(7\theta) - 0.110282\sin(8\theta) - 0.00340622si\ cm^{-1}$$

A list of torsional eigenvalues (in cm^{-1}) calculated for the (first) torsional vibration in TS1

1	66.8566055796270 (ZPE)
2	90.6556435201120
3	135.635785628552
4	204.087157451529
5	225.493070170724
6	303.330484163356
7	362.713129210742
8	425.193673321536
9	487.198837976727
10	585.222954401800
11	623.504689327563
12	775.821859759148
13	795.208741929463
14	999.189164560921
15	1006.99617047763
16	1254.47663965656
17	1257.90951643050

18 1543.84222410686
19 1544.44574866352
20 1866.34616286730
21 1866.86971658541
22 2223.27319610835
23 2223.52751401327
24 2614.37317445240
25 2614.45503999403
26 3039.58048153673
27 3039.59927040674
28 3498.88800625279
29 3498.89594421667
30 3992.29633916516
31 3992.29869383931
32 4519.79083111815
33 4519.79149392488
34 5081.36203836743
35 5081.36252079148
36 5677.00317149446
37 5677.00340125797
38 6306.70862491898
39 6306.70867429695
40 6970.47424448772
41 6970.47425295067
42 7668.29695702972
43 7668.29696508292
44 8400.17438162826
45 8400.17438532941
46 9166.10464086833
47 9166.10464131234
48 9966.08625299281
49 9966.08625317893
50 10800.1180368427
51 10800.1180369972
52 11668.1990386978
53 11668.1990387409
54 12570.3284819938
55 12570.3284820083
56 13506.5057293700
57 13506.5057293733
58 14476.7302535700
59 14476.7302535723
60 15481.0016153338
61 15481.0016153346
62 16519.3194462890
63 16519.3194462894
64 17591.6834356247
65 17591.6834356248
66 18698.0933195971
67 18698.0933195973
68 19838.5488732110
69 19838.5488732115
70 21013.0499035688
71 21013.0499035689
72 22221.5962445176
73 22221.5962445176

74 23464.1877523114
75 23464.1877523116
76 24740.8243020741
77 24740.8243020746
78 26051.5057848985
79 26051.5057848987
80 27396.2321054528
81 27396.2321054528
82 28775.0031799964
83 28775.0031799965
84 30187.8189347268
85 30187.8189347269
86 31634.6793043951
87 31634.6793043951
88 33115.5842311416
89 33115.5842311416
90 34630.5336635129
91 34630.5336635130
92 36179.5275556281
93 36179.5275556282
94 37762.5658664695
95 37762.5658664697
96 39379.6485592757
97 39379.6485592758
98 41030.7756010219
99 41030.7756010221
100 42715.9469619731
101 42715.9469619732
102 44435.1626152981
103 44435.1626152982
104 46188.4225367352
105 46188.4225367353
106 47975.7267043022
107 47975.7267043023
108 49797.0750980441
109 49797.0750980444
110 51652.4676998129
111 51652.4676998131

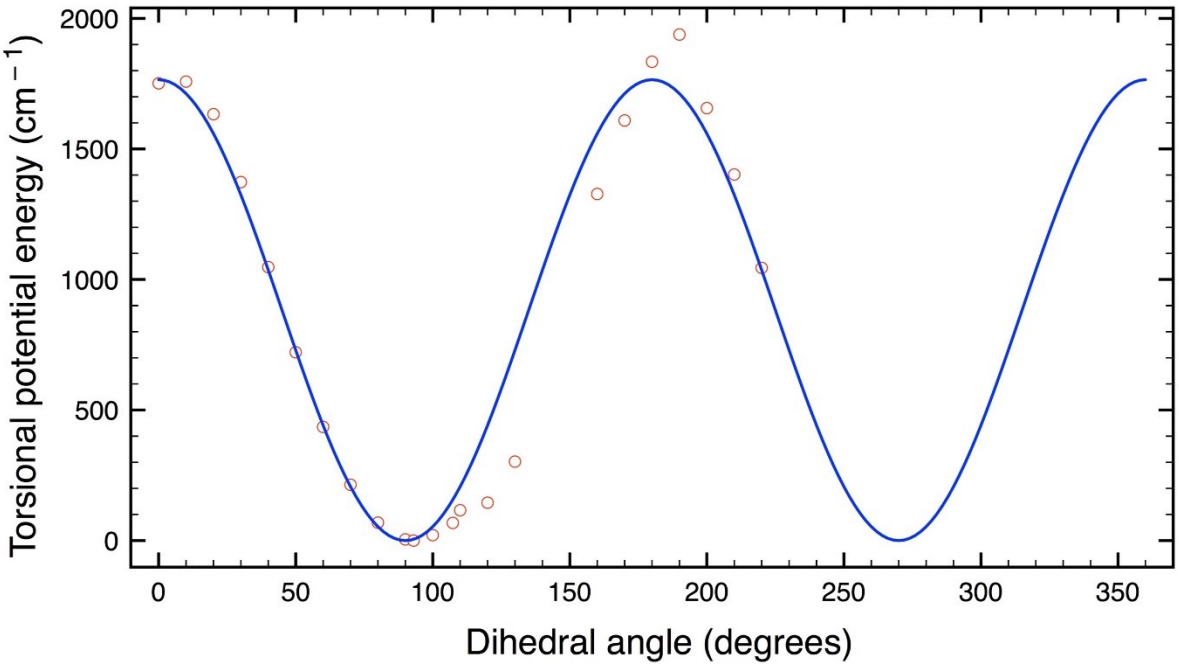

Fig. S5: (Second) torsional potential energy curve (cm^{-1}) in TS1 calculated at fc-CCSD(T)/ANO1 level of theory.

$V(\theta\ in\ rad) = 912.329 + 912.329\cos(2\theta),\ in\ cm^{-1}$

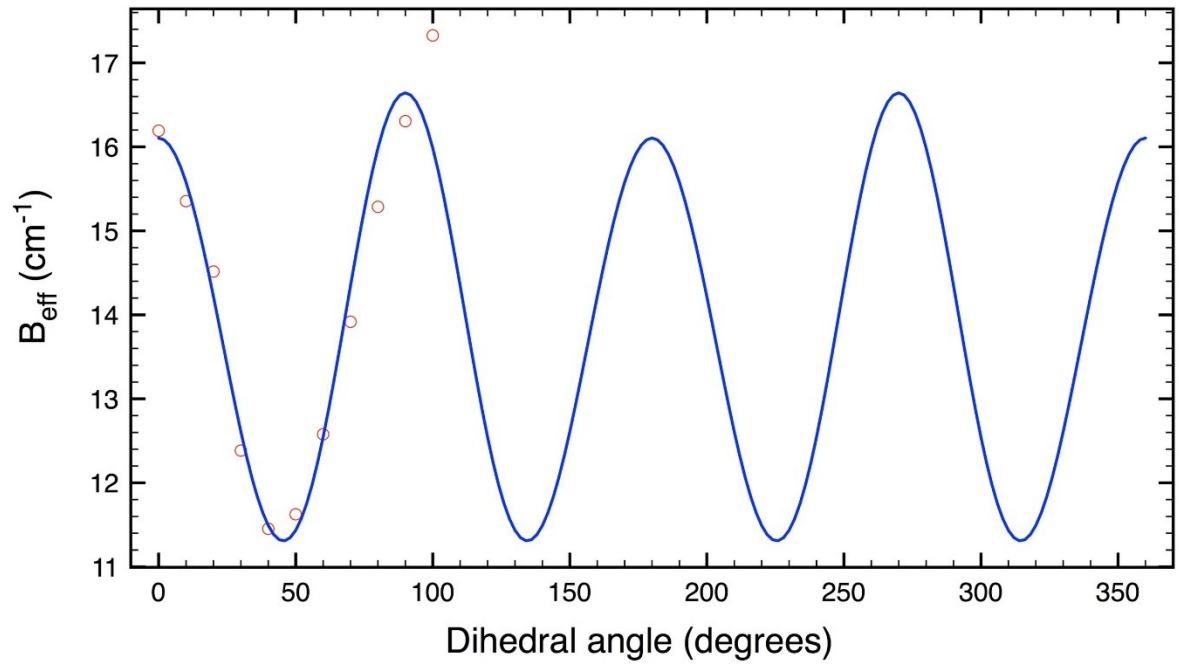

Fig. S6: Effective rotational constant for the (second) torsional vibration in TS1 calculated at fc-CCSD(T)/ANO1 level of theory.

$B_{eff}(\theta\ in\ rad) = 13.842 - 0.157805\cos(2\theta) + 2.53207\cos(4\theta) - 0.111167\cos(6\theta),\ in\ cm^{-1}$

A list of torsional eigenvalues (in cm^{-1}) calculated for the (second) torsional vibration in TS1

1 157.938765745004 (ZPE)
2 157.938766138411
3 478.798503308855
4 478.798546076736
5 767.696776097367
6 767.698608279295
7 1030.26268423918
8 1030.30489975628
9 1269.91042148368
10 1270.50760849790
11 1485.37851792595
12 1490.84778299697
13 1665.02806336978
14 1695.99357918308
15 1802.01363879341
16 1897.98227225581
17 1938.09007787866
18 2114.02465765428
19 2122.99838840100
20 2356.66569088383
21 2358.11152607795
22 2630.05616455975
23 2630.25216549286
24 2934.08237635438
25 2934.10633349302
26 3267.85781478259
27 3267.86055598156
28 3630.67819867462
29 3630.67849925763
30 4022.07028790178
31 4022.07031997761
32 4441.71604732780
33 4441.71605069320
34 4889.39533964759
35 4889.39533999719
36 5364.95121632478
37 5364.95121636103
38 5868.26893062000
39 5868.26893062382
40 6399.26279946729
41 6399.26279946781
42 6957.86768011892
43 6957.86768011902
44 7544.03326794898
45 7544.03326794911
46 8157.72018112232
47 8157.72018112239
48 8798.89721172466

49 8798.89721172484
50 9467.53935823074
51 9467.53935823084
52 10163.6263931146
53 10163.6263931147
54 10887.1418041930
55 10887.1418041931
56 11638.0720015236
57 11638.0720015239
58 12416.4057159230
59 12416.4057159231
60 13222.1335376955
61 13222.1335376957
62 14055.2475592564
63 14055.2475592565
64 14915.7410956429
65 14915.7410956431
66 15803.6084640259
67 15803.6084640260
68 16718.8448083691
69 16718.8448083692
70 17661.4459589376
71 17661.4459589376
72 18631.4083189423
73 18631.4083189425
74 19628.7287724795
75 19628.7287724796
76 20653.4046093013
77 20653.4046093014
78 21705.4334629871
79 21705.4334629872
80 22784.8132598487
81 22784.8132598488
82 23891.5421764906
83 23891.5421764907
84 25025.6186043851
85 25025.6186043851
86 26187.0411201680
87 26187.0411201681
88 27375.8084606208
89 27375.8084606209
90 28591.9195015120
91 28591.9195015121
92 29835.3732396331
93 29835.3732396331
94 31106.1687774860
95 31106.1687774861
96 32404.3053101875
97 32404.3053101875
98 33729.7821142272
99 33729.7821142273
100 35082.5985377882
101 35082.5985377882
102 36462.7539923846
103 36462.7539923846
104 37870.2479456156

105 37870.2479456158
106 39305.0799148704
107 39305.0799148704
108 40767.2494618406
109 40767.2494618407
110 42256.7561877278
111 42256.7561877278
112 43773.5997290436
113 43773.5997290436
114 45317.7797539227
115 45317.7797539227
116 46889.2959588779
117 46889.2959588780
118 48488.1480659354
119 48488.1480659355
120 50114.3358201041
121 50114.3358201042