

Computational Study of the Reaction Mechanism of the Methylperoxy Self-Reaction

Yan-Ni Liang,[†] Jun Li,[‡] Quan-De Wang,[†] Fan Wang,^{,†} and Xiang-Yuan Li[‡]*

[†] College of Chemistry, Sichuan University, Chengdu, 610065, People's Republic of China

[‡] College of Chemical Engineering, Sichuan University, Chengdu, 610065, People's Republic of China

Supporting Information

The reactant ($\text{CH}_3\text{O}_2\cdot$), intermediates (IM1–IM6), transition states (TS1–TS8) and products ($\cdot\text{CH}_2\text{O}_2\cdot$, CH_3OCH_3 , $\text{CH}_3\text{O}\cdot$, CH_3OOCH_3 , CH_3OOOH) structures optimized at the B3LYP/6-311++g(2df,2p) level.

$\text{CH}_3\text{O}_2\cdot$

C						
O	1	B1				
O	2	B2	1	A1		
H	1	B3	2	A2	3	D1
H	1	B4	2	A3	3	D2
H	1	B5	2	A4	3	D3

Variables:

B1	1.44609396
B2	1.31484132
B3	1.08757329
B4	1.08678245
B5	1.08752987
A1	111.49349247
A2	109.05763361
A3	105.51092781
A4	109.06855507
D1	-60.56329576
D2	179.99166186
D3	60.51927973

$\text{CH}_3\text{O}\cdot$

C						
H	1	B1				
H	1	B2	2	A1		
H	1	B3	3	A2	2	D1
O	1	B4	3	A3	4	D2

Variables:

B1	1.09772262
B2	1.09744480
B3	1.10679965
B4	1.36249233
A1	111.72468619
A2	106.35879508
A3	113.29026838
D1	115.41677402
D2	115.32306802

$\cdot\text{CH}_2\text{O}_2\cdot$

C						
H	1	B1				
H	1	B2	2	A1		
O	1	B3	2	A2	3	D1
O	4	B4	1	A3	2	D2

Variables:

B1	1.07928907
B2	1.07930656

B3	1.37751062
B4	1.34935218
A1	124.92279796
A2	116.76513994
A3	111.14709522
D1	-165.35766298
D2	83.22203753

CH₃OCH₃

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

Variables:

B1	1.41020248
B2	1.09690158
B3	1.08786081
B4	1.09690158
B5	1.41020248
B6	1.08786081
B7	1.09690158
B8	1.09690158
A1	111.44582020
A2	107.41197779
A3	111.44582020
A4	112.86204961
A5	107.41197779
A6	111.44582020
A7	111.44582020
D1	-119.32264311
D2	-119.32264311
D3	180.00000000
D4	180.00000000
D5	-60.67735689
D6	60.67735689

CH₃OOCH₃

C					
O	1	B1			
O	2	B2	1	A1	
H	1	B3	2	A2	3
H	1	B4	2	A3	3
H	1	B5	2	A4	3
C	3	B6	2	A5	1
H	7	B7	3	A6	2
H	7	B8	3	A7	2
H	7	B9	3	A8	2
					D1
					D2
					D3
					D4
					D5
					D6
					D7

Variables:

B1	1.41077118
B2	1.46221626
B3	1.09226324
B4	1.08937628
B5	1.09233057
B6	1.41082840
B7	1.08936331
B8	1.09225457
B9	1.09232777
A1	105.17442493
A2	111.27171599
A3	104.71594202
A4	111.27259910
A5	105.18637261
A6	104.71433631
A7	111.26705283
A8	111.27090965
D1	-61.47440463
D2	179.99628811
D3	61.48267780
D4	-180.00000000
D5	-179.98378090
D6	-61.45198227
D7	61.50261895

CH₃OOOH

H

C	1	B1				
H	2	B2	1	A1		
H	2	B3	1	A2	3	D1
H	2	B4	1	A3	3	D2
O	2	B5	1	A4	3	D3
O	6	B6	2	A5	1	D4
O	7	B7	6	A6	2	D5

Variables:

B1	3.51280178
B2	1.08966922
B3	1.08989693
B4	1.08899243
B5	2.93105488
B6	1.43016088
B7	1.42415704
A1	72.13805437
A2	117.48598972
A3	127.94879157
A4	13.87146674
A5	50.86972871
A6	107.99850016
D1	-104.60087472
D2	101.59246275
D3	-57.34685107
D4	-80.66574960

D5	36.19542224					
IM1						
O						
O	1	B1				
O	2	B2	1	A1		
O	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
H	5	B5	4	A4	3	D3
H	5	B6	4	A5	3	D4
H	5	B7	4	A6	3	D5
C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	2	D8
H	9	B11	1	A10	2	D9

Variables:

B1	1.42877012
B2	1.41311333
B3	1.42877012
B4	1.42511333
B5	1.09029810
B6	1.08977202
B7	1.08898873
B8	1.42511333
B9	1.08898873
B10	1.08977202
B11	1.09029810
A1	108.99191618
A2	108.99191618
A3	108.48185038
A4	110.88961535
A5	110.95798983
A6	104.25118795
A7	108.48185038
A8	104.25118795
A9	110.95798983
A10	110.88961535
D1	79.77946898
D2	80.79712660
D3	58.99763643
D4	-64.60349658
D5	177.43697072
D6	80.79712660
D7	177.43697072
D8	-64.60349658
D9	58.99763643

IM2

O						
O	1	B1				
O	2	B2	1	A1		
O	3	B3	2	A2	1	D1
C	3	B4	2	A3	1	D2

H	5	B5	3	A4	2	D3
H	5	B6	3	A5	2	D4
H	5	B7	2	A6	1	D5
C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	2	D8
H	9	B11	1	A10	2	D9

Variables:

B1	1.46611161
B2	1.35795422
B3	1.46611161
B4	2.31893391
B5	1.08996775
B6	1.09053955
B7	1.09000318
B8	1.42281437
B9	1.08996775
B10	1.09053955
B11	1.09000318
A1	108.77274969
A2	108.77274969
A3	122.12908071
A4	141.21752690
A5	89.33614831
A6	78.73270920
A7	106.76739764
A8	104.12255119
A9	111.14646302
A10	111.61014148
D1	-84.42214525
D2	-47.15492786
D3	-84.23649330
D4	154.92682674
D5	1.24845854
D6	119.20502426
D7	175.58794084
D8	58.05478944
D9	-65.47139576

IM3

O					
O	1	B1			
O	2	B2	1	A1	
O	3	B3	2	A2	1
C	3	B4	2	A3	1
H	5	B5	2	A4	1
H	5	B6	1	A5	6
H	5	B7	7	A6	6
C	1	B8	2	A7	3
H	9	B9	1	A8	2
H	9	B10	1	A9	2
H	9	B11	1	A10	2

Variables:

B1	1.43162544
B2	1.40088001
B3	1.44235742
B4	2.31896269
B5	1.09037450
B6	1.09003602
B7	1.08937766
B8	1.42785267
B9	1.09024363
B10	1.08944552
B11	1.08832241
A1	108.88361595
A2	109.10028427
A3	103.88380201
A4	67.71271291
A5	116.54925277
A6	109.89041517
A7	109.44559778
A8	110.80561522
A9	103.84310388
A10	111.35999822
D1	91.91490705
D2	128.88342627
D3	121.29990705
D4	106.39652740
D5	121.31677768
D6	-95.23933519
D7	-54.17572968
D8	-171.85338801
D9	69.62577337

IM4

O					
O	1	B1			
O	1	B2	2	A1	
O	3	B3	1	A2	2
C	3	B4	1	A3	2
H	3	B5	1	A4	2
H	5	B6	4	A5	3
H	5	B7	4	A6	3
C	1	B8	2	A7	4
H	9	B9	1	A8	2
H	9	B10	1	A9	2
H	9	B11	1	A10	2

Variables:

B1	1.30652933
B2	2.15019206
B3	1.30652933
B4	2.29986474
B5	2.71668317
B6	1.08561110

B7	1.08413852
B8	1.44989254
B9	1.08924961
B10	1.08561110
B11	1.08413852
A1	92.45959840
A2	87.37966537
A3	97.16228501
A4	120.37857920
A5	105.73347979
A6	109.82819690
A7	112.99713153
A8	107.39853510
A9	105.73347979
A10	109.82819690
D1	5.50817803
D2	-28.65904555
D3	-29.37765345
D4	159.65131035
D5	39.16204559
D6	-106.21817721
D7	-81.43282995
D8	159.65131035
D9	39.16204559

IM5

O

O	1	B1				
O	1	B2	2	A1		
O	3	B3	1	A2	2	D1
C	4	B4	3	A3	1	D2
H	5	B5	4	A4	3	D3
H	5	B6	4	A5	3	D4
H	5	B7	4	A6	3	D5
C	1	B8	2	A7	4	D6
H	1	B9	2	A8	3	D7
H	1	B10	2	A9	10	D8
H	9	B11	1	A10	2	D9

Variables:

B1	1.30681552
B2	2.15132628
B3	1.30681552
B4	1.45139417
B5	1.08567278
B6	1.08482374
B7	1.08855997
B8	1.45139417
B9	2.07633542
B10	2.03264545
B11	1.08855997
A1	92.72587977
A2	87.27412024

A3	111.67477932
A4	105.57965532
A5	109.04932050
A6	107.50369905
A7	111.67477932
A8	90.37879310
A9	141.45014560
A10	107.50369905
D1	0.00000000
D2	-98.99846281
D3	166.73569128
D4	46.73538992
D5	-74.13342594
D6	98.99846280
D7	77.92074232
D8	10.15864014
D9	74.13342594

IM6

O

O	1	B1				
O	2	B2	1	A1		
O	3	B3	2	A2	1	D1
C	3	B4	2	A3	1	D2
H	5	B5	2	A4	1	D3
H	5	B6	1	A5	6	D4
H	5	B7	6	A6	7	D5
C	5	B8	8	A7	7	D6
H	5	B9	8	A8	7	D7
H	9	B10	5	A9	8	D8
H	9	B11	5	A10	8	D9

Variables:

B1	1.31352459
B2	3.97224574
B3	1.31334744
B4	2.28917209
B5	1.08715678
B6	1.08791134
B7	1.08662656
B8	4.41001391
B9	4.78510375
B10	1.08665201
B11	1.08734312
A1	83.50829977
A2	88.25987832
A3	62.66574304
A4	8.53076760
A5	110.30328687
A6	111.47528566
A7	147.75178132
A8	151.34509968
A9	141.70827285

A10	37.80851309
D1	143.76640110
D2	170.19229339
D3	145.64411469
D4	95.95787629
D5	-124.27566639
D6	146.12015866
D7	121.78270649
D8	88.68806278
D9	136.49579553

cis -TS1-2 (IM1-IM2)

O						
O	1	B1				
O	2	B2	1	A1		
O	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
H	5	B5	4	A4	3	D3
H	5	B6	4	A5	3	D4
H	5	B7	4	A6	3	D5
C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	10	D8
H	9	B11	11	A10	10	D9

Variables:

B1	1.37427017
B2	1.57518652
B3	1.37427017
B4	1.43759774
B5	1.08678062
B6	1.08871631
B7	1.08884910
B8	1.43759774
B9	1.08871631
B10	1.08678062
B11	1.08884910
A1	109.79349910
A2	109.79349910
A3	109.03976614
A4	110.68987365
A5	104.37942917
A6	109.91045991
A7	109.03976614
A8	104.37942917
A9	110.68987365
A10	110.88915626
D1	26.29410212
D2	-101.63234161
D3	63.69945105
D4	-177.22249525
D5	-59.13166042
D6	-101.63234161

D7	-177.22249525					
D8	-119.07805370					
D9	-122.52341308					
trans -TS1-2 (IM1-IM2)						
O						
O	1	B1				
O	2	B2	1	A1		
O	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
H	5	B5	4	A4	3	D3
H	5	B6	4	A5	3	D4
H	5	B7	4	A6	3	D5
C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	10	D8
H	9	B11	10	A10	11	D9

Variables:

B1	1.37673409
B2	1.55374736
B3	1.37673409
B4	1.43324499
B5	1.08889574
B6	1.08820496
B7	1.08934459
B8	1.43324499
B9	1.08820496
B10	1.08889574
B11	1.08934459
A1	104.34390521
A2	104.34390521
A3	109.53693672
A4	110.67030587
A5	104.48324633
A6	110.39434646
A7	109.53693672
A8	104.48324633
A9	110.67030587
A10	110.25078949
D1	-165.47966553
D2	-89.52669050
D3	65.19110821
D4	-176.34243617
D5	-57.82460967
D6	-89.52669050
D7	-176.34243617
D8	-118.46645562
D9	122.52415899

cis -TS1-3 (IM1-IM3)

O					
O	1	B1			
O	2	B2	1	A1	

O	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
H	5	B5	4	A4	3	D3
H	5	B6	4	A5	3	D4
H	5	B7	4	A6	3	D5
C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	10	D8
H	9	B11	11	A10	10	D9

Variables:

B1	1.51012006
B2	1.34694244
B3	1.47429877
B4	1.42172094
B5	1.09034225
B6	1.08971488
B7	1.09053675
B8	1.41223649
B9	1.09089643
B10	1.08993798
B11	1.09008982
A1	112.99316527
A2	109.51772093
A3	107.65854811
A4	111.19067794
A5	104.21986564
A6	111.10986775
A7	113.03259352
A8	102.13138361
A9	112.47885094
A10	110.52591592
D1	-90.40411627
D2	-81.20353391
D3	63.62677996
D4	-178.55166876
D5	-60.32388638
D6	13.12043633
D7	-178.63656213
D8	-117.69141200
D9	-120.28289070

trans -TS1-3 (IM1-IM3)

O					
O	1	B1			
O	2	B2	1	A1	
O	3	B3	2	A2	1
C	4	B4	3	A3	2
H	5	B5	4	A4	3
H	5	B6	4	A5	3
H	5	B7	4	A6	3
C	1	B8	2	A7	3
H	9	B9	1	A8	2

H	9	B10	1	A9	10	D8
H	9	B11	10	A10	11	D9

Variables:

B1	1.48971854
B2	1.35348787
B3	1.45465864
B4	1.42159249
B5	1.09071319
B6	1.08947761
B7	1.09072093
B8	1.41223502
B9	1.08950558
B10	1.09233616
B11	1.09260160
A1	106.23688815
A2	109.22832438
A3	107.94073229
A4	111.21433610
A5	104.23861670
A6	111.15706705
A7	104.05616395
A8	104.14775245
A9	111.62084018
A10	109.34639752
D1	-84.71188347
D2	-82.85660335
D3	63.94853742
D4	-178.23037019
D5	-59.91297023
D6	-171.12788939
D7	-179.70905882
D8	-118.15316147
D9	121.01663949

TS1 (R→P1)

O					
O	1	B1			
O	1	B2	2	A1	
O	3	B3	1	A2	2
C	2	B4	1	A3	3
H	5	B5	2	A4	1
H	5	B6	1	A5	6
H	5	B7	7	A6	6
C	5	B8	7	A7	8
H	9	B9	5	A8	7
H	9	B10	5	A9	7
H	9	B11	5	A10	7

Variables:

B1	1.33725335
B2	2.90104141
B3	1.24300442
B4	2.13192975

B5	1.07809004
B6	1.07797391
B7	1.08490608
B8	3.59148307
B9	1.08589408
B10	1.09772201
B11	1.08729905
A1	99.34454511
A2	40.90798852
A3	107.97500850
A4	96.47110270
A5	95.67586481
A6	112.19927680
A7	108.19611449
A8	98.53343239
A9	69.95954877
A10	146.25058219
D1	-66.67884671
D2	16.27121455
D3	-87.93614516
D4	-118.26564456
D5	-137.05409674
D6	-143.01173955
D7	-50.17780675
D8	-159.25928781
D9	104.57536975

TS2 (IM1→P2)

O					
O	1	B1			
O	2	B2	1	A1	
O	3	B3	2	A2	1
C	4	B4	3	A3	2
H	5	B5	4	A4	3
H	5	B6	4	A5	3
H	5	B7	4	A6	3
C	1	B8	2	A7	3
H	9	B9	1	A8	2
H	9	B10	1	A9	2
H	9	B11	1	A10	2

Variables:

B1	1.83686888
B2	1.21991239
B3	2.05440017
B4	1.28538831
B5	1.10149224
B6	1.23750609
B7	1.10126903
B8	1.34578244
B9	1.09691421
B10	1.13280263
B11	1.09662870

A1	109.93813942
A2	100.15928355
A3	99.77809200
A4	117.39467070
A5	101.98646988
A6	117.41747598
A7	104.40579316
A8	112.88732756
A9	107.42243013
A10	113.21503506
D1	91.84704915
D2	5.07059671
D3	105.81238395
D4	-3.12324740
D5	-109.53928002
D6	4.06215696
D7	-117.95390956
D8	-3.85189329
D9	112.02827197

TS3 (IM1→P3)

O						
O	1	B1				
O	2	B2	1	A1		
O	3	B3	2	A2	1	D1
C	4	B4	3	A3	2	D2
H	5	B5	4	A4	3	D3
H	5	B6	4	A5	3	D4
H	5	B7	4	A6	3	D5
C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	2	D8
H	9	B11	1	A10	2	D9

Variables:

B1	2.36915018
B2	1.22676328
B3	1.55437864
B4	1.36025169
B5	1.18059984
B6	1.08927759
B7	1.09766640
B8	1.37684299
B9	1.09884215
B10	1.09890563
B11	1.10405749
A1	98.68684536
A2	114.02632482
A3	109.71351587
A4	107.93571222
A5	106.75969709
A6	112.87409998
A7	150.71369322

A8	113.12607946
A9	113.15365861
A10	107.59145014
D1	59.04811266
D2	-4.93861555
D3	-64.44083833
D4	172.28608295
D5	47.50726052
D6	103.39888845
D7	131.43154622
D8	-102.41121503
D9	14.53991826

TS4 (IM2→P4)

O					
O	1	B1			
O	2	B2	1	A1	
O	3	B3	2	A2	1
C	4	B4	3	A3	2
H	5	B5	4	A4	3
H	5	B6	4	A5	3
H	5	B7	4	A6	3
C	1	B8	5	A7	4
H	9	B9	1	A8	5
H	9	B10	1	A9	5
H	9	B11	1	A10	5

Variables:

B1	2.15903630
B2	1.29231510
B3	1.32702080
B4	2.10412653
B5	1.07731216
B6	1.07725511
B7	1.07681042
B8	1.38672039
B9	1.09848844
B10	1.09318368
B11	1.10004811
A1	91.82171902
A2	113.46937892
A3	114.08954567
A4	137.43162411
A5	92.64145824
A6	73.02131124
A7	112.83153965
A8	107.97157485
A9	111.23826883
A10	113.13390494
D1	52.14942625
D2	-6.78665135
D3	0.94610052
D4	-135.52125774

D5	107.83435943					
D6	150.87522344					
D7	102.19507444					
D8	-139.20473465					
D9	-16.90449693					

TS5 (IM3→P5)

O						
O	1	B1				
O	2	B2	1	A1		
O	2	B3	1	A2	3	D1
C	3	B4	2	A3	1	D2
H	5	B5	2	A4	1	D3
H	5	B6	1	A5	6	D4
H	5	B7	6	A6	7	D5
C	5	B8	6	A7	7	D6
H	9	B9	5	A8	6	D7
H	9	B10	5	A9	6	D8
H	9	B11	5	A10	6	D9

Variables:

B1	1.51374233
B2	1.25540963
B3	2.59222647
B4	2.68331374
B5	1.10094831
B6	1.18107454
B7	1.10127100
B8	4.13820616
B9	1.09127636
B10	1.08919913
B11	1.09004707
A1	109.55176904
A2	96.98468989
A3	88.78949466
A4	117.71553226
A5	51.68033900
A6	113.71632019
A7	99.26924769
A8	123.35842937
A9	54.05871933
A10	127.40366403
D1	-94.84645082
D2	-94.81949679
D3	25.19675980
D4	101.73519951
D5	-109.24302090
D6	71.11644711
D7	-174.91942184
D8	91.77041547
D9	2.68653810

TS6 (IM3→P6)

O

O	1	B1			
O	2	B2	1	A1	
O	3	B3	2	A2	1
C	4	B4	3	A3	2
H	5	B5	4	A4	3
H	4	B6	3	A5	2
H	5	B7	7	A6	6
C	1	B8	2	A7	3
H	9	B9	1	A8	2
H	9	B10	1	A9	2
H	9	B11	1	A10	2

Variables:

B1	1.88808839
B2	1.28618060
B3	1.32090836
B4	2.18376195
B5	1.08210100
B6	2.45801213
B7	1.07725866
B8	1.31967751
B9	1.10024839
B10	1.09994330
B11	1.19509986
A1	107.60257743
A2	112.44761339
A3	107.06879420
A4	138.50823654
A5	133.10940898
A6	115.22859586
A7	105.85150919
A8	115.53034700
A9	113.84625316
A10	108.25776669
D1	55.91744795
D2	43.85702709
D3	-46.99185982
D4	44.42877460
D5	-136.55169904
D6	-85.34035402
D7	-106.35656269
D8	118.60797209
D9	8.64051733

TS7 (R→P7)

O					
O	1	B1			
O	1	B2	2	A1	
O	3	B3	1	A2	2
C	4	B4	3	A3	1
H	5	B5	4	A4	3
H	5	B6	4	A5	3
H	5	B7	4	A6	3

C	1	B8	2	A7	3	D6
H	9	B9	1	A8	2	D7
H	9	B10	1	A9	10	D8
H	9	B11	11	A10	10	D9

Variables:

B1	1.24715635
B2	3.94283922
B3	1.35815670
B4	1.42959952
B5	1.08893724
B6	1.09131962
B7	1.08804390
B8	1.88819150
B9	1.07434908
B10	1.07400657
B11	1.07335691
A1	113.78324186
A2	112.04323291
A3	110.35547877
A4	109.99574638
A5	110.20954979
A6	105.54702882
A7	113.56026799
A8	93.85070451
A9	91.92065754
A10	120.28205353
D1	106.02343042
D2	98.59664930
D3	56.27747607
D4	-65.31336180
D5	175.75539817
D6	0.90552889
D7	-62.48058199
D8	-119.56990754
D9	-168.83515654

TS8 (R→P8)

O					
O	1	B1			
O	2	B2	1	A1	
O	3	B3	2	A2	1
C	4	B4	3	A3	2
H	5	B5	4	A4	3
H	2	B6	1	A5	5
H	5	B7	4	A6	3
C	1	B8	2	A7	3
H	9	B9	1	A8	2
H	9	B10	1	A9	10
H	9	B11	10	A10	11

Variables:

B1	1.40340974
B2	4.50973657

B3	1.33124848
B4	1.41111368
B5	1.08492965
B6	1.09460925
B7	1.08534586
B8	1.42493944
B9	1.08971465
B10	1.09150504
B11	1.08893621
A1	98.72564715
A2	14.23799347
A3	109.70017319
A4	113.01340995
A5	105.39481903
A6	112.92392381
A7	108.72267376
A8	110.55328352
A9	110.80651117
A10	110.27914873
D1	-57.17737632
D2	5.27669789
D3	-65.94886712
D4	-0.11832164
D5	71.58678871
D6	78.11643431
D7	57.43029183
D8	-122.54186149
D9	121.72387672

TS8 Mulliken spin density analysis

1	O	0.085313
2	O	0.276162
3	O	0.762362
4	O	0.266331
5	C	0.623477
6	H	0.006636
7	H	-0.034482
8	H	0.009316
9	C	-0.002480
10	H	0.004534
11	H	0.002568
12	H	0.000263

TABLE5: Vibrational Frequencies,^a Rotational Constants (B) and Average of S^2 at the B3LYP/6-311++g(2df,2p) Level for the Main Species in the Self-Reaction of $\text{CH}_3\text{O}_2\cdot$ System

Species	B/MHz	Frequencies (cm^{-1})	$\langle S^2 \rangle$
$\text{CH}_3\text{O}_2\cdot$	53170, 11293 9904	131, 492, 914, 1126, 1157, 1221, 1446, 1474, 1485, 3055, 3143, 3157	0.750
$\text{CH}_3\text{O}\cdot$	158111, 28111, 27908	679, 957, 1105, 1355, 1367, 1512, 2895, 2968, 3011	0.750
$\cdot\text{CH}_2\text{O}_2\cdot$	58260, 12168, 10865	184, 350, 559, 962, 1057, 1103, 1444, 3134, 3287	2.000
CH_3OCH_3	39654, 9972, 8860	204, 236, 409, 938, 1117, 1161, 1191, 1194, 1265, 1463, 1486, 1489, 1494, 1499, 1516, 2966, 2978, 3009, 3014, 3114, 3115	0.000
CH_3OOCH_3	31883, 4557, 4201	40, 211, 264, 304, 484, 841, 1051, 1062, 1171, 1172, 1176, 1264, 1447, 1456, 1462, 1463, 512, 1519, 3011, 3014, 3072, 3072, 3116, 3117	0.000
CH_3OOOH	19697, 5510, 4946	150, 197, 378, 439, 559, 755, 909, 999, 1170, 1205, 1389, 1448, 1470, 1507, 3034, 3110, 3126, 3731	0.000
IM1	11265, 1827, 1798	72, 89, 152, 203, 216, 302, 458, 560, 602, 614, 832, 888, 990, 1004, 1168, 1170, 1202, 1209, 1448, 1448, 1471, 1471, 1507, 1507, 3031, 3032, 3107, 3107, 3126, 3126	0.000
IM2	6056, 2465, 2019	73, 81, 126, 190, 201, 365, 421, 479, 568, 638, 799, 946, 1000, 1010, 1171, 1172, 1199, 1210, 1448, 1449, 1466, 1466, 1508, 1518, 3027, 3028, 3100, 3100, 3116, 3117	0.000
IM3	7486, 2184, 1927	61, 93, 141, 205, 210, 351, 422, 544, 593, 611, 812, 900, 991, 1000, 1170, 1171, 1202, 1206, 1448, 1449, 1470, 1472, 1507, 1510, 3029, 3035, 3104, 3113, 3121, 3127	0.000
IM4	5988, 2500, 2339	120, 126, 157, 188, 189, 267, 364, 481, 486, 563, 901, 923, 1055, 1140, 1145, 1155, 1202, 1246, 1437, 1444, 1465, 1470, 1480, 1488, 3055, 3058, 3144, 3147, 3178, 3184	0.000

IM5	7260, 2492, 2079	110, 137, 179, 190, 224, 276, 367, 480, 532, 559, 907, 913, 1063, 1142, 1148, 1159, 1208, 1247, 1442, 1443, 1469, 1469, 1480, 1481, 3058, 3059, 3150, 3150, 3177, 3177,	0.000
IM6	5263, 1357, 1141	18, 27, 36, 62, 74, 82, 137, 152, 492, 493, 908, 908, 1128, 1130, 1159, 1161, 1228, 1230, 1450, 1450, 1475, 1477, 1486, 1491, 3053, 3054, 3145, 3145, 3160, 3160	2.000
cis-TS1-2 (IM1-IM2)	5903, 2631, 2177	158 <i>i</i> , 135, 140, 152, 188, 303, 377, 454, 613, 617, 900, 947, 996, 1000, 1162, 1164, 1206, 1207, 1448, 1451, 1472, 1474, 1503, 1503, 3046, 3047, 3127, 3128, 3144, 3144	0.000
trans-TS1-2 (IM1-IM2)	9892, 1767, 1668	53 <i>i</i> , 115, 157, 164, 187, 336, 341, 475, 504, 683, 916, 962, 998, 1036, 1163, 1164, 1206, 1206, 1448, 1451, 1473, 1474, 1501, 1503, 3038, 3040, 3117, 3118, 3135, 3136	0.000
cis-TS1-3 (IM1-IM3)	8015, 2177, 1954	145 <i>i</i> , 77, 153, 209, 234, 286, 399, 526, 600, 644, 712, 921, 997, 1019, 1167, 1171, 1199, 1203, 1439, 1446, 1456, 1468, 1508, 1520, 3027, 3028, 3102, 3103, 3109, 3117	0.000
trans-TS1-3 (IM1-IM3)	10686, 1737, 1699	44 <i>i</i> , 78, 143, 204, 234, 312, 347, 539, 591, 679, 798, 940, 1005, 1034, 1170, 1172, 1201, 1215, 1445, 1448, 1461, 1470, 1507, 1515, 3010, 3025, 3072, 3097, 3115, 3118	0.000
TS1 ^b (R→P1)	4285, 3205, 2114	537 <i>i</i> , 86, 139, 205, 216, 280, 312, 353, 418, 430, 525, 858, 863, 940, 1038, 1152, 1195, 1205, 1349, 1411, 1450, 1470, 1485, 1490, 2967, 3080, 3104, 3162, 3210, 3280	0.000
TS2 (IM1→P2)	5543, 2319, 2197	659 <i>i</i> , 100, 150, 170, 260, 332, 408, 424, 551, 592, 672, 835, 1020, 1121, 1143, 1193, 1255, 1263, 1356, 1394, 1401, 1439, 1508, 1535, 1755, 2604, 2911, 2966, 2989, 3030	0.000
TS3 ^b (IM1→P3)	5458, 2092, 1725	493 <i>i</i> , 82, 84, 176, 241, 252, 304, 342, 393, 439, 723, 882, 1040, 1104, 1121, 1141, 1149, 1258, 1316, 1383, 1402, 1416, 1419, 1500, 1892, 2916, 2953, 2986, 2987, 3118	0.000
TS4 (IM2→P4)	5028, 2725, 2054	772 <i>i</i> , 46, 81, 147, 175, 223, 242, 272, 319, 431, 703, 835, 843, 982, 1043, 1063, 1112, 1160, 1232, 1420, 1433, 1446, 1483, 1503, 2940, 2989, 3046, 3122, 3261, 3295	0.051
TS5 (IM3→P5)	4807 2386 1771	662 <i>i</i> , 87, 92, 109, 126, 194, 328, 357, 390, 487, 708, 771, 1002, 1028, 1172, 1187, 1205, 1254, 1265, 1343, 1441, 1460, 1511,	0.026

		1517, 1835, 2916, 2984, 3027, 3104, 3123	
TS6 (IM3→P6)	3992, 3227, 2262	949 <i>i</i> , 121, 123, 201, 213, 224, 329, 378, 454, 480, 646, 741, 818, 977, 1004, 1083, 1138, 1146, 1223, 1307, 1362, 1429, 1461, 1498, 1840, 2925, 2998, 3103, 3241, 3271	0.000
TS7(R→P7)	11267, 1009, 974	881 <i>i</i> , 25, 74, 96, 119, 146, 189, 225, 359, 417, 485, 925, 992, 1010, 1024, 1127, 1145, 1200, 1358, 1404, 1407, 1450, 1472, 1491, 3028, 3104, 3137, 3143, 3327, 3336	2.000
TS8(R→P8)	7092, 1379, 1215	1349 <i>i</i> , 30, 38, 64, 121, 153, 232, 379, 463, 504, 579, 906, 927, 994, 1050, 1106, 1135, 1165, 1198, 1243, 1442, 1453, 1470, 1482, 1504, 3026, 3084, 3099, 3127, 3207	2.000

^a Imaginary frequencies are denoted by “*i*”.

^b Spin-restricted calculations for this species.