Kinetics of the OH reaction with 2-Methyl-2-Propen-1-ol and the Analogue Alkene

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Supplementary Material

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A: Cartesian coordinates (angstroms), vibrational frequencies (cm-1) and electronic energies (hartrees) for the stationary points on the MPO221 + OH Potential Energy Surface calculated at BHandHLYP/cc-pVDZ

MPO221 BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	0.405521	1.453824	-0.044616
H	-0.556298	1.945408	-0.130942
H	1.290309	2.079575	0.004963
C	0.494514	0.129517	-0.022740
C	1.796681	-0.606424	0.058735
H	2.645642	0.079354	0.062073
H	1.846968	-1.221080	0.965030
H	1.913812	-1.289430	-0.790918
C	-0.728340	-0.745876	-0.091120
H	-0.644245	-1.531229	0.677175
H	-0.741138	-1.267412	-1.054801
O	-1.948318	-0.068297	0.001485
H	-1.978770	0.364946	0.853995

Frequencies

129.82	179.90	290.68	355.31	398.60	451.09
559.16	741.83	875.71	974.53	995.72	1010.53
1045.49	1105.54	1169.87	1258.23	1318.29	1430.53
1446.58	1471.48	1474.69	1505.46	1514.40	1528.30
1805.67	3058.55	3107.89	3144.45	3163.47	3216.30
3241.73	3338.62	3949.62			

E(BHandHLYP).....-232.304825

σ-PC_{pri} BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	-0.364713	0.832071	1.116212
H	0.649476	0.788098	1.493015
H	-1.004955	1.632824	1.471848
C	-0.818853	-0.095393	0.274560
C	-2.229286	-0.124020	-0.229910
H	-2.822244	0.695099	0.180712
H	-2.262274	-0.061618	-1.324004
H	-2.717228	-1.067374	0.041571
C	0.063019	-1.213399	-0.219149
H	-0.061575	-1.293900	-1.312466
H	-0.311028	-2.158462	0.192750
O	1.402498	-1.114063	0.142043
H	1.741921	-0.306044	-0.253990
O	1.510972	1.564312	-0.805509
H	0.685333	1.762173	-1.271525

Frequencies

53.63	95.71	116.39	144.38	181.16	288.00
324.46	377.64	400.04	445.19	539.64	569.89
752.76	874.50	973.81	992.14	1008.74	1045.20
1107.27	1186.00	1277.91	1318.60	1444.56	1459.63
1471.58	1474.19	1505.36	1511.76	1524.98	1788.60
3062.38	3111.58	3137.77	3169.13	3218.20	3236.20
3336.05	3717.45	3868.50			

E(BHandHLYP).....-308.0200863

σ-PC_{ter} BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	-0.540445	0.429555	1.359686
H	0.409528	0.714785	1.795666
H	-1.449792	0.821209	1.804301
C	-0.582368	-0.414084	0.325448
C	-1.858155	-0.876977	-0.302374
H	-2.733331	-0.513735	0.239348
H	-1.918682	-0.525748	-1.337796
H	-1.902390	-1.971697	-0.332100
C	0.679985	-0.985337	-0.268090
H	0.551694	-1.050943	-1.358618
H	0.802322	-2.013915	0.091746
O	1.838781	-0.290255	0.073981
H	1.714932	0.599179	-0.269190
O	0.182565	1.769442	-0.928948
H	-0.157096	2.455111	-0.336605

Frequencies

61.58	131.74	159.34	183.39	190.51	244.55
296.45	393.38	418.25	461.12	553.61	628.16
746.48	874.97	970.09	993.81	1002.95	1050.50
1102.61	1177.11	1274.48	1322.34	1439.26	1453.88
1468.05	1492.19	1506.65	1513.21	1524.33	1765.56
3077.97	3113.95	3139.21	3176.32	3216.55	3236.54
3341.23	3853.18	3877.66			

E(BHandHLYP).....-308.0204422

π-PC BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	-0.597750	-2.335504	1.549995
H	-1.309545	-3.027122	1.111298
H	0.291899	-2.744539	2.015888
C	-0.826625	-1.024483	1.571813
C	-2.063708	-0.398634	1.004424
H	-1.816710	0.319974	0.214735
H	-2.741934	-1.146729	0.590710
H	-2.602355	0.160216	1.778356
C	0.143801	-0.060930	2.209678
H	0.291785	0.790098	1.525490
H	-0.331066	0.356560	3.105599
O	1.355918	-0.617658	2.610933
H	1.864025	-0.804442	1.816685
O	2.009162	-1.369767	-0.116828
H	1.094250	-1.697942	-0.030592

Frequencies

63.12	115.05	142.01	174.02	197.57	289.20
299.10	395.02	429.82	452.01	557.64	617.84
755.50	874.37	973.74	990.43	1011.18	1044.56
1107.38	1182.54	1279.49	1317.11	1443.03	1458.48
1468.77	1482.12	1505.40	1510.84	1522.21	1788.67
3058.40	3111.22	3136.82	3168.63	3217.71	3235.30
3334.76	3716.82	3874.19			

E(BHandHLYP).....-308.0215015

TS_{pri} BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	-0.194462	0.849889	1.025133
H	0.711958	0.662201	1.581190
H	-0.774651	1.724592	1.296398
C	-0.719432	-0.112611	0.227318
C	-2.077508	-0.017406	-0.387843
H	-2.621323	0.864214	-0.043603
H	-2.018639	0.012565	-1.482537
H	-2.673371	-0.902978	-0.136648
C	0.116243	-1.306017	-0.149577
H	-0.051361	-1.515221	-1.219951
H	-0.245714	-2.191700	0.388170
O	1.467718	-1.158359	0.144987
H	1.719806	-0.289199	-0.192185
O	1.156440	1.587279	-0.432133
H	0.521274	1.754226	-1.139150

Frequencies

295.12i	125.53	151.28	163.23	193.29	308.77
315.70	393.11	435.00	555.64	711.92	723.22
832.96	869.70	983.33	1000.93	1012.87	1040.65
1094.18	1180.47	1270.99	1320.94	1436.06	1441.70
1463.28	1501.60	1510.68	1516.45	1528.11	1672.18
3038.69	3104.31	3121.85	3158.80	3214.49	3258.34
3370.16	3791.20	3873.24			

E(BHandHLYP).....-308.0178656

TS_{ter} BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	0.117085	-0.873830	1.099986
H	-0.844291	-0.626673	1.533057
H	0.589615	-1.809905	1.378193
C	0.692989	-0.037866	0.195383
C	2.076086	-0.259471	-0.328902
H	2.442129	-1.260400	-0.092917
H	2.097306	-0.123700	-1.411791
H	2.765642	0.468281	0.114927
C	0.090149	1.321388	-0.067876
H	0.410102	1.656019	-1.063726
H	0.499198	2.033145	0.658434
O	-1.295856	1.337500	0.066519
H	-1.600037	0.650419	-0.534828
O	-0.471044	-0.845019	-1.389618
H	-0.635065	-1.757374	-1.121662

Frequencies

284.63i	168.10	176.67	212.28	224.37	266.94
308.14	394.24	398.59	542.54	641.87	692.82
734.15	859.12	915.62	974.12	1012.12	1047.18
1082.71	1176.18	1266.04	1324.60	1434.23	1440.67
1464.02	1494.29	1504.41	1515.91	1529.83	1643.18
3094.86	3119.53	3148.23	3195.15	3227.73	3238.93
3351.61	3864.46	3872.97			

E(BHandHLYP).....-308.0183809

IM_{pri} BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	0.178608	1.105963	0.532893
H	0.568624	0.726031	1.483841
H	-0.534072	1.906920	0.763442
C	-0.474192	0.025479	-0.256270
C	-1.949909	-0.035220	-0.433013
H	-2.395555	0.961347	-0.507730
H	-2.221400	-0.596666	-1.334020
H	-2.443871	-0.544710	0.410130
C	0.337502	-1.178678	-0.622451
H	0.239268	-1.363856	-1.708508
H	-0.090812	-2.070885	-0.139988
O	1.678039	-1.115632	-0.229629
H	1.985164	-0.218727	-0.386743
O	1.327051	1.632642	-0.131312
H	1.035520	1.999293	-0.966574

Frequencies

85.67	106.30	138.77	216.59	257.67	337.71
388.48	455.14	557.49	623.05	807.89	934.01
971.43	996.88	1048.80	1071.04	1163.69	1201.77
1257.42	1287.60	1358.77	1384.20	1426.07	1447.60
1466.06	1499.27	1504.76	1512.93	1524.68	1530.04
3001.71	3054.72	3067.77	3106.00	3136.46	3151.25
3185.92	3872.55	3937.17			

E(BHandHLYP).....-308.0588574

IM_{ter} BHandHLYP/cc-pVDZ

Cartesian Coordinates

C	-0.359763	0.560051	1.354042
H	0.575923	0.739092	1.869806
H	-1.295223	0.645563	1.896300
C	-0.337771	0.277270	-0.109806
C	-1.648760	-0.310634	-0.600310
H	-2.480788	0.361607	-0.368499
H	-1.619775	-0.452589	-1.683137
H	-1.852087	-1.273485	-0.122129
C	0.843069	-0.622190	-0.472095
H	0.788744	-0.840753	-1.548573
H	0.776602	-1.567748	0.071121
O	2.059849	-0.024015	-0.133761
H	2.019942	0.861853	-0.500328
O	-0.047446	1.485374	-0.835331
H	-0.572142	2.193440	-0.463560

Frequencies

131.02	166.58	236.65	253.58	301.50	350.24
367.15	397.71	459.28	508.94	563.73	597.45
813.58	924.75	941.83	983.16	1036.48	1149.26
1174.50	1204.41	1262.31	1290.40	1404.12	1423.00
1447.69	1475.77	1492.05	1517.65	1520.10	1533.27
3081.45	3120.46	3186.65	3194.59	3213.28	3232.94
3356.99	3915.50	3953.35			

E(BHandHLYP).....-308.0582132

B: Cartesian coordinates (angstroms), vibrational frequencies (cm-1) and electronic energies (hartrees) for the stationary points on the MPO221 + OH Potential Energy Surface calculated at BHandHLYP/aug- cc-pVDZ

MPO221 BHandHLYP/aug-cc-pVDZ

Cartesian Coordinates

C	-0.095712	1.028694	0.778944
H	0.964151	1.065943	0.990333
H	-0.681630	1.906624	1.018692
C	-0.664749	-0.056670	0.266886
C	-2.135901	-0.156599	-0.003630
H	-2.656972	0.750313	0.299015
H	-2.328707	-0.326838	-1.066610
H	-2.574708	-1.000230	0.536977
C	0.116245	-1.293730	-0.081514
H	-0.154339	-1.607210	-1.098091
H	-0.185142	-2.107783	0.582263
O	1.509608	-1.183737	0.050775
H	1.824459	-0.502643	-0.537324

Frequencies

99.22	194.56	253.34	270.24	414.16	442.46
580.93	743.68	851.93	984.84	1002.73	1010.55
1080.56	1111.88	1121.21	1265.95	1291.50	1363.66
1445.78	1475.23	1499.64	1504.42	1528.10	1545.33
1794.35	3073.68	3111.82	3140.65	3178.36	3213.48
3232.24	3320.73	4008.05			

E(BHandHLYP).....-232.3247623

σ-PC_{pri} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.302402	0.818239	1.115085
H	0.686400	0.738776	1.540203
H	-0.922576	1.644463	1.437610
C	-0.773074	-0.107358	0.272487
C	-2.168834	-0.079219	-0.269828
H	-2.735065	0.763873	0.122987
H	-2.166613	-0.020774	-1.362049
H	-2.699903	-0.999219	-0.009148
C	0.067803	-1.264274	-0.193379
H	-0.056750	-1.366780	-1.279730
H	-0.319406	-2.186664	0.248375
O	1.419464	-1.187010	0.151333
H	1.767403	-0.380804	-0.230608
O	1.213874	1.602393	-0.761234
H	0.450745	1.864660	-1.285944

Frequencies

60.85	100.16	142.45	145.88	183.64	202.90
290.80	400.29	439.53	462.11	542.79	589.41
752.30	871.21	983.73	995.30	1004.08	1044.88
1100.71	1168.47	1266.81	1318.96	1435.83	1449.08
1478.13	1481.35	1507.78	1520.16	1530.47	1746.60
3067.83	3104.98	3139.87	3157.08	3209.93	3250.32
3354.18	3904.36	3916.22			

E(BHandHLYP).....-308.0496335

σ-PC_{ter} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.528714	0.452886	1.340551
H	0.411958	0.742677	1.786454
H	-1.439823	0.845835	1.773552
C	-0.570335	-0.403565	0.313503
C	-1.849980	-0.877373	-0.298322
H	-2.717840	-0.488227	0.231598
H	-1.908147	-0.564582	-1.343291
H	-1.899334	-1.969809	-0.286851
C	0.677070	-0.995048	-0.284104
H	0.564161	-1.011078	-1.374030
H	0.763768	-2.035589	0.039750
O	1.863447	-0.354282	0.089096
H	1.799375	0.550039	-0.217304
O	0.122538	1.774663	-0.876238
H	-0.250597	2.480044	-0.337909

Frequencies

66.83	137.10	139.90	158.91	181.87	229.08
288.72	400.12	420.25	495.50	532.20	580.82
735.63	873.10	974.53	993.61	998.02	1050.07
1098.01	1163.88	1266.96	1322.37	1438.23	1447.54
1474.86	1479.57	1509.75	1519.98	1530.31	1744.68
3094.38	3112.09	3147.68	3170.79	3213.01	3240.71
3342.60	3901.95	3926.96			

E(BHandHLYP).....-308.050449

π-PC BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.595657	-2.336681	1.544545
H	-1.308863	-3.017813	1.098358
H	0.287447	-2.760343	2.004242
C	-0.824093	-1.025707	1.578258
C	-2.062268	-0.399284	1.011720
H	-1.814927	0.317567	0.223911
H	-2.735324	-1.148619	0.598495
H	-2.600264	0.156198	1.784908
C	0.133347	-0.052567	2.216656
H	0.301654	0.781754	1.523764
H	-0.348237	0.377299	3.098922
O	1.347376	-0.599226	2.648128
H	1.888375	-0.786839	1.881840
O	2.005895	-1.410507	-0.195804
H	1.086689	-1.696134	-0.059758

Frequencies

53.19	99.42	130.39	139.81	181.42	252.47
288.90	395.63	400.00	448.68	534.76	559.77
747.79	874.35	978.64	991.01	1007.51	1046.75
1104.65	1165.04	1270.77	1315.94	1444.73	1452.03
1466.59	1476.12	1509.33	1518.86	1528.17	1779.45
3076.52	3108.43	3144.72	3162.37	3212.60	3237.01
3331.89	3742.75	3926.00			

E(BHandHLYP).....-308.0496316

TS_{pri} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.110248	0.894087	0.985885
H	0.834558	0.749021	1.483625
H	-0.675179	1.780499	1.240348
C	-0.667701	-0.090801	0.247218
C	-2.055086	-0.008719	-0.303202
H	-2.566809	0.894251	0.026031
H	-2.047401	-0.029564	-1.396811
H	-2.644149	-0.872425	0.018754
C	0.114425	-1.320245	-0.119245
H	-0.069171	-1.540515	-1.179686
H	-0.267515	-2.177320	0.443215
O	1.482766	-1.230502	0.146288
H	1.796629	-0.419112	-0.258445
O	1.180198	1.569062	-0.646794
H	0.494206	1.800724	-1.277515

Frequencies

200.05i	115.29	130.37	152.71	168.96	257.23
297.55	397.82	435.83	548.74	623.21	676.81
807.30	867.67	984.88	998.33	1011.00	1042.62
1093.22	1166.26	1264.24	1320.54	1431.70	1447.04
1470.34	1489.33	1506.16	1519.75	1529.65	1685.85
3064.95	3104.12	3133.63	3155.73	3211.01	3261.18
3368.55	3877.66	3925.33			

E(BHandHLYP).....-308.0491307

TS_{ter} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.448143	0.451796	1.407709
H	0.488213	0.646168	1.910139
H	-1.355245	0.860208	1.833659
C	-0.482568	-0.267501	0.257875
C	-1.766605	-0.673459	-0.392634
H	-2.619603	-0.159204	0.047088
H	-1.735867	-0.458782	-1.460233
H	-1.917139	-1.750401	-0.273840
C	0.752824	-0.948681	-0.271594
H	0.669762	-1.020102	-1.360187
H	0.783584	-1.968290	0.120847
O	1.946641	-0.327243	0.106195
H	1.892381	0.571266	-0.220402
O	0.024524	1.521453	-0.859050
H	-0.356716	2.252571	-0.367084

Frequencies

225.53i	139.82	181.76	194.50	209.82	252.33
298.92	393.87	399.92	531.90	588.40	687.88
706.18	860.58	938.70	975.12	1007.63	1047.74
1084.12	1164.27	1261.14	1325.26	1436.63	1442.54
1469.39	1482.41	1509.24	1523.34	1533.66	1652.43
3110.06	3116.84	3156.19	3187.43	3221.18	3242.04
3350.53	3920.77	3923.89			

E(BHandHLYP).....-308.0494352

IM_{pri} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.174830	1.111597	0.536592
H	0.598721	0.747937	1.475796
H	-0.550572	1.892839	0.776782
C	-0.469395	0.015401	-0.235232
C	-1.942193	-0.035187	-0.443178
H	-2.378185	0.963555	-0.504196
H	-2.196237	-0.573796	-1.360213
H	-2.452989	-0.559946	0.376765
C	0.330053	-1.194016	-0.602258
H	0.235189	-1.379118	-1.683505
H	-0.090803	-2.081253	-0.112250
O	1.681339	-1.141253	-0.221183
H	2.016122	-0.262618	-0.399166
O	1.296048	1.675559	-0.155383
H	0.988037	2.053602	-0.975301

Frequencies

77.74	80.58	119.37	192.94	249.51	340.06
371.86	441.75	551.55	559.21	805.70	933.80
970.31	997.03	1041.64	1051.73	1145.89	1194.64
1247.10	1287.21	1361.24	1381.08	1416.53	1446.07
1453.06	1488.79	1501.93	1516.45	1533.17	1534.88
3026.85	3051.37	3078.88	3117.14	3130.23	3161.02
3180.52	3917.57	3974.95			

E(BHandHLYP).....-308.0886748

IM_{ter} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.368152	0.569052	1.356347
H	0.552150	0.784624	1.879728
H	-1.304473	0.609075	1.896780
C	-0.339518	0.286133	-0.107367
C	-1.648658	-0.312880	-0.594316
H	-2.482622	0.350759	-0.358835
H	-1.621542	-0.457154	-1.674036
H	-1.836818	-1.274359	-0.112874
C	0.835040	-0.617428	-0.479139
H	0.789335	-0.812941	-1.556036
H	0.753837	-1.567065	0.048367
O	2.070764	-0.054614	-0.127020
H	2.102369	0.819449	-0.511038
O	-0.062001	1.500995	-0.832767
H	-0.589337	2.209194	-0.474056

Frequencies

110.06	150.16	232.22	247.01	270.62	346.40
366.35	402.69	453.77	465.76	569.24	601.60
810.29	924.92	935.40	986.76	1031.60	1140.52
1165.21	1199.63	1258.91	1285.43	1400.86	1419.94
1448.33	1474.47	1498.52	1524.25	1527.35	1537.35
3101.43	3119.17	3189.14	3195.09	3209.01	3236.68
3358.84	3961.72	3988.71			

E(BHandHLYP).....-308.0892122

C: Cartesian coordinates (angstroms), vibrational frequencies (cm-1) and electronic energies (hartrees) for the stationary points on the M2 + OH Potential Energy Surface calculated at BHandHLYP/cc-pVDZ

M2 BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	0.010683	1.445627	-0.168029
C	0.000939	0.125323	-0.020688
H	0.940716	2.001671	-0.229325
H	-0.911046	2.014993	-0.232378
C	-1.274057	-0.659091	0.065735
H	-1.326803	-1.405545	-0.735516
H	-1.327934	-1.211354	1.011289
H	-2.153071	-0.015653	-0.006406
C	1.264218	-0.677350	0.069909
H	1.308933	-1.424395	-0.731264
H	2.152627	-0.046628	0.000829
H	1.306970	-1.230433	1.015535

Frequencies

175.37	222.49	388.30	449.77	457.28	726.71
851.75	965.58	989.52	1017.22	1047.20	1114.24
1137.87	1343.94	1444.51	1455.92	1476.64	1495.02
1507.00	1513.87	1527.36	1806.28	3103.85	3109.48
3160.97	3164.26	3211.59	3212.97	3230.60	3321.63

E(BHandHLYP).....-157.1235288

σ-PC_{ter} BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	0.364354	-0.174911	1.418042
C	-0.457088	-0.026215	0.378153
H	0.784597	0.682574	1.933416
H	0.628415	-1.159426	1.792647
C	-1.048948	-1.198751	-0.342782
H	-2.143595	-1.148371	-0.333777
H	-0.730389	-1.193286	-1.389646
H	-0.745245	-2.147310	0.105216
C	-0.855363	1.323677	-0.135821
H	-1.941307	1.455876	-0.067368
H	-0.373451	2.127991	0.422882
H	-0.579801	1.424291	-1.189520
O	1.767845	0.061122	-1.139078
H	2.299682	-0.493159	-0.550335

Frequencies

66.11	79.16	93.66	115.84	166.97	209.89
332.80	391.01	449.81	459.51	726.34	852.57
951.67	993.09	1018.54	1043.80	1117.71	1137.36
1345.73	1442.05	1454.88	1472.40	1495.65	1504.86
1515.55	1527.17	1780.37	3112.79	3118.20	3181.39
3185.29	3211.42	3219.56	3226.23	3319.93	3848.53

E(BHandHLYP).....-232.8327446

π-PC BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	-0.534326	-0.724861	1.341535
H	-1.129865	-1.569707	1.673032
H	0.327546	-0.458484	1.945293
C	-0.862045	-0.028717	0.254228
C	-2.048708	-0.383215	-0.591841
H	-1.729718	-0.655529	-1.604230
H	-2.610807	-1.220470	-0.173814
H	-2.724028	0.473781	-0.689839
C	-0.049977	1.140315	-0.218633
H	0.364783	0.941276	-1.213218
H	-0.675101	2.035595	-0.306979
O	0.825570	-1.759929	-1.722932
H	0.562343	-1.640825	-0.793868
H	0.777128	1.361579	0.458596

Frequencies

58.18	61.22	121.03	175.99	219.15	332.77
386.07	392.19	450.97	469.88	737.31	850.26
969.98	992.18	1017.14	1051.57	1116.97	1140.63
1349.92	1446.87	1459.48	1475.24	1496.58	1512.40
1516.39	1527.81	1791.36	3110.78	3115.34	3174.35
3176.40	3215.34	3216.37	3229.38	3322.46	3758.16

E(BHandHLYP).....-232.8338157

TS_{pri} BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	-0.168808	0.917821	-0.381888
C	0.000753	0.776149	-1.718413
H	0.097173	1.841720	0.117637
H	-0.776226	0.219313	0.177430
C	-0.439670	-0.459903	-2.435027
H	-1.103047	-0.211625	-3.271952
H	0.422425	-0.986904	-2.860544
H	-0.960451	-1.149537	-1.769236
C	0.709534	1.807513	-2.540046
H	0.060670	2.171693	-3.345548
H	1.021933	2.665935	-1.941459
H	1.595964	1.383876	-3.028405
O	1.504963	-0.168984	0.277551
H	2.162602	0.265751	-0.279088

Frequencies

319.59i	95.64	107.49	139.54	177.11	194.60
386.79	444.61	449.32	732.38	824.44	846.21
967.07	990.33	1016.71	1034.60	1103.21	1116.46
1348.90	1440.22	1455.55	1462.22	1492.26	1503.21
1510.74	1526.68	1676.31	3099.67	3107.64	3154.25
3161.99	3207.86	3222.15	3254.55	3356.24	3866.69

E(BHandHLYP).....-232.8290677

TS_{ter} BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	0.407325	-0.169072	1.394124
C	-0.294503	-0.013555	0.237968
H	0.824640	0.685326	1.914469
H	0.607766	-1.155407	1.800155
C	-0.987716	-1.177082	-0.406542
H	-2.055261	-1.160152	-0.157276
H	-0.893411	-1.122315	-1.492246
H	-0.575361	-2.130341	-0.069196
C	-0.727625	1.345140	-0.225506
H	-1.776798	1.511605	0.044833
H	-0.122829	2.132442	0.226342
H	-0.642139	1.423493	-1.310730
O	1.439871	-0.009277	-0.921699
H	1.995551	-0.668867	-0.488758

Frequencies

351.37i	146.93	170.52	220.13	226.11	243.47
390.56	405.45	441.00	659.63	758.67	841.12
874.62	988.06	1003.87	1045.16	1100.20	1108.99
1347.70	1433.39	1455.80	1464.49	1494.16	1506.34
1511.19	1527.95	1643.44	3116.86	3122.84	3193.66
3200.42	3226.63	3231.64	3234.70	3335.94	3867.05

E(BHandHLYP).....-232.8293023

IM_{pri} BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	0.847502	-0.362422	-0.653306
C	-0.397200	-0.087839	0.125908
H	1.070553	-1.439601	-0.628425
H	0.704343	-0.103174	-1.714148
C	-0.754365	1.328717	0.420055
H	-1.383268	1.754974	-0.379894
H	-1.330215	1.416248	1.347875
H	0.138657	1.951654	0.497643
C	-1.471648	-1.118916	0.141239
H	-2.115416	-1.049526	-0.751982
C	-1.064819	-2.134910	0.161112
H	-2.131491	-0.997554	1.006824
O	1.957818	0.399814	-0.241622
H	2.108848	0.212930	0.684515

Frequencies

32.71	89.43	102.80	192.47	328.71	360.35
403.21	529.37	787.94	951.51	974.65	1015.69
1036.61	1071.50	1076.13	1202.53	1338.07	1349.19
1410.63	1439.43	1443.46	1458.17	1495.37	1499.41
1507.57	1520.76	1533.24	3036.76	3067.60	3091.27
3137.47	3144.16	3154.77	3188.33	3190.90	3944.92

E(BHandHLYP).....-232.873043

E(CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ)....-232.36172956

IM_{ter} BHandHLYP/ cc-pVDZ

Cartesian Coordinates

C	0.131679	1.312666	-0.781820
C	0.002832	0.042458	-0.003428
H	0.918605	2.010471	-0.514938
H	-0.412122	1.465383	-1.707788
C	-1.372499	-0.586160	-0.206876
H	-1.540837	-0.843292	-1.256752
H	-1.460272	-1.493638	0.395263
H	-2.162821	0.107346	0.099066
C	1.104949	-0.941647	-0.386014
H	1.030507	-1.225221	-1.438607
H	2.084953	-0.492698	-0.209524
H	1.024071	-1.841700	0.230563
O	0.216275	0.301574	1.378128
H	-0.411953	0.970184	1.649676

Frequencies

148.96	230.38	279.14	328.91	345.80	365.92
413.92	457.24	481.60	562.38	796.60	935.87
965.37	974.28	1027.08	1044.29	1172.80	1276.32
1308.83	1390.18	1434.46	1446.03	1481.11	1499.65
1508.08	1522.39	1532.59	3116.02	3125.81	3190.13
3205.83	3213.35	3218.79	3226.89	3345.66	3940.09

E(BHandHLYP).....-232.8722004

E(CCSD(T)/cc-pVDZ//BHandHLYP/cc-pVDZ)....-232.36410512

D: : Cartesian coordinates (angstroms), vibrational frequencies (cm-1) and electronic energies (hartrees) for the stationary points on the M2 + OH Potential Energy Surface calculated at BHandHLYP/aug- cc-pVDZ

M2 BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.010670	1.445465	-0.167705
C	0.000929	0.124147	-0.020500
H	0.938235	2.000991	-0.228872
H	-0.908607	2.014264	-0.231912
C	-1.274109	-0.660180	0.065774
H	-1.324748	-1.404259	-0.734489
H	-1.326184	-1.210085	1.009978
H	-2.149409	-0.015827	-0.006706
C	1.264263	-0.678428	0.069889
H	1.306956	-1.422924	-0.730437
H	2.148964	-0.046705	0.000607
H	1.305214	-1.229295	1.014064

Frequencies

174.91	223.27	392.26	454.35	459.39	722.84
849.82	970.32	990.77	1016.88	1041.11	1114.84
1132.18	1343.80	1444.39	1453.28	1481.61	1496.93
1510.35	1516.84	1532.42	1790.99	3100.42	3105.81
3153.92	3157.37	3205.75	3207.08	3230.45	3318.30

E(BHandHLYP).....-157.1324603

σ-PC_{pri} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.395868	-0.168315	1.201100
C	-0.568999	-0.025581	0.288209
H	0.917822	0.685397	1.610066
H	0.669005	-1.143137	1.585510
C	-1.314806	-1.199196	-0.270971
H	-2.384531	-1.107175	-0.064065
H	-1.211730	-1.240665	-1.359098
H	-0.964188	-2.141202	0.149172
C	-0.973126	1.316094	-0.238893
H	-2.033981	1.500015	-0.046429
H	-0.390880	2.117008	0.212982
H	-0.832168	1.358826	-1.321895
O	2.128491	0.084073	-0.698737
H	1.880654	-0.806158	-0.972125

Frequencies

24.00	50.39	95.12	151.27	169.34	217.77
394.16	434.88	453.05	460.34	737.97	849.84
976.92	990.89	1017.66	1035.76	1114.97	1129.21
1347.37	1444.31	1454.54	1479.30	1496.65	1508.99
1516.90	1533.50	1758.81	3103.33	3109.46	3157.35
3164.00	3205.23	3217.27	3239.68	3334.96	3889.61

E(BHandHLYP).....-232.8533002

σ-PC_{ter} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.387345	-0.192875	1.366826
C	-0.458797	-0.020508	0.346522
H	0.830034	0.650303	1.880876
H	0.640714	-1.182857	1.726238
C	-1.096454	-1.175562	-0.361620
H	-2.185282	-1.121537	-0.275516
H	-0.853994	-1.144356	-1.425843
H	-0.764859	-2.131299	0.042413
C	-0.854062	1.339546	-0.139127
H	-1.933484	1.480074	-0.033512
H	-0.344360	2.128369	0.411528
H	-0.614204	1.446632	-1.198724
O	1.813059	0.061747	-0.983204
H	2.377667	-0.518367	-0.461416

Frequencies

67.02	102.33	107.88	132.05	178.21	222.82
395.11	409.38	453.03	466.62	727.28	851.26
964.89	993.32	1019.12	1037.75	1118.51	1131.41
1348.93	1443.85	1455.27	1477.70	1498.21	1509.54
1519.34	1533.45	1756.11	3108.89	3114.28	3171.18
3175.26	3208.40	3215.17	3229.77	3322.98	3896.93

E(BHandHLYP)..... -232.8540993

π-PC BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.475863	-0.760438	1.210913
H	-1.039939	-1.631913	1.519806
H	0.412659	-0.519778	1.781600
C	-0.875289	0.001024	0.192425
C	-2.111530	-0.307992	-0.597541
H	-1.868609	-0.448783	-1.654374
H	-2.610202	-1.205577	-0.235005
H	-2.815812	0.526559	-0.545334
C	-0.116111	1.220183	-0.237899
H	0.196123	1.131248	-1.282070
H	-0.751920	2.107240	-0.174176
O	1.131936	-2.211570	-1.357397
H	0.648133	-1.772811	-0.638340
H	0.769220	1.383417	0.374722

Frequencies

33.20	40.48	123.07	171.63	223.35	333.37
396.90	432.77	452.60	468.83	739.28	849.40
978.82	992.01	1017.97	1043.52	1117.73	1134.82
1348.61	1448.74	1456.69	1481.03	1497.87	1511.40
1518.63	1533.55	1778.72	3106.32	3111.36	3162.21
3165.61	3211.09	3212.27	3229.02	3319.80	3744.77

E(BHandHLYP).....-232.8553091

TS_{pri} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	-0.188012	0.951845	-0.394991
C	0.008387	0.797912	-1.721425
H	0.031568	1.886918	0.097519
H	-0.716610	0.206243	0.182181
C	-0.387900	-0.454176	-2.440169
H	-1.099470	-0.226586	-3.239164
H	0.477983	-0.919010	-2.921414
H	-0.845779	-1.180767	-1.769973
C	0.673704	1.853226	-2.545559
H	0.023752	2.164854	-3.368602
H	0.928929	2.727480	-1.949753
H	1.591645	1.465861	-2.996552
O	1.800031	0.313372	0.277919
H	1.829587	-0.514355	-0.209008

Frequencies

192.50i	83.01	103.18	148.27	159.34	202.51
393.47	450.19	459.30	669.31	797.22	845.70
983.58	991.46	1017.16	1030.15	1107.43	1118.75
1350.45	1443.24	1454.79	1469.98	1495.13	1507.36
1515.15	1533.70	1691.93	3099.32	3105.60	3151.13
3157.05	3205.56	3218.04	3257.11	3355.43	3918.81

E(BHandHLYP).....-232.8527261

TS_{ter} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.414881	-0.174564	1.380702
C	-0.309806	-0.016285	0.240829
H	0.839261	0.675784	1.896482
H	0.619175	-1.159109	1.781967
C	-1.007894	-1.175965	-0.402241
H	-2.073115	-1.143445	-0.155901
H	-0.913450	-1.123291	-1.485825
H	-0.605850	-2.128719	-0.060708
C	-0.735073	1.342281	-0.226129
H	-1.784829	1.504516	0.034230
H	-0.136382	2.127361	0.231173
H	-0.642710	1.418824	-1.308694
O	1.474182	-0.020045	-0.913008
H	2.061120	-0.635405	-0.466941

Frequencies

294.80i	145.26	173.82	215.72	226.38	245.26
395.00	409.64	447.04	667.65	737.50	841.70
908.89	986.60	1008.50	1044.09	1105.01	1111.12
1351.55	1438.57	1457.04	1469.84	1499.40	1511.25
1518.03	1535.21	1646.74	3113.36	3119.31	3187.28
3192.23	3220.82	3227.64	3234.44	3335.91	3920.86

E(BHandHLYP).....-232.8520136

IM_{pri} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.715691	-0.178774	1.178033
C	-0.505270	0.007878	0.351188
H	0.809546	0.634802	1.904793
H	0.662659	-1.126267	1.724219
C	-1.057485	-1.163564	-0.384861
H	-2.112623	-1.020983	-0.628774
H	-0.526787	-1.317978	-1.334703
H	-0.957028	-2.085853	0.190359
C	-0.843783	1.377838	-0.125907
H	-1.902753	1.462217	-0.379943
H	-0.606123	2.136217	0.622449
H	-0.275330	1.631253	-1.031615
O	1.857887	-0.185559	0.315228
H	2.645900	-0.304636	0.837791

Frequencies

52.36	117.80	120.57	199.01	262.53	373.97
402.29	533.08	788.55	946.22	995.89	1020.30
1039.48	1045.01	1074.77	1251.26	1259.30	1344.37
1371.56	1437.40	1442.43	1478.02	1497.70	1503.62
1509.58	1526.34	1550.89	3056.00	3060.47	3086.79
3128.43	3137.31	3139.68	3182.32	3184.83	3985.74

E(BHandHLYP).....-232.8939089

IM_{ter} BHandHLYP/ aug-cc-pVDZ

Cartesian Coordinates

C	0.024758	1.318065	-0.780625
C	-0.000237	0.040310	-0.006126
H	0.796009	2.047238	-0.570103
H	-0.629499	1.479791	-1.626583
C	-1.325859	-0.689791	-0.194346
H	-1.480810	-0.948742	-1.243151
H	-1.334904	-1.604720	0.397495
H	-2.161074	-0.063133	0.125251
C	1.171237	-0.855981	-0.397130
H	1.098992	-1.147804	-1.445014
H	2.113525	-0.331510	-0.241935
H	1.169531	-1.754470	0.221861
O	0.205412	0.318604	1.380884
H	-0.447917	0.951153	1.667636

Frequencies

117.22	227.87	277.26	330.23	334.22	358.69
422.27	461.61	483.16	576.79	794.51	937.95
964.84	971.53	1026.63	1049.54	1171.58	1261.90
1311.21	1383.59	1436.40	1450.09	1495.26	1507.49
1515.17	1529.47	1539.29	3116.25	3124.74	3187.61
3201.16	3209.73	3213.37	3230.92	3350.08	3980.23

E(BHandHLYP).....-232.8933573

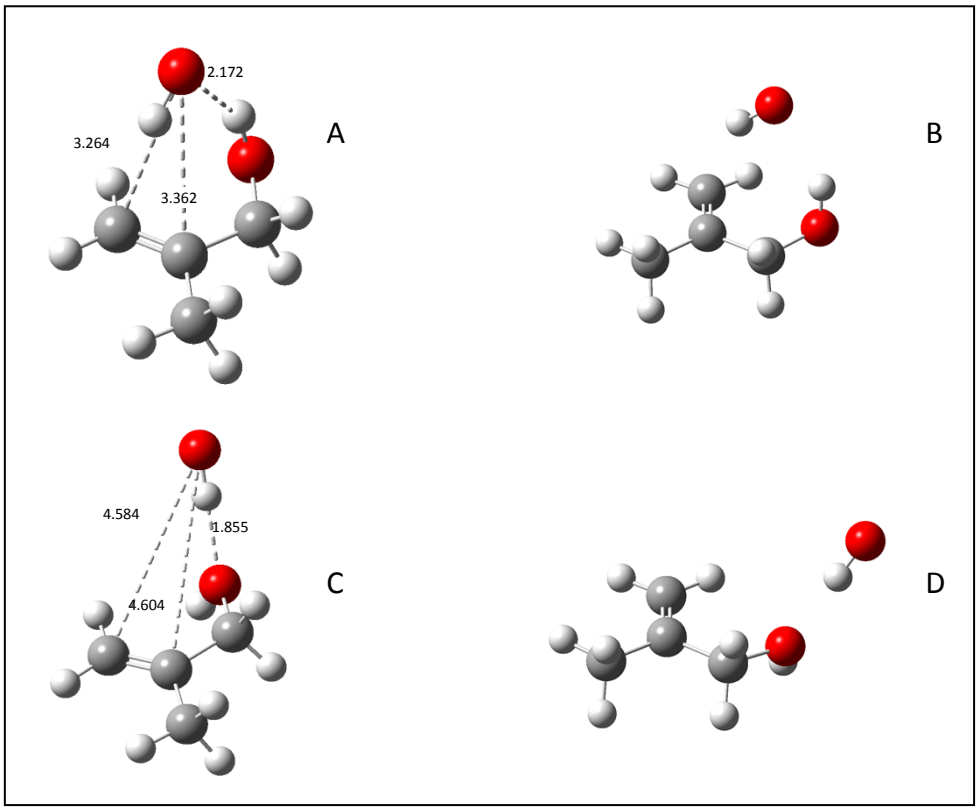

Figure: Reaction Profile showing the contribution of both π-PC (denoted as 1π-PC in this Figure) and 2π-PC paths. A: Comparison of the optimized geometries, located at the BHandHLYP/aug-cc-pVDZ level, for the π-PC. A: 1π-PC, as reported at the manuscript, representing an upward OH attack to MPO221. B: 1π-PC, from another view. C: 2π-PC, representing an upward OH attack to the mirror image of MPO221 and resembling Zhang´s PC. C: 2π-PC, from another view.

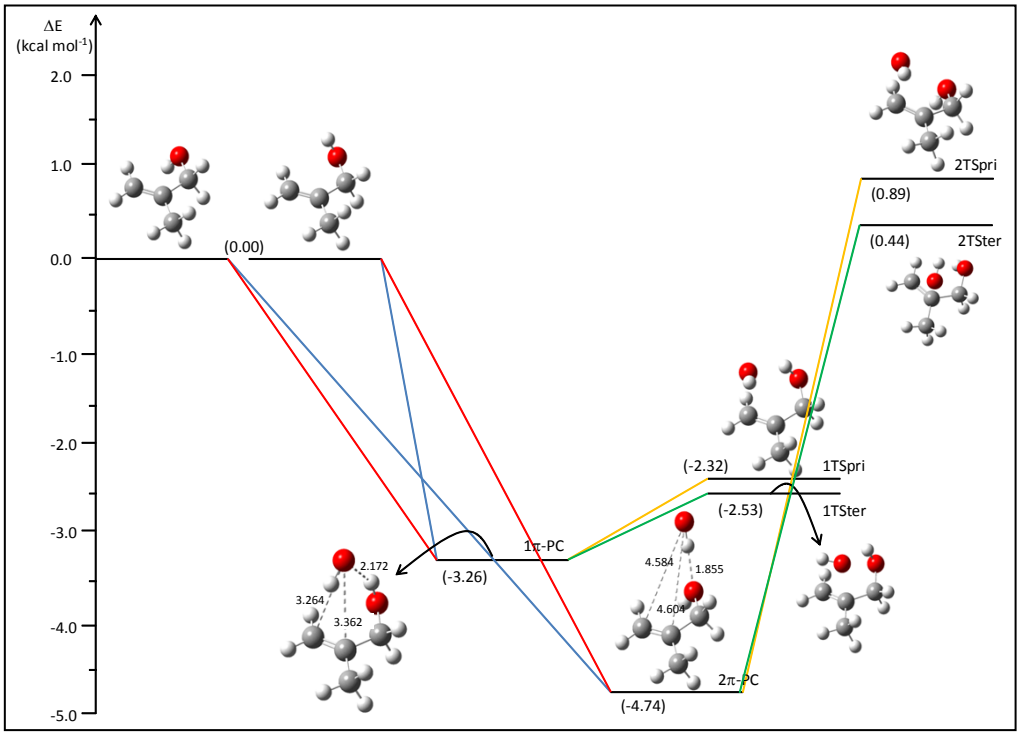

Figure: Reaction Profile showing the contribution of both π-PC (denoted as 1π-PC in this Figure) and 2π-PC paths. B: Reaction profile showing the contribution of both upward and downward attack to MPO221, resulting from two conformers (mirror images) of the reactant. The blue lines represent the upward attacks; the red lines represent the downward attack; the yellow lines represent the connection between the π-PC and TSpri along the π-PC → IMpri reaction path; the green lines represent the connection between the π-PC and TSter along the π-PC → IMter reaction path.

Table: Electronic energies (hartree) claculated for the stationary points along the MPO221 + OH reaction path at different theoretical levels with the cc-pVDZ basis set.

	BHandHLYP	M06-2X	PMP2	QCISD_opt	CCSD	CCSD(T)
Reactants	-308.0083691	-308.0405827	-307.2678462	-307.3371760	-307.3359543	-307.3625151
π-PC	-308.0215015	-308.0564629	-307.2806319	-307.3487047	-307.3473857	-307.3747570
TSpri	-308.0178656	-308.0561336	-307.2768660	-307.3426968	-307.3406502	-307.3690064
TSter	-308.0183809	-308.0564510	-307.2788224	-307.3444477	-307.3422644	-307.3703280