

Supplementary Information

Insights into the Cr(III) catalysed isomerization mechanism of glucose to fructose in the presence of water using *ab initio* molecular dynamics

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1. Car – Parrinello Molecular Dynamics and Metadynamics Sample Input File

Sample input file for the CPMD – metadynamics simulation for the rate limiting hydride transfer step (fully condensed phase system) is provided here. The xyz coordinates of all the atoms in the system are embedded in the input file.

```
&CPMD
MOLECULAR DYNAMICS CP
RESTART WAVEFUNCTION COORDINATES VELOCITIES ACCUMULATORS NOSEE NOSEP NOSEC
TEMPERATURE
  350.0
NOSE IONS MASSIVE
  375.0 1800.0
NOSE ELECTRONS
  0.18 10000.0
LSD
MAXSTEP
  50000
TRAJECTORY XYZ SAMPLE FORCES
  1
TIMESTEP
  4.0
EMASS
  600.0
PRINT FORCES ON
FILEPATH
/home/samir/samir/isomerization/hydride/mtd-1/
&END

&DFT
FUNCTIONAL PBE
GC-CUTOFF
  1.0d-08
&END

&SYSTEM
ANGSTROM
SYMMETRY
  1
CELL
  16.0 1.0 1.0 0.0 0.0 0.0
DUAL
  4.0
MULTIPLICITY
  4
CUTOFF
  100.0
&END
```

&ATOMS

*Cr_MT_PBE_SEMI.psp KLEINMAN-BYLANDER

LMAX=D LOC=D

1

8.121000	6.943000	6.807000
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*Cl_MT_PBE.psp KLEINMAN-BYLANDER

LMAX=D LOC=D

2

11.532000	6.282000	4.853000
4.432000	8.716000	8.211000

*C_MT_PBE.psp KLEINMAN-BYLANDER

LMAX=P LOC=P

6

9.128000	8.493000	8.855000
8.256000	7.420000	9.530000
7.083000	8.015000	10.299000
7.539000	8.752000	11.602000
6.608000	9.974000	11.882000
6.881000	10.695000	13.214000

*H_MT_PBE.psp KLEINMAN-BYLANDER

LMAX=S LOC=S

261

5.505000	9.537000	11.911000
9.775000	9.110000	9.560000
8.989000	7.051000	10.312000
6.610000	8.739000	9.657000
8.567000	9.038000	11.350000
3.026000	11.953000	9.399000
6.169000	5.097000	7.106000
7.969000	10.819000	13.400000
6.290000	11.595000	13.142000
6.958000	7.076000	12.521000
5.350000	7.151000	10.011000
6.555000	9.075000	14.241000
8.307000	7.881000	4.230000
9.744000	7.316000	4.855000
10.319000	5.675000	6.121000
5.791000	8.571000	7.119000
6.742000	8.800000	5.793000
11.192000	2.057000	7.435000
7.107000	4.543000	5.946000
10.917000	3.105000	8.530000
9.810000	4.876000	7.492000
5.837000	11.089000	10.436000
3.963000	10.765000	9.254000
12.757000	9.391000	5.157000
11.473000	8.490000	5.132000
10.760000	10.705000	2.452000
10.698000	9.940000	3.723000
8.394000	9.656000	3.319000
6.851000	9.164000	3.173000
-0.630000	4.110000	6.860000
-0.090000	2.950000	5.840000

4.760000	12.681000	11.281000
5.800000	13.641000	12.091000
14.981000	14.951000	7.840000
14.961000	15.211000	6.230000
1.761000	7.120000	8.560000
1.941000	5.640000	9.220000
2.570000	14.041000	10.081000
3.930000	14.931000	10.041000
14.841000	15.991000	13.651000
14.441000	14.511000	14.211000
5.200000	3.360000	15.081000
3.570000	3.340000	15.031000
2.040000	15.301000	5.380000
1.590000	13.801000	5.830000
6.130000	10.481000	0.690000
6.520000	9.771000	2.110000
0.770000	5.550000	5.800000
1.210000	6.970000	6.470000
1.841000	8.930000	6.200000
0.811000	9.870000	5.370000
1.271000	11.101000	3.800000
0.551000	11.551000	5.200000
5.640000	12.781000	7.350000
5.900000	14.081000	6.390000
13.301000	11.551000	13.651000
13.451000	12.331000	15.081000
12.111000	2.521000	-0.599000
11.941000	0.971000	-0.139000
14.071000	14.231000	10.331000
14.511000	13.291000	9.071000
6.220000	7.980000	2.020000
5.200000	7.620000	3.240000
11.951000	2.950000	9.311000
13.431000	2.910000	10.001000
7.600000	6.020000	15.541000
7.560000	5.500000	13.991000
13.741000	5.120000	1.621000
14.721000	4.070000	0.831000
9.141000	4.440000	12.961000
9.571000	3.590000	11.631000
9.240000	4.110000	1.460000
8.840000	2.540000	1.660000
14.451000	11.151000	4.970000
13.131000	12.111000	4.890000
9.621000	15.281000	4.250000
10.041000	14.761000	5.750000
1.331000	10.511000	7.970000
1.431000	10.771000	9.580000
12.331000	14.731000	15.701000
11.751000	15.241000	14.261000
4.030000	9.821000	2.000000
2.940000	8.611000	1.930000
14.531000	6.700000	8.030000
15.381000	7.940000	7.410000
4.110000	12.671000	0.411000
3.980000	12.481000	2.031000
10.511000	1.141000	2.870000

11.421000	1.321000	1.520000
1.220000	3.450000	14.851000
1.920000	2.360000	15.841000
4.970000	1.821000	4.090000
5.400000	1.361000	2.580000
13.761000	0.700000	3.360000
14.991000	1.230000	4.300000
10.201000	0.411000	9.250000
8.911000	0.581000	8.270000
4.270000	6.100000	4.770000
2.880000	6.890000	5.130000
7.120000	1.000000	1.240000
5.830000	1.050000	0.240000
13.791000	5.470000	15.181000
13.761000	6.860000	14.341000
8.930000	14.161000	8.820000
7.320000	14.041000	8.530000
14.661000	11.121000	0.980000
13.421000	12.151000	0.710000
8.871000	2.770000	4.020000
10.341000	2.340000	4.610000
9.961000	6.220000	14.671000
11.571000	6.300000	14.401000
12.481000	16.441000	7.280000
12.951000	15.701000	8.660000
3.880000	11.251000	8.060000
4.330000	11.241000	6.480000
13.151000	2.611000	5.270000
12.211000	2.491000	6.610000
1.700000	5.550000	13.451000
0.720000	6.300000	14.531000
5.990000	1.380000	11.841000
4.730000	2.410000	11.911000
13.741000	10.891000	8.600000
14.551000	12.021000	7.750000
14.361000	4.950000	9.991000
15.391000	6.060000	10.581000
1.631000	12.881000	6.710000
0.191000	13.641000	6.880000
2.451000	11.841000	15.751000
1.621000	13.191000	16.121000
9.841000	13.241000	13.951000
11.471000	13.211000	13.891000
10.711000	12.391000	11.811000
10.701000	12.321000	10.171000
0.431000	11.801000	11.381000
-0.479000	11.011000	10.281000
9.400000	0.690000	13.071000
9.870000	1.450000	14.441000
4.960000	8.250000	13.011000
3.680000	7.260000	12.781000
12.951000	4.600000	13.261000
11.851000	4.030000	12.191000
0.180000	16.461000	12.971000
1.620000	15.831000	13.401000
3.600000	11.831000	4.450000
3.710000	10.201000	4.410000

5.780000	6.030000	7.910000
6.120000	5.710000	9.480000
13.021000	14.251000	4.280000
11.571000	13.501000	4.200000
13.191000	14.581000	12.291000
12.061000	13.711000	11.511000
3.330000	14.661000	12.421000
4.510000	15.361000	13.321000
4.700000	8.060000	15.511000
4.420000	6.630000	16.250999
14.951000	8.170000	0.651000
16.471001	8.260000	0.051000
12.851000	8.620000	9.791000
13.971000	7.700000	10.541000
0.900000	12.611000	13.501000
0.590000	14.081000	12.871000
0.241000	2.910000	4.380000
-0.259000	4.440000	4.140000
9.601000	16.171000	0.121000
10.191000	14.821000	0.841000
13.371000	7.450000	0.570000
13.211000	8.650000	-0.530000
10.751000	12.491000	7.940000
11.301000	14.021000	8.130000
2.870000	4.260000	9.891000
4.160000	5.140000	9.421000
4.930000	4.600000	2.961000
5.530000	4.800000	1.451000
-0.850000	13.471000	1.690000
0.180000	12.271000	2.130000
0.460000	1.151000	9.000000
1.820000	2.041000	8.930000
5.700000	16.421000	9.190000
5.480000	14.891000	8.680000
10.431000	7.640000	13.241000
9.061000	7.690000	12.351000
2.480000	4.800000	0.521000
1.310000	5.910000	0.811000
8.220000	4.830000	2.790000
7.210000	6.060000	3.170000
2.220000	16.211000	2.201000
2.450000	14.671000	1.701000
6.370000	3.750000	12.391000
6.970000	5.180000	11.891000
13.711000	9.961000	11.601000
12.571000	10.991000	12.161000
12.161000	8.240000	3.510000
12.981000	8.410000	2.100000
13.361000	1.361000	10.741000
12.291000	0.351000	11.461000
1.991000	1.180000	4.560000
0.951000	0.480000	5.610000
0.890000	1.201000	3.041000
1.940000	2.451000	3.091000
8.250000	13.061000	15.171000
7.440000	12.921000	13.761000
1.840000	3.770000	6.860000

2.540000	3.110000	8.180000
14.121000	0.441000	0.510000
15.421000	0.271000	-0.460000
3.590000	13.811000	14.561000
2.880000	12.361000	14.771000
9.691000	10.511000	7.500000
10.981000	10.301000	6.530000
6.320000	14.291000	4.210000
5.460000	15.661000	4.470000
1.590000	13.491000	2.630000
2.670000	14.011000	3.740000
0.280000	9.801000	1.801000
1.900000	9.831000	1.681000
7.620000	1.870000	14.491000
6.800000	2.080000	15.881000
13.831000	9.080000	13.351000
15.361000	8.680000	13.741000
10.841000	13.241000	1.210000
12.171000	13.501000	2.120000
7.350000	6.300000	1.821000
7.760000	4.850000	1.171000
2.990000	1.821000	15.581000
3.830000	0.471000	15.921000
0.471000	7.940000	12.171000
0.751000	9.510000	11.811000
1.681000	10.251000	15.321000
1.221000	9.171000	14.181000
6.150000	2.781000	9.401000
7.600000	2.021000	9.461000
13.121000	2.401000	0.931000
14.641000	1.841000	0.721000
10.601000	10.371000	0.050000
11.641000	9.281000	0.680000
1.901000	15.571000	7.810000
2.621000	14.901000	9.110000
5.940000	13.411000	0.621000
6.690000	14.861000	0.551000
2.201000	1.020000	12.711000
2.271000	1.810000	11.281000
4.580000	3.520000	4.580000
3.890000	3.840000	6.030000
0.121000	14.621000	10.771000
1.311000	14.371000	11.861000
3.550000	4.880000	13.521000
3.570000	5.210000	11.921000
8.440000	15.961000	5.930000
7.330000	15.241000	6.890000
9.381000	-0.380000	11.231000
10.941000	-0.020000	11.541000
7.240000	12.431000	3.180000
8.610000	13.271000	3.420000
6.130000	16.490999	13.411000
7.070000	15.641000	12.391000
12.411000	5.330000	6.950000
13.151000	4.180000	7.840000
7.980000	0.111000	2.830000
8.430000	1.171000	3.990000

2.960000	1.570000	6.510000
3.020000	0.000000	6.950000

*O_MT_PBE.psp KLEINMAN-BYLANDER
LMAX=P LOC=P

131		
6.845000	5.366000	6.404000
6.189000	6.979000	10.589000
6.281000	10.020000	14.376000
6.702000	11.035000	10.845000
7.617000	7.837000	12.670000
7.897000	6.406000	8.558000
9.316000	8.352000	7.632000
8.751000	7.304000	4.852000
9.661000	5.639000	6.905000
6.615000	8.199000	6.521000
11.009000	2.954000	7.559000
4.007000	11.717000	9.442000
11.763000	9.501000	5.066000
10.089000	10.347000	3.054000
7.625000	9.206000	3.798000
0.190000	3.680000	6.470000
5.690000	12.751000	11.651000
15.551000	15.111000	7.030000
1.431000	6.180000	8.560000
3.350000	14.351000	10.611000
14.601000	15.051000	13.391000
4.380000	3.920000	14.991000
2.300000	14.341000	5.380000
6.060000	9.641000	1.230000
1.220000	6.430000	5.630000
0.891000	9.220000	6.120000
0.411000	11.081000	4.320000
6.130000	13.651000	7.260000
12.931000	12.281000	14.231000
11.871000	1.921000	0.161000
14.661000	14.171000	9.531000
5.980000	7.290000	2.700000
12.811000	3.450000	9.441000
8.070000	6.050000	14.651000
13.941000	4.690000	0.741000
9.911000	4.100000	12.421000
8.650000	3.480000	1.950000
13.621000	11.441000	5.450000
10.081000	14.561000	4.770000
1.951000	10.661000	8.730000
12.271000	15.501000	15.061000
3.210000	9.431000	2.420000
14.581000	7.350000	7.280000
4.610000	12.661000	1.271000
11.111000	1.761000	2.370000
2.020000	2.850000	14.981000
4.640000	1.431000	3.230000
14.001000	1.070000	4.260000
9.401000	0.981000	9.040000
3.820000	7.000000	4.800000
6.140000	1.220000	1.170000

13.511000	5.900000	14.331000
8.030000	14.021000	9.240000
14.341000	11.881000	0.410000
9.351000	2.360000	4.800000
10.761000	6.830000	14.641000
12.271000	15.701000	7.930000
4.590000	11.521000	7.410000
12.711000	1.971000	5.910000
0.780000	5.560000	13.861000
5.610000	2.220000	11.471000
14.291000	11.731000	8.670000
14.661000	5.900000	9.921000
0.641000	12.801000	6.570000
1.541000	12.231000	15.881000
10.641000	13.471000	13.401000
11.111000	11.951000	11.001000
0.381000	10.991000	10.791000
9.150000	0.890000	14.021000
4.100000	8.130000	12.511000
12.741000	3.860000	12.621000
0.640000	15.641000	13.311000
3.670000	11.001000	5.010000
5.660000	5.370000	8.650000
12.521000	13.481000	3.880000
12.721000	14.451000	11.421000
3.540000	15.101000	13.291000
4.020000	7.510000	15.981000
15.871000	7.790000	0.701000
13.601000	8.620000	10.451000
0.370000	13.101000	12.821000
0.221000	3.670000	3.740000
9.801000	15.731000	1.001000
13.031000	8.380000	0.420000
10.681000	13.331000	8.490000
3.390000	5.090000	10.061000
5.110000	4.150000	2.081000
0.080000	13.261000	2.000000
0.880000	2.011000	9.270000
5.040000	15.681000	9.100000
10.021000	7.960000	12.381000
1.890000	5.200000	1.221000
8.150000	5.720000	3.250000
2.520000	15.641000	1.441000
6.710000	4.640000	12.691000
13.471000	10.591000	12.341000
13.021000	8.550000	3.090000
12.521000	1.311000	11.281000
1.261000	1.350000	5.230000
1.300000	1.941000	2.511000
8.300000	12.731000	14.221000
2.630000	3.260000	7.200000
15.041000	0.071000	0.440000
3.720000	12.881000	14.901000
10.391000	10.981000	6.960000
5.900000	14.871000	4.910000
2.550000	13.481000	2.900000
1.050000	10.131000	1.261000

6.720000	2.030000	14.891000
14.401000	8.560000	13.981000
11.831000	13.351000	1.190000
7.160000	5.650000	1.081000
3.900000	1.411000	15.601000
0.741000	8.830000	12.541000
1.301000	9.341000	15.171000
6.610000	1.901000	9.531000
14.081000	2.511000	1.201000
10.831000	9.841000	0.870000
2.611000	15.691000	8.510000
6.720000	13.911000	0.241000
2.241000	1.920000	12.271000
4.280000	4.240000	5.200000
1.051000	14.871000	11.041000
3.170000	5.470000	12.801000
8.120000	15.861000	6.870000
10.011000	0.340000	11.541000
7.700000	13.301000	3.010000
6.180000	15.671000	12.841000
13.001000	4.530000	6.910000
8.750000	0.461000	3.370000
3.070000	0.630000	6.180000

METADYNAMICS COLLECTIVE VARIABLES

DEFINE VARIABLES

2

COOR_RF INDAT 4 2 6 6 1.5 SCF 1.0 KCV 1.0 MCV 150

11 12

COOR_RF INDAT 5 2 6 6 1.5 SCF 1.0 KCV 1.0 MCV 150

11 12

END DEFINE

LAGRANGE TEMPERATURE

375.0

LAGRANGE TEMPCONTROL

375.0 200.0

HILLS = 0.1 0.0005

METASTEPNUM

10000

MOVEMENT CHECK

0.015

MINSTEPNUM INTERMETA

25

MAXSTEPNUM INTERMETA

50

CHECK DELAY

10

METASTORE NO TRAJECTORY

20 1 100000

MONITOR

10

END METADYNAMICS

&END
