Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Photoinduced water splitting with oxotitanium porphyrin: a computational study

Andrzej L. Sobolewski and Wolfgang Domcke

Electronic Supplementary Information

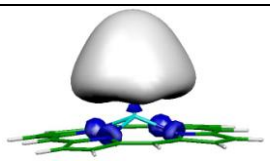
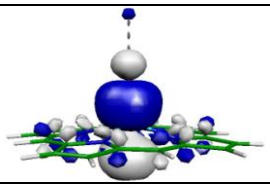
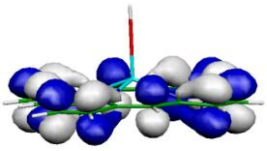
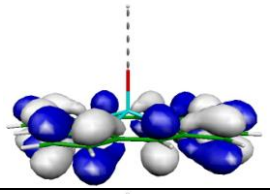
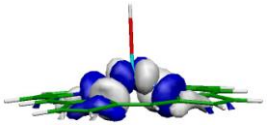
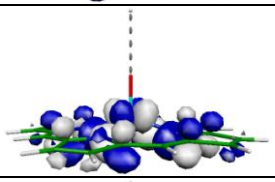
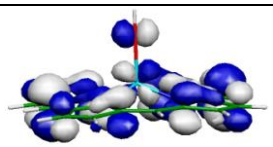
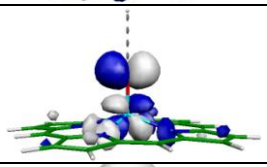
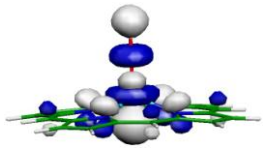
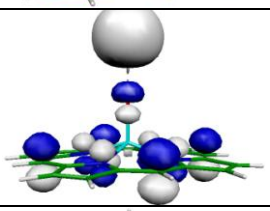
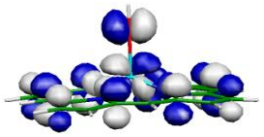
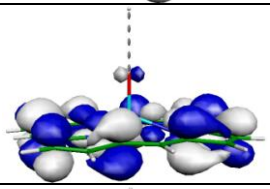
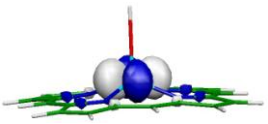
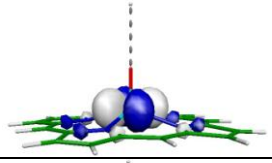
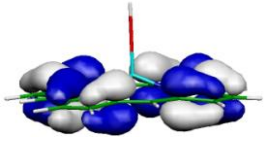
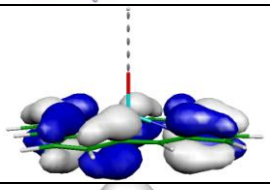
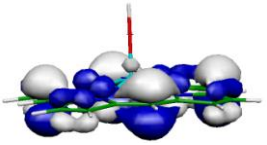
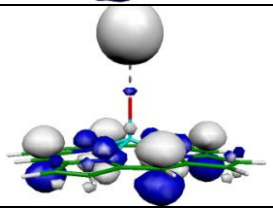
	$24a_1$	
	$11b_1$	
	$12b_2$	
	$25e$	
	$23a_1$	
	$24e$	
	$10b_1$	
	$7a_2$	
	$22a_1$	

Fig. S1. The Kohn-Sham frontier orbitals of the TiPOH$^{\bullet}$ radical at the equilibrium geometry of the $^2A_1$ state ($R_{OH} \approx 1.0$ Å, left column) and at the dissociation limit ($R_{OH} = 2.7$ Å, right column). Only one component of the degenerate (e) orbitals is shown.

Cartesian coordinates (in Ångstrom) of the $S_0(C_{4v})$ equilibrium geometry of TiOP optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   38
FINAL HEAT OF FORMATION = -1912.629930
Ti     0.000000     0.000000    -0.613368
 O     0.000000     0.000000    -2.232562
 N    -1.452033     1.452033    -0.032815
 N    -1.452033    -1.452033    -0.032815
 N     1.452033    -1.452033    -0.032815
 N     1.452033     1.452033    -0.032815
 C    -3.490306     2.523372     0.111980
 C    -3.490306    -2.523372     0.111980
 C     3.490306    -2.523372     0.111980
 C     3.490306     2.523372     0.111980
 C    -2.813352     1.248881     0.024067
 C    -2.813352    -1.248881     0.024067
 C     2.813352    -1.248881     0.024067
 C     2.813352     1.248881     0.024067
 C    -1.248881     2.813352     0.024067
 C    -1.248881    -2.813352     0.024067
 C     1.248881    -2.813352     0.024067
 C     1.248881     2.813352     0.024067
 C     2.523372     3.490306     0.111980
 C    -2.523372     3.490306     0.111980
 C    -2.523372    -3.490306     0.111980
 C     2.523372    -3.490306     0.111980
 C    -3.441909     0.000000     0.032758
 C     0.000000    -3.441909     0.032758
 C     3.441909     0.000000     0.032758
 C     0.000000     3.441909     0.032758
 H     2.651598     4.569465     0.177983
 H    -2.651598    -4.569465     0.177983
 H    -2.651598     4.569465     0.177983
 H     2.651598    -4.569465     0.177983
 H     4.569465     2.651598     0.177983
 H     4.569465    -2.651598     0.177983
 H    -4.569465    -2.651598     0.177983
 H    -4.569465     2.651598     0.177983
 H     0.000000     4.532646     0.083480
 H     4.532646     0.000000     0.083480
 H     0.000000    -4.532646     0.083480
 H    -4.532646     0.000000     0.083480
```

Cartesian coordinates (in Ångstrom) of the $S_0(C_{4v})$ equilibrium geometry of TiOP optimized with the MP2/cc-pVDZ(TZVP at Ti) method.

```
   38
FINAL HEAT OF FORMATION = -1909.564650
Ti     0.000000     0.000000    -0.552751
 O     0.000000     0.000000    -2.198537
 N    -1.456704     1.456704    -0.017651
 N    -1.456704    -1.456704    -0.017651
 N     1.456704    -1.456704    -0.017651
 N     1.456704     1.456704    -0.017651
 C    -3.503630     2.530150     0.106304
 C    -3.503630    -2.530150     0.106304
 C     3.503630    -2.530150     0.106304
 C     3.503630     2.530150     0.106304
 C    -2.820875     1.255546     0.029636
 C    -2.820875    -1.255546     0.029636
 C     2.820875    -1.255546     0.029636
 C     2.820875     1.255546     0.029636
 C    -1.255546     2.820875     0.029636
 C    -1.255546    -2.820875     0.029636
 C     1.255546    -2.820875     0.029636
 C     1.255546     2.820875     0.029636
 C     2.530150     3.503630     0.106304
 C    -2.530150     3.503630     0.106304
 C    -2.530150    -3.503630     0.106304
 C     2.530150    -3.503630     0.106304
 C    -3.450557     0.000000     0.030346
 C     0.000000    -3.450557     0.030346
 C     3.450557     0.000000     0.030346
 C     0.000000     3.450557     0.030346
 H     2.658771     4.586004     0.165263
 H    -2.658771    -4.586004     0.165263
 H    -2.658771     4.586004     0.165263
 H     2.658771    -4.586004     0.165263
 H     4.586004     2.658771     0.165263
 H     4.586004    -2.658771     0.165263
 H    -4.586004    -2.658771     0.165263
 H    -4.586004     2.658771     0.165263
 H     0.000000     4.545418     0.072721
 H     4.545418     0.000000     0.072721
 H     0.000000    -4.545418     0.072721
 H    -4.545418     0.000000     0.072721
```

Cartesian coordinates (in Ångstrom) of the $S_0(C_1)$ equilibrium geometry of the TiOP-H_2O complex optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   41
FINAL HEAT OF FORMATION = -1989.026460
 N     0.156436     0.195496     2.026217
 C    -0.951193     0.284651     2.842239
 C    -0.533178     0.340437     4.223527
 C     0.832766     0.287034     4.230987
 C     1.259440     0.198695     2.853320
 C    -2.273484     0.348540     2.400043
 C    -2.703695     0.367889     1.071487
 N    -1.880809     0.288764    -0.031985
 C    -2.693723     0.383981    -1.142234
 C    -4.069854     0.519334    -0.724727
 C    -4.075458     0.509894     0.643483
 C    -2.249788     0.382002    -2.467751
 C    -0.921702     0.322274    -2.898159
 N     0.177597     0.217445    -2.072287
 C     1.289493     0.233297    -2.887196
 C     0.877583     0.343397    -4.267637
 C    -0.488707     0.398361    -4.274366
 C     2.614122     0.186165    -2.443714
 C     3.043734     0.152134    -1.114437
 C     4.422849     0.179722    -0.684317
 C     4.415793     0.170887     0.682933
 C     3.032316     0.138494     1.098421
 N     2.216035     0.122945    -0.012366
Ti     0.144449    -0.369623    -0.024239
 O     0.073565    -1.999658    -0.029158
 C     2.588637     0.156204     2.423414
 O    -2.017888    -2.883453     1.695169
 H     1.502532     0.312947     5.088730
 H    -1.153757     0.494887    -5.130844
 H     5.267767     0.196189     1.360101
 H    -4.917659     0.621741    -1.400032
 H    -1.208348     0.418544     5.073728
 H    -4.928895     0.601478     1.313155
 H     1.556421     0.384769    -5.117668
 H     5.281716     0.214111    -1.352300
 H     3.356738     0.168253     3.199143
 H    -3.046319     0.408742     3.168130
 H    -3.014501     0.466826    -3.242445
 H     3.390409     0.209571    -3.210976
 H    -2.675742    -2.790484     0.990299
 H    -1.184215    -2.807808     1.192130
```

Cartesian coordinates (in Ångstrom) of the S_0(*Cs*) equilibrium geometry of the TiOP-H_2O complex optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   41
FINAL HEAT OF FORMATION = -1989.024830
 C     4.441178     0.197661    -0.683619
 C     3.059746     0.160289    -1.106404
 N     2.238221     0.131880     0.000000
 C     3.059746     0.160289     1.106404
 C     4.441178     0.197661     0.683619
 C     2.622121     0.187540    -2.433505
 C     1.294770     0.226903    -2.870274
 N     0.187147     0.209175    -2.050075
 C    -0.916665     0.298301    -2.871139
 C    -0.491060     0.369323    -4.250261
 C     0.875292     0.325463    -4.249770
 C    -2.243331     0.343911    -2.434872
 C    -2.681753     0.344832    -1.107537
 N    -1.862498     0.273014     0.000000
 C    -2.681753     0.344832     1.107537
 C    -4.058393     0.455894     0.684211
 C    -4.058393     0.455894    -0.684211
 C    -2.243331     0.343911     2.434872
 C    -0.916665     0.298301     2.871139
 C    -0.491060     0.369323     4.250261
 C     0.875292     0.325463     4.249770
 C     1.294770     0.226903     2.870274
 N     0.187147     0.209175     2.050075
Ti     0.167529    -0.365444     0.000000
 O     0.074207    -1.991548     0.000000
 C     2.622121     0.187540     2.433505
 O    -2.545353    -3.266553     0.000000
 H     1.549644     0.365715     5.103386
 H    -1.161107     0.452581    -5.104128
 H     5.296595     0.232432     1.356012
 H    -4.911446     0.534020    -1.355913
 H    -1.161107     0.452581     5.104128
 H    -4.911446     0.534020     1.355913
 H     1.549644     0.365715    -5.103386
 H     5.296595     0.232432    -1.356012
 H     3.393990     0.210773     3.205324
 H    -3.012877     0.410650     3.206349
 H    -3.012877     0.410650    -3.206349
 H     3.393990     0.210773    -3.205324
 H    -2.962548    -2.393788     0.000000
 H    -1.597260    -3.038488     0.000000
```

Cartesian coordinates (in Ångstrom) of the ^{1}LMCT(A'') inner minimum geometry of the TiOP-H_2O complex optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   41
FINAL HEAT OF FORMATION = -1988.925310
 N     2.217970     0.005757     0.000000
 C     3.043919     0.008894    -1.106615
 C     4.423927    -0.020039    -0.684857
 C     4.423927    -0.020039     0.684857
 C     3.043919     0.008894     1.106615
 C     2.608839     0.078708    -2.434093
 C     1.285115     0.194519    -2.870064
 N     0.179575     0.215526    -2.047990
 C    -0.916315     0.368320    -2.869564
 C    -0.489206     0.439128    -4.249529
 C     0.873767     0.331772    -4.249919
 C    -2.241748     0.463088    -2.434896
 C    -2.684300     0.461917    -1.108092
 N    -1.868882     0.322523     0.000000
 C    -2.684300     0.461917     1.108092
 C    -4.050123     0.652799     0.685358
 C    -4.050123     0.652799    -0.685358
 C    -2.241748     0.463088     2.434896
 C    -0.916315     0.368320     2.869564
 N     0.179575     0.215526     2.047990
 C     1.285115     0.194519     2.870064
 C     0.873767     0.331772     4.249919
 C    -0.489206     0.439128     4.249529
Ti     0.131835    -0.396629     0.000000
 O    -0.039860    -2.267372     0.000000
 C     2.608839     0.078708     2.434093
 O    -2.535637    -3.205349     0.000000
 H     1.548897     0.349351     5.103950
 H    -1.154113     0.561957    -5.102904
 H     5.281705    -0.025325     1.355457
 H    -4.898836     0.781632    -1.355040
 H    -1.154113     0.561957     5.102904
 H    -4.898836     0.781632     1.355040
 H     1.548897     0.349351    -5.103950
 H     5.281705    -0.025325    -1.355457
 H     3.382104     0.075025     3.205296
 H    -3.005343     0.581805     3.206488
 H    -3.005343     0.581805    -3.206488
 H     3.382104     0.075025    -3.205296
 H    -2.723584    -2.255903     0.000000
 H    -1.557570    -3.241183     0.000000
```

Cartesian coordinates (in Ångstrom) of the ^{1}LMCT(*A′*) inner minimum geometry of the TiOP-H_2O complex optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   41
FINAL HEAT OF FORMATION = -1988.926440
 N     2.251476     0.069270     0.000000
 C     3.075645     0.078049    -1.104335
 C     4.459380     0.085549    -0.683651
 C     4.459380     0.085549     0.683651
 C     3.075645     0.078049     1.104335
 C     2.639591     0.098773    -2.432673
 C     1.312617     0.155591    -2.871315
 N     0.204372     0.163668    -2.047244
 C    -0.896079     0.302901    -2.871165
 C    -0.470165     0.351652    -4.248883
 C     0.896535     0.261079    -4.249056
 C    -2.218702     0.421765    -2.433713
 C    -2.655099     0.458001    -1.105594
 N    -1.838086     0.346844     0.000000
 C    -2.655099     0.458001     1.105594
 C    -4.026519     0.635531     0.684416
 C    -4.026519     0.635531    -0.684416
 C    -2.218702     0.421765     2.433713
 C    -0.896079     0.302901     2.871165
 N     0.204372     0.163668     2.047244
 C     1.312617     0.155591     2.871315
 C     0.896535     0.261079     4.249056
 C    -0.470165     0.351652     4.248883
Ti     0.165312    -0.393372     0.000000
 O    -0.009364    -2.272432     0.000000
 C     2.639591     0.098773     2.432673
 O    -2.823189    -3.066780     0.000000
 H     1.569151     0.275190     5.105114
 H    -1.135702     0.453932    -5.104474
 H     5.315994     0.097073     1.355601
 H    -4.876222     0.749739    -1.355496
 H    -1.135702     0.453932     5.104474
 H    -4.876222     0.749739     1.355496
 H     1.569151     0.275190    -5.105114
 H     5.315994     0.097073    -1.355601
 H     3.412301     0.102381     3.204358
 H    -2.984496     0.522438     3.205670
 H    -2.984496     0.522438    -3.205670
 H     3.412301     0.102381    -3.204358
 H    -3.136961    -2.151780     0.000000
 H    -1.854390    -2.958370     0.000000
```

Cartesian coordinates (in Ångstrom) of the ^{1}LMCT(*A*″) outer (biradicalic) minimum geometry of the TiOP-H_2O complex optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   41
FINAL HEAT OF FORMATION = -1988.928680
 C    -0.504798     0.376004     4.251174
 C    -0.928000     0.276997     2.870533
 N     0.173213     0.175192     2.049851
 C     1.277777     0.220454     2.869271
 C     0.861755     0.341133     4.250364
 C    -2.256300     0.308076     2.435441
 C    -2.699073     0.289232     1.107664
 N    -1.880485     0.205426     0.000000
 C    -2.699073     0.289232    -1.107664
 C    -4.077288     0.388837    -0.686316
 C    -4.077288     0.388837     0.686316
 C    -2.256300     0.308076    -2.435441
 C    -0.928000     0.276997    -2.870533
 N     0.173213     0.175192    -2.049851
 C     1.277777     0.220454    -2.869271
 C     0.861755     0.341133    -4.250364
 C    -0.504798     0.376004    -4.251174
 C     2.606314     0.188423    -2.431313
 C     3.044404     0.154641    -1.103448
 N     2.222962     0.104884     0.000000
 C     3.044404     0.154641     1.103448
 C     4.428250     0.215109     0.683541
 C     4.428250     0.215109    -0.683541
Ti     0.153125    -0.473649     0.000000
 O     0.058433    -2.282345     0.000000
 C     2.606314     0.188423     2.431313
 O    -2.600500    -2.855048     0.000000
 H     1.536179     0.402010     5.103069
 H    -1.174323     0.470463    -5.104714
 H     5.283431     0.265273     1.355708
 H    -4.932267     0.471138    -1.355893
 H    -1.174323     0.470463     5.104714
 H    -4.932267     0.471138     1.355893
 H     1.536179     0.402010    -5.103069
 H     5.283431     0.265273    -1.355708
 H     3.378697     0.230649     3.202448
 H    -3.024879     0.385853     3.207654
 H    -3.024879     0.385853    -3.207654
 H     3.378697     0.230649    -3.202448
 H    -3.248782    -2.116988     0.000000
 H    -0.690932    -2.901248     0.000000
```

Cartesian coordinates (in Ångstrom) of the ^{1}LMCT(*A′*) outer (biradicalic) minimum geometry of the TiOP-H_2O complex optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   41
FINAL HEAT OF FORMATION = -1988.932060
 C    -0.484176     0.391966     4.253883
 C    -0.907262     0.289323     2.872190
 N     0.195779     0.195008     2.052559
 C     1.298734     0.242477     2.870813
 C     0.882089     0.364672     4.252925
 C    -2.235316     0.297252     2.437011
 C    -2.679564     0.272712     1.107157
 N    -1.860374     0.238762     0.000000
 C    -2.679564     0.272712    -1.107157
 C    -4.062540     0.305243    -0.686636
 C    -4.062540     0.305243     0.686636
 C    -2.235316     0.297252    -2.437011
 C    -0.907262     0.289323    -2.872190
 N     0.195779     0.195008    -2.052559
 C     1.298734     0.242477    -2.870813
 C     0.882089     0.364672    -4.252925
 C    -0.484176     0.391966    -4.253883
 C     2.627475     0.199789    -2.431606
 C     3.064104     0.154461    -1.103484
 N     2.242923     0.107732     0.000000
 C     3.064104     0.154461     1.103484
 C     4.449555     0.204497     0.683207
 C     4.449555     0.204497    -0.683207
Ti     0.160939    -0.446230     0.000000
 O    -0.076249    -2.237023     0.000000
 C     2.627475     0.199789     2.431606
 O    -2.873189    -2.946196     0.000000
 H     1.556034     0.428313     5.105818
 H    -1.153946     0.482631    -5.107673
 H     5.305035     0.249656     1.355359
 H    -4.921121     0.341568    -1.355695
 H    -1.153946     0.482631     5.107673
 H    -4.921121     0.341568     1.355695
 H     1.556034     0.428313    -5.105818
 H     5.305035     0.249656    -1.355359
 H     3.400943     0.240563     3.201695
 H    -3.005628     0.351667     3.209593
 H    -3.005628     0.351667    -3.209593
 H     3.400943     0.240563    -3.201695
 H    -3.304845    -2.060153     0.000000
 H    -0.949593    -2.680493     0.000000
```

Cartesian coordinates (in Ångstrom) of the $^2B_1$ minimum geometry of the TiPOH$^\bullet$ radical optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   39
FINAL HEAT OF FORMATION = -1913.219530
Ti     0.000000     0.000000    -0.609511
 O     0.000000     0.000000    -2.399081
 H     0.000000     0.000000    -3.357618
 N    -1.448107     1.448107     0.040487
 N    -1.448107    -1.448107     0.040487
 N     1.448107    -1.448107     0.040487
 N     1.448107     1.448107     0.040487
 C    -3.488507     2.521364     0.215121
 C    -3.488507    -2.521364     0.215121
 C     3.488507    -2.521364     0.215121
 C     3.488507     2.521364     0.215121
 C    -2.809134     1.248414     0.112400
 C    -2.809134    -1.248414     0.112400
 C     2.809134    -1.248414     0.112400
 C     2.809134     1.248414     0.112400
 C    -1.248414     2.809134     0.112400
 C    -1.248414    -2.809134     0.112400
 C     1.248414    -2.809134     0.112400
 C     1.248414     2.809134     0.112400
 C     2.521364     3.488507     0.215121
 C    -2.521364     3.488507     0.215121
 C    -2.521364    -3.488507     0.215121
 C     2.521364    -3.488507     0.215121
 C    -3.438942     0.000000     0.124429
 C     0.000000    -3.438942     0.124429
 C     3.438942     0.000000     0.124429
 C     0.000000     3.438942     0.124429
 H     2.649074     4.567298     0.291982
 H    -2.649074    -4.567298     0.291982
 H    -2.649074     4.567298     0.291982
 H     2.649074    -4.567298     0.291982
 H     4.567298     2.649074     0.291982
 H     4.567298    -2.649074     0.291982
 H    -4.567298    -2.649074     0.291982
 H    -4.567298     2.649074     0.291982
 H     0.000000     4.529435     0.187631
 H     4.529435     0.000000     0.187631
 H     0.000000    -4.529435     0.187631
 H    -4.529435     0.000000     0.187631
```

Cartesian coordinates (in Ångstrom) of the $^2A_1$ minimum geometry of the TiPOH$^\bullet$ radical optimized with the DFT/B3LYP/cc-pVDZ(TZVP at Ti) method.

```
   39
FINAL HEAT OF FORMATION = -1913.163110
Ti     0.000000     0.000000    -0.630872
 O     0.000000     0.000000    -2.483317
 H     0.000000     0.000000    -3.454724
 N    -1.454121     1.454121     0.026087
 N    -1.454121    -1.454121     0.026087
 N     1.454121    -1.454121     0.026087
 N     1.454121     1.454121     0.026087
 C    -3.489543     2.522566     0.227497
 C    -3.489543    -2.522566     0.227497
 C     3.489543    -2.522566     0.227497
 C     3.489543     2.522566     0.227497
 C    -2.811786     1.249909     0.108027
 C    -2.811786    -1.249909     0.108027
 C     2.811786    -1.249909     0.108027
 C     2.811786     1.249909     0.108027
 C    -1.249909     2.811786     0.108027
 C    -1.249909    -2.811786     0.108027
 C     1.249909    -2.811786     0.108027
 C     1.249909     2.811786     0.108027
 C     2.522566     3.489543     0.227497
 C    -2.522566     3.489543     0.227497
 C    -2.522566    -3.489543     0.227497
 C     2.522566    -3.489543     0.227497
 C    -3.441274     0.000000     0.120452
 C     0.000000    -3.441274     0.120452
 C     3.441274     0.000000     0.120452
 C     0.000000     3.441274     0.120452
 H     2.648734     4.567409     0.316539
 H    -2.648734    -4.567409     0.316539
 H    -2.648734     4.567409     0.316539
 H     2.648734    -4.567409     0.316539
 H     4.567409     2.648734     0.316539
 H     4.567409    -2.648734     0.316539
 H    -4.567409    -2.648734     0.316539
 H    -4.567409     2.648734     0.316539
 H     0.000000     4.530952     0.191565
 H     4.530952     0.000000     0.191565
 H     0.000000    -4.530952     0.191565
 H    -4.530952     0.000000     0.191565
```