Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: A comparative test of different density functionals for calculations of NH_3-SCR over Cu-CHA

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Excitation energies of triplet O_2 to singlet O_2 in gas phase

The excitation energies of triplet O_2 to singlet O_2 in gas phase have been investigated. For triplet O_2, there is simply just one case with the two spin-parallel electrons occupying the degenerate antibonding molecular orbitals π_x^* and π_y^* respectively. However, for singlet O_2, three possible arrangements of electrons in the antibonding molecular orbitals π_x^* and π_y^* are possible (see Figure S1). The singlet states are not described properly in DFT and it has been argued that a spin unpolarized calculation is preferable for this spin state.[S1] The results show a clear functional dependence of the triplet-singlet excitation.

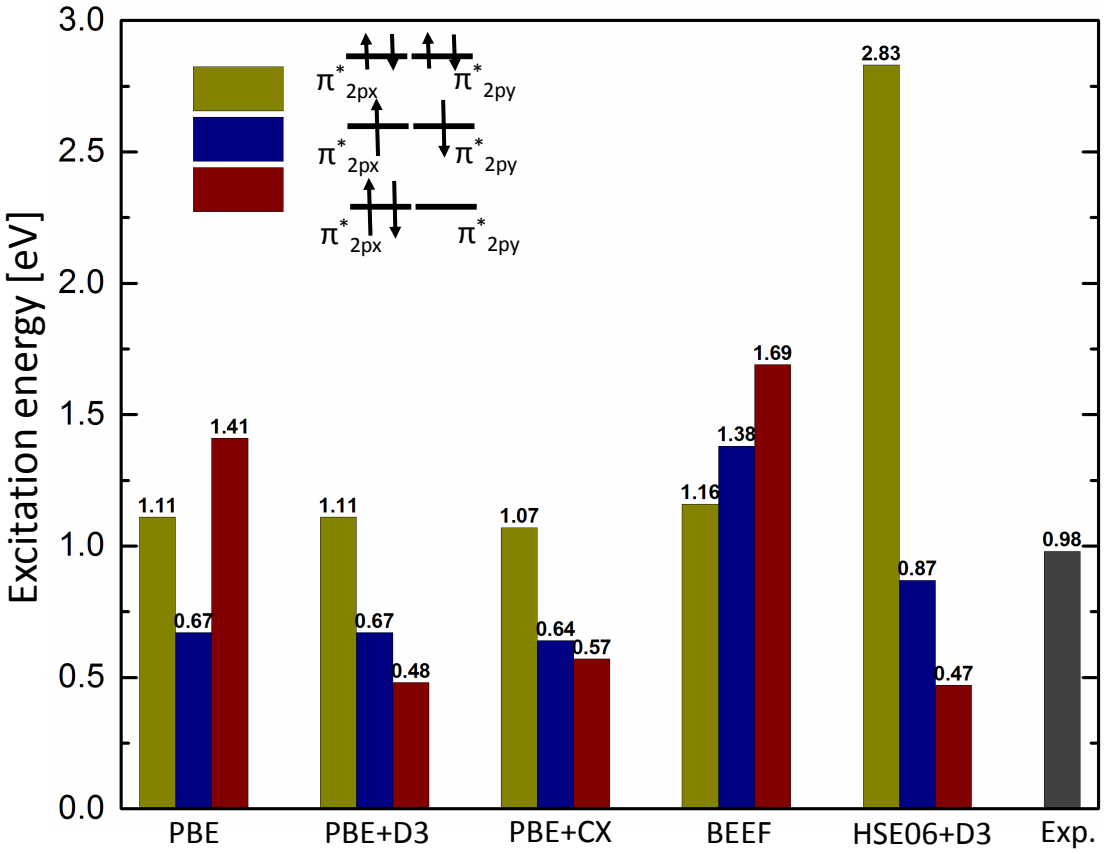

Figure S1: The excitation energies of triplet O_2 to singlet O_2 in gas phase calculated by different functionals compared with experimental value. Here, three cases of the singlet state are considered. A long arrow refers to one electron, whereas a short arrow corresponds to half an electron.

O_2 adsorption over $Cu^+(NH_3)_2$-pairs in gas phase

Figure S2 shows that the zeolite stabilizes the O_2 adsorption by 0.5±0.1 eV for PBE-cx and BEEF. For the BEEF functional, the zeolite stabilization is needed in order to obtain an exothermic adsorption of molecular O_2 adsorption (C2).

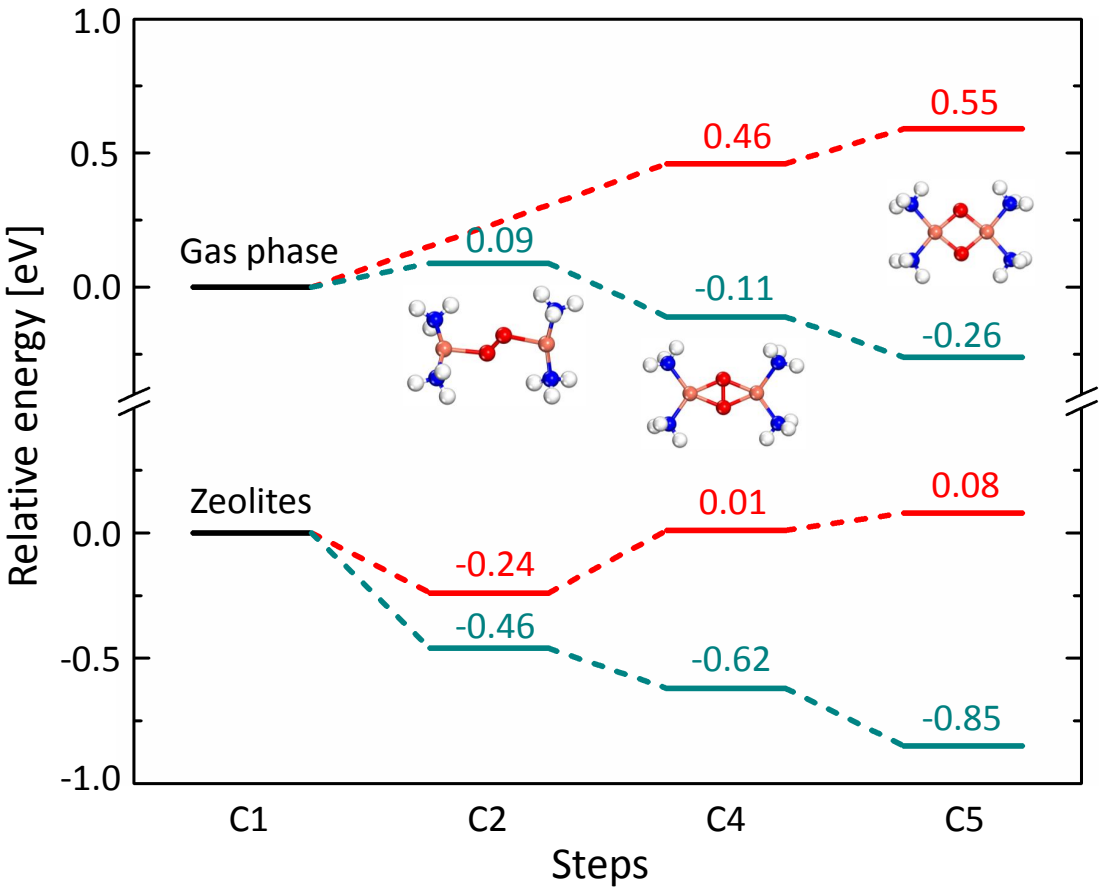

Figure S2: The potential energy landscape of O_2 dissociation on pairs of $Cu(NH_3)_2^+$ in the gas-phase. The dissociation steps in zeolites are also shown in the figure for comparison. All energies are zero-point energy corrected. The BEEF (PBE-cx) results are shown in red (turquoise). Atom color codes: copper (pink), nitrogen (blue), oxygen (red), carbon (grey) and hydrogen (white).

Geometries of Cu_2O_2 crystal structure from enzymatic catalysis

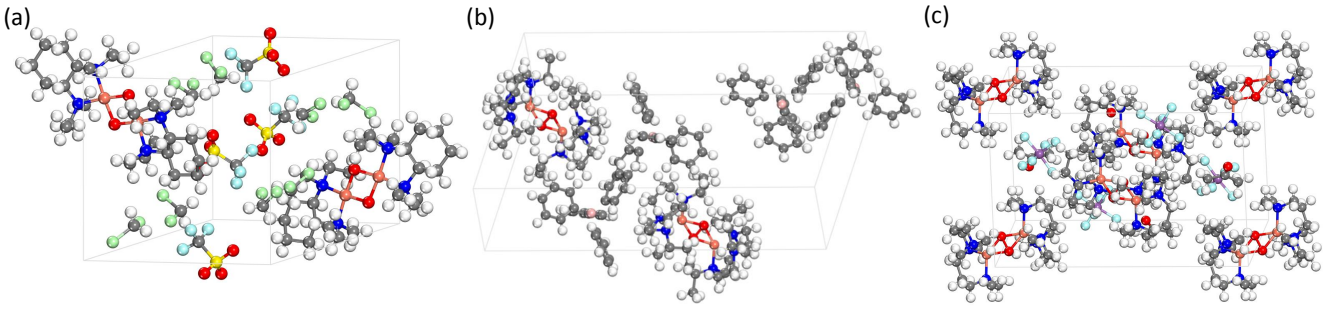

Figure S3: The geometries of Cu_2O_2 crystal structure from enzymatic catalysis: (a) bis Cu_2O_2 crystal taken from Ref. [62], (b) side-on Cu_2O_2 crystal taken from Ref. [63], (c) side-on Cu_2O_2 crystal taken from Ref. [64].

Structures

The C1-5 structures are added to the ESI as .cif files. The corresponding wavenumbers form the vibrational analysis are given below.

The vibrational wavenumbers for C1:

1 f = 3432.026211 cm-1

2 f = 3416.093311 cm-1

3 f = 3393.784482 cm-1

4 f = 3386.297972 cm-1

5 f = 3369.088250 cm-1

6 f = 3358.733490 cm-1

7 f = 3344.085117 cm-1

8 f = 3293.423151 cm-1

9 f = 3273.627732 cm-1

10 f = 3272.638503 cm-1

11 f = 3224.750826 cm-1

12 f = 3125.639873 cm-1

13 f = 1629.414427 cm-1

14 f = 1622.442476 cm-1

15 f = 1621.359058 cm-1

16 f = 1611.137319 cm-1

17 f = 1603.938142 cm-1

18 f = 1599.439692 cm-1

19 f = 1597.376882 cm-1

20 f = 1592.240733 cm-1

21 f = 1295.199455 cm-1

22 f = 1282.649049 cm-1

23 f = 1279.137856 cm-1

24 f = 1273.000911 cm-1

25 f = 758.127285 cm-1

26 f = 752.901047 cm-1

27 f = 734.900888 cm-1

28 f = 710.838462 cm-1

29 f = 707.723581 cm-1

30 f = 702.259613 cm-1

31 f = 687.094958 cm-1

32 f = 662.450901 cm-1

33 f = 548.567234 cm-1

34 f = 546.743088 cm-1

35 f = 467.533424 cm-1

36 f = 462.354693 cm-1

37 f = 294.452161 cm-1

38 f = 250.803728 cm-1

39 f = 241.760318 cm-1

40 f = 207.210343 cm-1

41 f = 192.953559 cm-1

42 f = 184.164603 cm-1

43 f = 182.016603 cm-1

44 f = 160.609697 cm-1

45 f = 130.554015 cm-1

46 f = 117.448957 cm-1

47 f = 107.556549 cm-1

48 f = 96.318427 cm-1

49 f = 67.245405 cm-1

50 f = 58.344244 cm-1

51 f = 54.741301 cm-1

52 f = 47.987158 cm-1

53 f = 42.021596 cm-1

54 f = 35.778719 cm-1

The vibrational wavenumbers for C2:

1 f = 3431.473427 cm-1

2 f = 3427.270626 cm-1

3 f = 3411.798101 cm-1

4 f = 3401.872855 cm-1

5 f = 3401.109711 cm-1

6 f = 3348.832422 cm-1

7 f = 3341.256851 cm-1

8 f = 3323.865923 cm-1

9 f = 3283.871198 cm-1

10 f = 3259.322178 cm-1

11 f = 3255.046320 cm-1

12 f = 3226.044113 cm-1

13 f = 1623.532860 cm-1

14 f = 1613.706454 cm-1

15 f = 1610.722002 cm-1

16 f = 1607.999946 cm-1

17 f = 1604.551102 cm-1

18 f = 1597.100764 cm-1

19 f = 1594.002411 cm-1

20 f = 1587.632445 cm-1

21 f = 1298.631191 cm-1

22 f = 1286.741739 cm-1

23 f = 1284.266356 cm-1

24 f = 1268.871007 cm-1

25 f = 1183.279334 cm-1

26 f = 784.417762 cm-1

27 f = 746.414570 cm-1

28 f = 744.005704 cm-1

29 f = 737.608224 cm-1

30 f = 691.245604 cm-1

31 f = 681.634649 cm-1

32 f = 672.700033 cm-1

33 f = 637.212692 cm-1

34 f = 533.101857 cm-1

35 f = 525.403887 cm-1

36 f = 450.538227 cm-1

37 f = 439.873479 cm-1

38 f = 307.911987 cm-1

39 f = 261.213529 cm-1

40 f = 230.524090 cm-1

41 f = 204.576427 cm-1

42 f = 202.539784 cm-1

43 f = 178.909329 cm-1

44 f = 166.527193 cm-1

45 f = 153.710110 cm-1

46 f = 147.010428 cm-1

47 f = 141.338236 cm-1

48 f = 129.584027 cm-1

49 f = 121.863169 cm-1

50 f = 116.927478 cm-1

51 f = 105.289254 cm-1

52 f = 90.792091 cm-1

53 f = 82.582496 cm-1

54 f = 71.511552 cm-1

55 f = 54.748598 cm-1

56 f = 53.439667 cm-1

57 f = 52.124912 cm-1

58 f = 38.974563 cm-1

59 f = 28.748836 cm-1

60 f = 24.350220 cm-1

The vibrational wavenumbers for C3:

1 f = 3427.451681 cm-1

2 f = 3423.034197 cm-1

3 f = 3420.470179 cm-1

4 f = 3401.224648 cm-1

5 f = 3358.284421 cm-1

6 f = 3332.486061 cm-1

7 f = 3320.508836 cm-1

8 f = 3290.959496 cm-1

9 f = 3264.715970 cm-1

10 f = 3256.368725 cm-1

11 f = 3230.141118 cm-1

12 f = 3175.560202 cm-1

13 f = 1621.499581 cm-1

14 f = 1619.315521 cm-1

15 f = 1617.922910 cm-1

16 f = 1610.501557 cm-1

17 f = 1608.473110 cm-1

18 f = 1601.439765 cm-1

19 f = 1592.515600 cm-1

20 f = 1586.438857 cm-1

21 f = 1310.536505 cm-1

22 f = 1298.336255 cm-1

23 f = 1295.592572 cm-1

24 f = 1283.238023 cm-1

25 f = 964.649405 cm-1

26 f = 790.622286 cm-1

27 f = 782.345460 cm-1

28 f = 756.775480 cm-1

29 f = 751.204122 cm-1

30 f = 700.495176 cm-1

31 f = 695.081888 cm-1

32 f = 684.529721 cm-1

33 f = 680.696315 cm-1

34 f = 539.248305 cm-1

35 f = 534.802657 cm-1

36 f = 481.229353 cm-1

37 f = 450.664927 cm-1

38 f = 447.063589 cm-1

39 f = 392.504585 cm-1

40 f = 264.776159 cm-1

41 f = 259.194337 cm-1

42 f = 253.999716 cm-1

43 f = 220.326495 cm-1

44 f = 202.355090 cm-1

45 f = 190.801479 cm-1

46 f = 188.083129 cm-1

47 f = 176.696211 cm-1

48 f = 173.486012 cm-1

49 f = 166.065530 cm-1

50 f = 137.188136 cm-1

51 f = 132.477965 cm-1

52 f = 122.389751 cm-1

53 f = 112.369753 cm-1

54 f = 98.278049 cm-1

55 f = 74.613941 cm-1

56 f = 68.668525 cm-1

57 f = 63.335660 cm-1

58 f = 47.640916 cm-1

59 f = 44.656416 cm-1

60 f = 33.301679 cm-1

The vibrational wavenumbers for C4:

1 f = 3432.874311 cm-1

2 f = 3421.648794 cm-1

3 f = 3420.681671 cm-1

4 f = 3418.543215 cm-1

5 f = 3378.849481 cm-1

6 f = 3341.812759 cm-1

7 f = 3308.618079 cm-1

8 f = 3303.436241 cm-1

9 f = 3259.312560 cm-1

10 f = 3247.017965 cm-1

11 f = 3215.862130 cm-1

12 f = 3212.653856 cm-1

13 f = 1630.574035 cm-1

14 f = 1624.338280 cm-1

15 f = 1612.637981 cm-1

16 f = 1607.143046 cm-1

17 f = 1601.525847 cm-1

18 f = 1592.734683 cm-1

19 f = 1587.843311 cm-1

20 f = 1586.020329 cm-1

21 f = 1313.356599 cm-1

22 f = 1305.939816 cm-1

23 f = 1253.661064 cm-1

24 f = 1238.673733 cm-1

25 f = 840.064912 cm-1

26 f = 776.055907 cm-1

27 f = 760.725343 cm-1

28 f = 748.371946 cm-1

29 f = 724.920537 cm-1

30 f = 720.478861 cm-1

31 f = 699.848682 cm-1

32 f = 682.016293 cm-1

33 f = 680.292587 cm-1

34 f = 573.504180 cm-1

35 f = 471.860470 cm-1

36 f = 461.618103 cm-1

37 f = 447.015287 cm-1

38 f = 440.437465 cm-1

39 f = 386.626096 cm-1

40 f = 300.128450 cm-1

41 f = 255.135159 cm-1

42 f = 235.507994 cm-1

43 f = 226.014512 cm-1

44 f = 215.428869 cm-1

45 f = 204.570623 cm-1

46 f = 196.015383 cm-1

47 f = 192.409006 cm-1

48 f = 179.804223 cm-1

49 f = 164.720497 cm-1

50 f = 155.364904 cm-1

51 f = 137.545401 cm-1

52 f = 130.161461 cm-1

53 f = 125.091849 cm-1

54 f = 103.223069 cm-1

55 f = 86.521055 cm-1

56 f = 66.833476 cm-1

57 f = 56.689283 cm-1

58 f = 51.109054 cm-1

59 f = 30.235685 cm-1

60 f = 25.974302 cm-1

The vibrational wavenumbers for C5:

1 f = 3442.413683 cm-1

2 f = 3441.473112 cm-1

3 f = 3412.281992 cm-1

4 f = 3382.701263 cm-1

5 f = 3372.403050 cm-1

6 f = 3370.586984 cm-1

7 f = 3309.168459 cm-1

8 f = 3261.218917 cm-1

9 f = 3228.397425 cm-1

10 f = 3221.959703 cm-1

11 f = 3133.471186 cm-1

12 f = 3053.363709 cm-1

13 f = 1620.332619 cm-1

14 f = 1611.506311 cm-1

15 f = 1609.733244 cm-1

16 f = 1602.141875 cm-1

17 f = 1591.378474 cm-1

18 f = 1587.981322 cm-1

19 f = 1569.875291 cm-1

20 f = 1556.147916 cm-1

21 f = 1322.729950 cm-1

22 f = 1276.766139 cm-1

23 f = 1265.588918 cm-1

24 f = 1257.892699 cm-1

25 f = 841.042429 cm-1

26 f = 817.412890 cm-1

27 f = 812.920560 cm-1

28 f = 772.684807 cm-1

29 f = 767.796484 cm-1

30 f = 744.949355 cm-1

31 f = 731.026154 cm-1

32 f = 705.007325 cm-1

33 f = 687.825093 cm-1

34 f = 637.303877 cm-1

35 f = 620.320722 cm-1

36 f = 597.810085 cm-1

37 f = 506.627096 cm-1

38 f = 488.957338 cm-1

39 f = 476.035635 cm-1

40 f = 457.052655 cm-1

41 f = 329.648225 cm-1

42 f = 298.921731 cm-1

43 f = 279.721252 cm-1

44 f = 260.671726 cm-1

45 f = 253.657726 cm-1

46 f = 235.737776 cm-1

47 f = 216.693247 cm-1

48 f = 212.136398 cm-1

49 f = 200.355062 cm-1

50 f = 194.687344 cm-1

51 f = 172.382700 cm-1

52 f = 154.638647 cm-1

53 f = 133.351298 cm-1

54 f = 105.561612 cm-1

55 f = 94.717267 cm-1

56 f = 78.232812 cm-1

57 f = 62.603400 cm-1

58 f = 51.201283 cm-1

59 f = 44.235261 cm-1

60 f = 28.960037 cm-1

References

(S1) Behler, J.; Delley, B.; Lorenz, S.; Reuter, K.; Scheffler, M. Dissociation of O_2 at Al(111): The Role of Spin Selection Rules. *Phys. Rev. Lett.* **2005**, *94*, 036104.