Electronic and geometrical effects of anchoring bio-mimetic catalyst onto oxidized carbon support A Density Functional Theory approach

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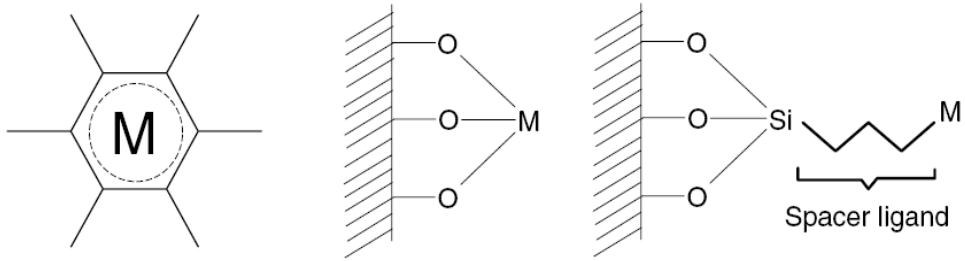
Introduction

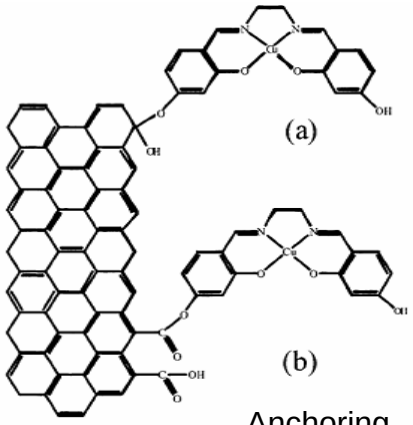
- A great challenge in the field of catalysis is the development of catalysts which possess the major advantages of both homogeneous (e.g., high activity, high selectivity, and mild reaction conditions) and heterogeneous (e.g., ease of catalyst recovery and high turnover numbers) catalysis.

- One way of bridging this 'gap' between homogeneous and heterogeneous catalysis is heterogenization of homogeneous catalysts.

- Heterogenization is achieved via either physisorption or through covalent grafting of a ligand or transition metal complex onto a solid support viz. Alumina, silica, MCM, carbon etc.,



Encapsulation (Ship-in-a-bottle) | Grafting | Tethering



Anchoring

Methods of heterogenization of homogeneous catalyst

- **Generally the activity and selectivity of the homogeneous catalysts are changed (either it increases or decreases) after heterogenization. This may be due to the changes in geometry and electronic properties of the catalytic site.**

- **In order to study these changes in advance, prior to carry out this reaction in the laboratory, a theoretical study should be carried out. Moreover, these properties of a catalyst can be obtained computationally more easily than by experimental means.**

- **In the present work, the electronic and geometrical effects of anchoring bio-mimetic galactose oxidase catalyst onto oxidized carbon support is studied by a Density Functional Theory (DFT).**

Computational Methods

Program: Gaussian 03

Theory: Density Functional Theory (DFT)

Graphical user interface: Gauss view 3.0

Basis set : 6-31G(d) for C, H, N and O
LanL2DZ for Cu

Functional: B3LYP hybrid

Drawing input structure

↓

Setting input parameters

↓

Geometry optimization

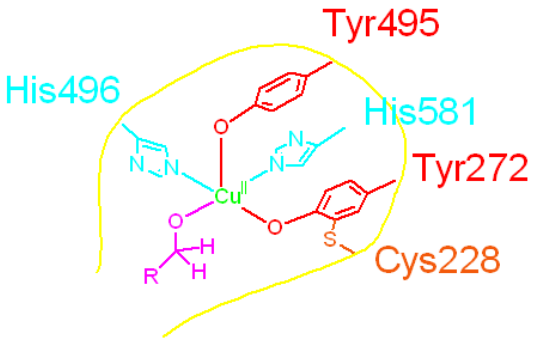
↓

Energy optimization

↓

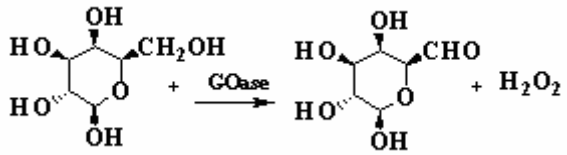
Surface analysis

Galactose Oxidase and its function



Active site of Galactose Oxidase

Oxidation of primary alcohol in galactose to aldehyde by GOase with O_2 as Oxidant



The overall alcohol oxidation reaction catalysed by GOase

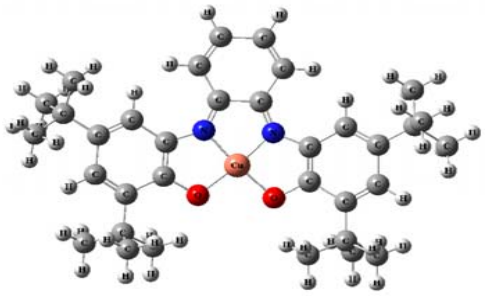
$$RCH_2OH \longrightarrow RCHO + 2e^- + 2H^+$$

$$2e^- + 2H^+ + O_2 \longrightarrow H_2O_2$$

$$RCH_2OH + O_2 \longrightarrow RCHO + H_2O_2$$

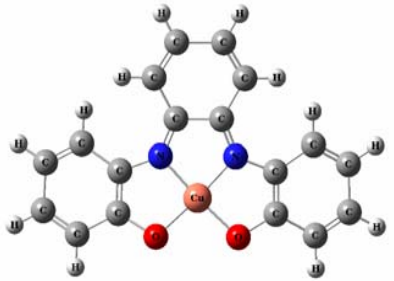
Synthetic model of Galactose Oxidase

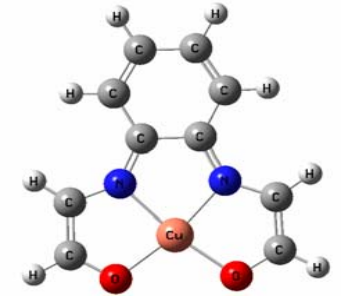
Full model



(Unable to optimize the geometry)

Truncated models

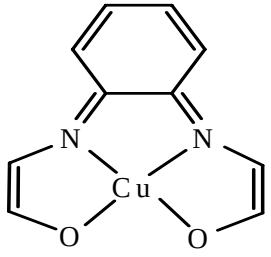




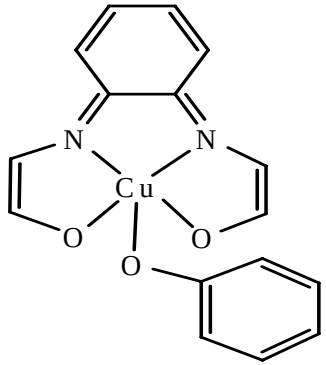
J. Am.Chem.Soc.1999, 121, 9599-9610

Truncated model structures taken for computational study

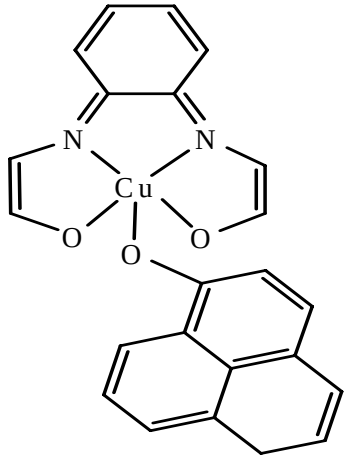
I



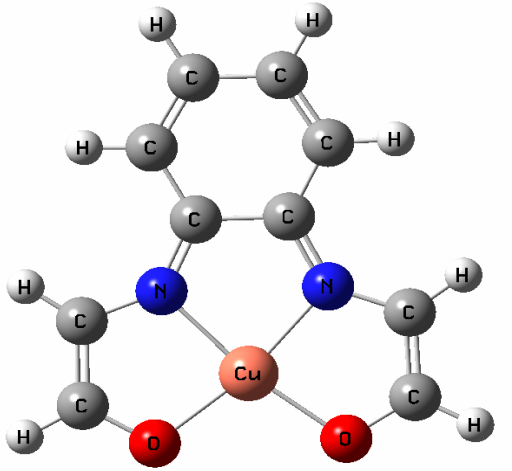
II



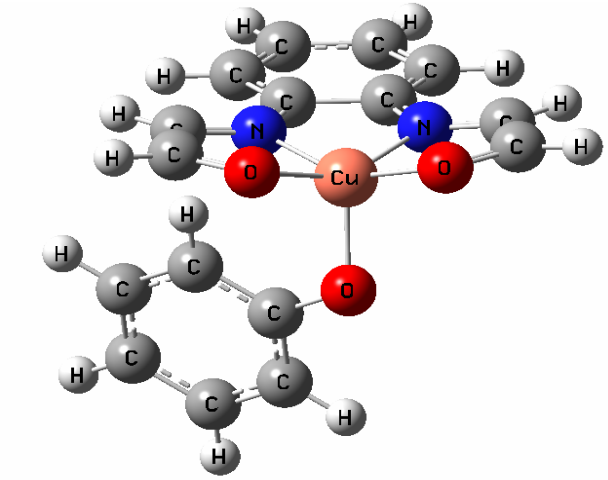
III



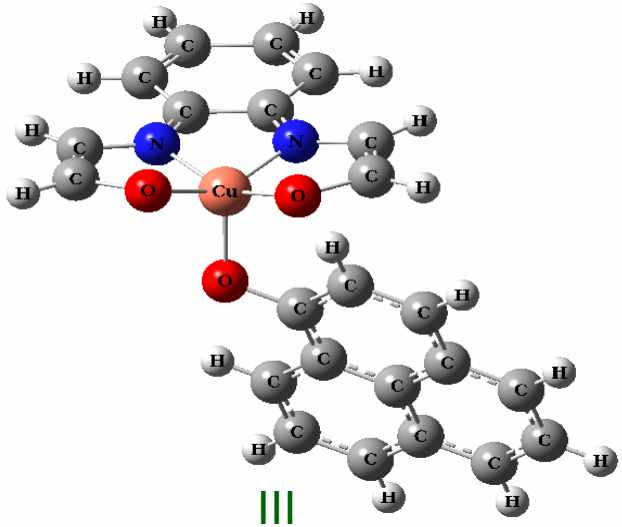
Chem draw models



I



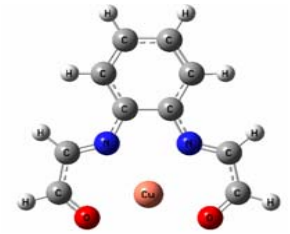
II



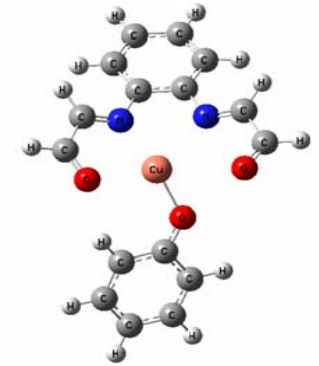
III

Gauss view models

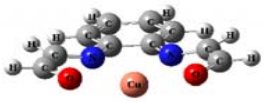
Comparison of optimised geometrical parameters of Model - I, II and III



Model-I

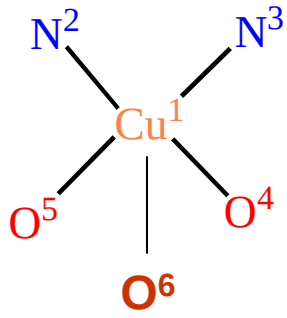


Model-I



Model-III

Atom numbering	Bond length (A°)		
	Model-I	Model-II	Model-III
Cu1-N2	2.231	1.998	2.165
Cu1-N3	2.231	2.354	2.166
Cu1-O4	2.136	3.192	2.393
Cu1-O5	2.135	2.624	2.479
Cu1-O6	-	1.895	2.025
O6 -C7	-	1.317	1.251
	Bond angle (degree)		
N2-Cu1-N3	72.58	74.73	75.86
N3-Cu1-O4	76.42	59.33	73.96
O4-Cu1-O5	134.54	113.32	120.32
O5-Cu1-N2	76.45	72.01	72.00
O4-Cu1-O6	-	78.14	98.98
O5-Cu1-O6	-	113.12	120.32



Percentage atomic orbital contributions to HOMO and LUMO level of model -I

Elements	% of atomic orbital contribution					
	HOMO			LUMO		
	s	p	d	s	p	d
Cu	1.09×10^{-7}	1.37×10^{-6}	5.50	2.13×10^{-8}	1.75	0.78
N	2.19×10^{-8}	18.53	-	1.55×10^{-5}	30.23	-
O	8.75×10^{-8}	18.80	-	7.28×10^{-6}	12.47	-
C	1.30×10^{-6}	57.17	-	2.16×10^{-5}	54.77	-
H	4.92×10^{-7}	-	-	1.48×10^{-5}	-	-
Total	2.01×10^{-6}	94.50	5.50	5.92×10^{-5}	99.22	0.78

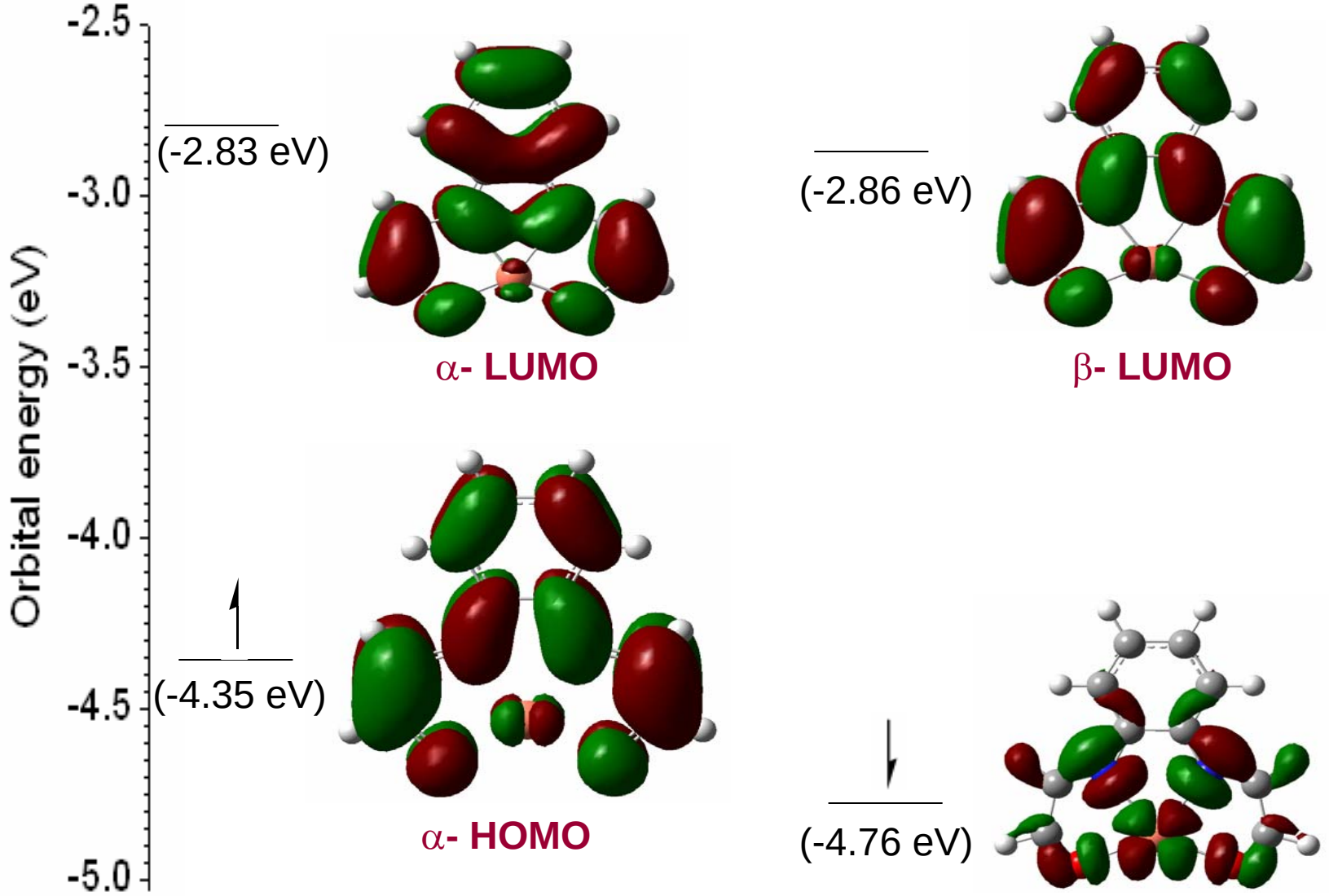
Percentage atomic orbital contributions to HOMO and LUMO level of model – II

Elements	% of atomic orbital contribution					
	HOMO			LUMO		
	s	p	d	s	p	d
Cu	0.02	1.04	3.56	0.32	0.05	4.58
N	0.04	3.47	-	0.17	19.91	-
O	0.07	31.03	-	0.04	18.56	-
C	0.50	60.13	-	2.49	53.36	-
H	0.16	-	-	0.51	-	-
Total	0.79	95.67	3.56	3.53	91.88	4.58

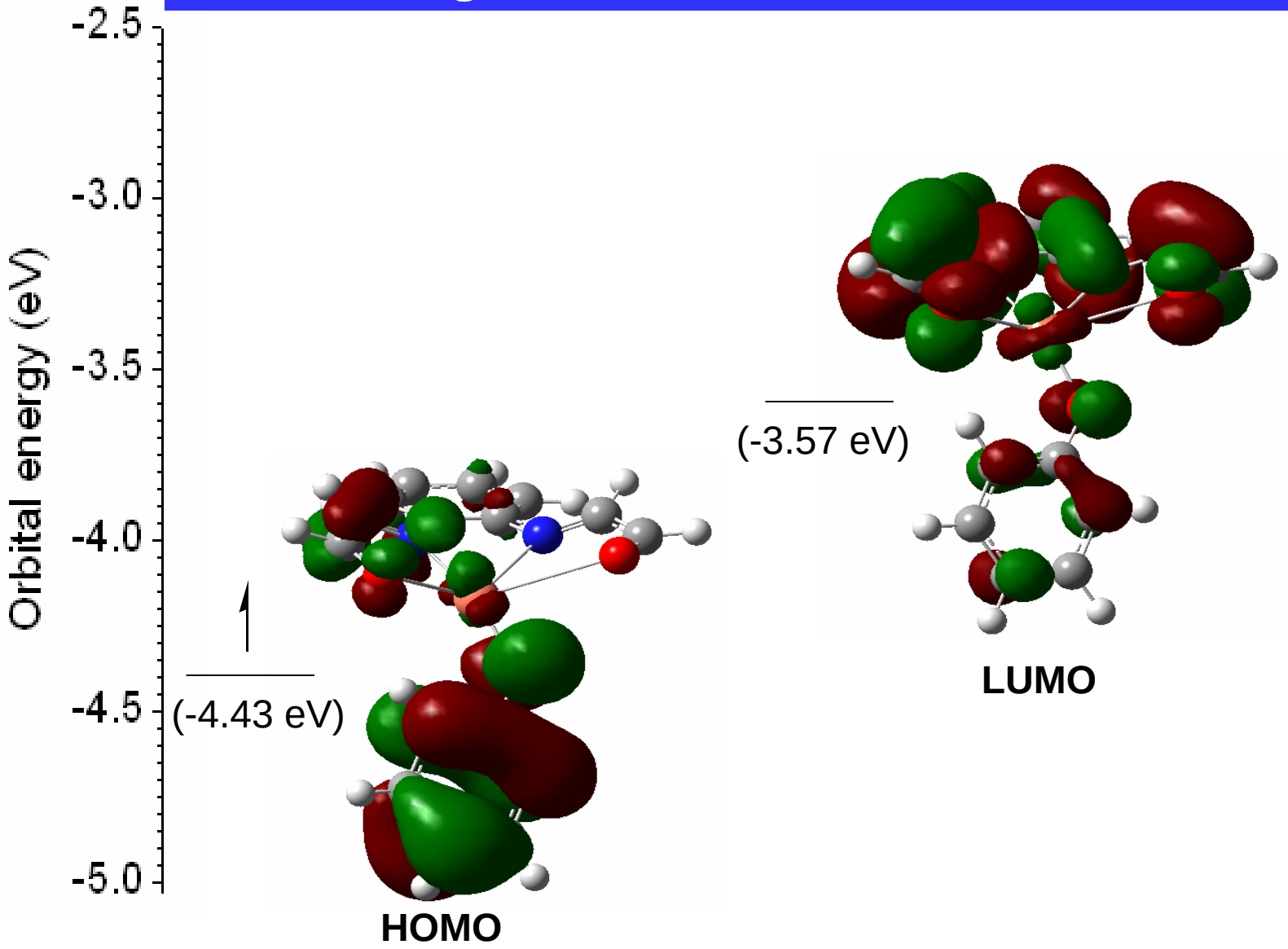
Percentage of atomic orbital contributions to HOMO and LUMO level of model - III

Elements	% of atomic orbital contribution					
	HOMO			LUMO		
	s	p	d	s	p	d
Cu	9.03E-06	6.38E-06	0.154204	0.722954	0.035241	0.642483
N	0.271045	1.097934	0.003088	0.131375	0.292254	0.000131
O	0.039622	0.987697	0.00011	0.121829	3.737995	8.88365E-05
C	70.6333633	26.61731	6.38119E-06	43.73752	50.46554	0.094397
H	1.63E-05	-	-	0.018195	-	-
Total	7.09E+01	2.87E+01	0.157408381	44.731873	54.53103	0.737099837

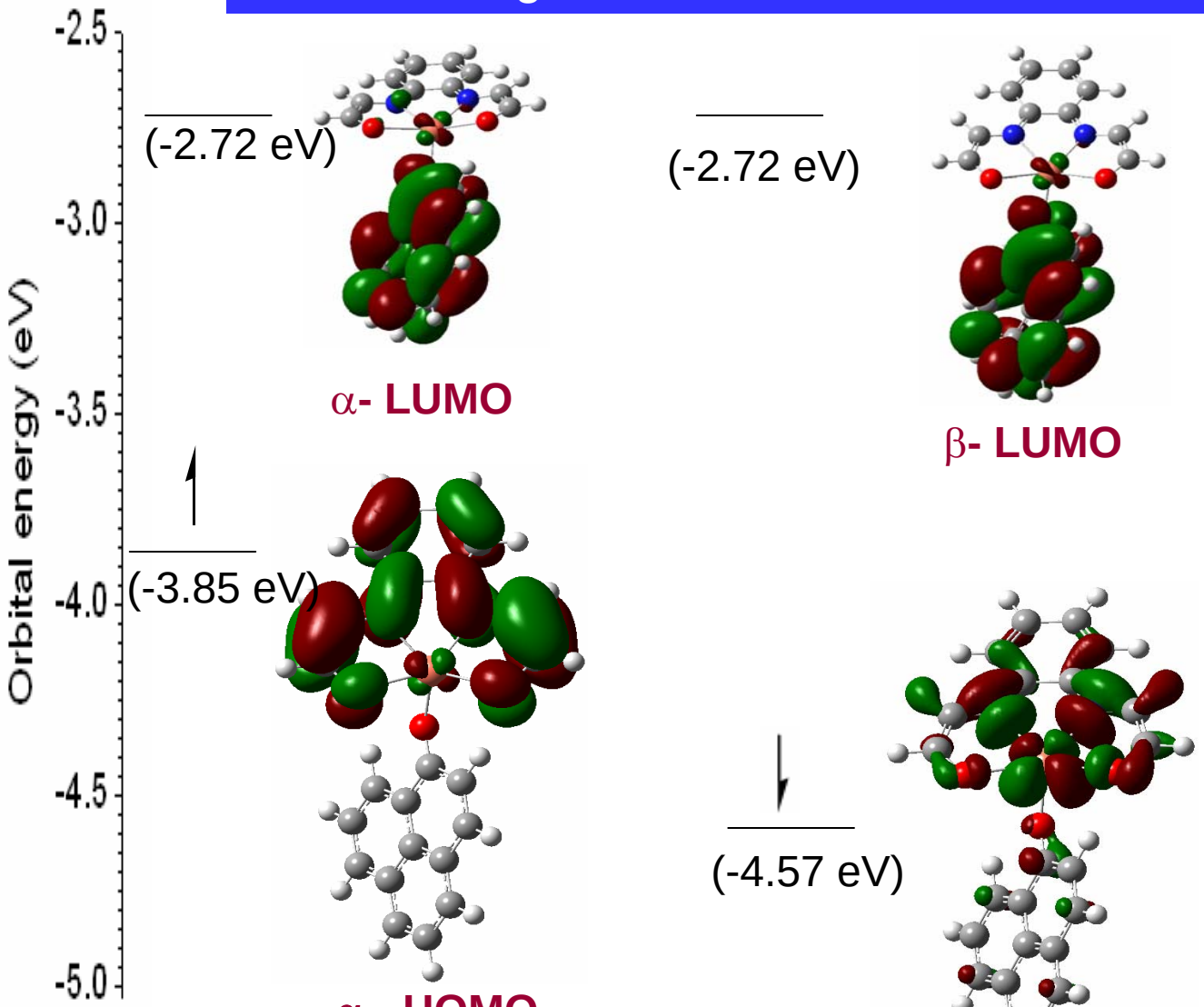
Relative energies of HOMO - LUMO orbitals of model - I



Relative energies of HOMO - LUMO orbitals of model - II

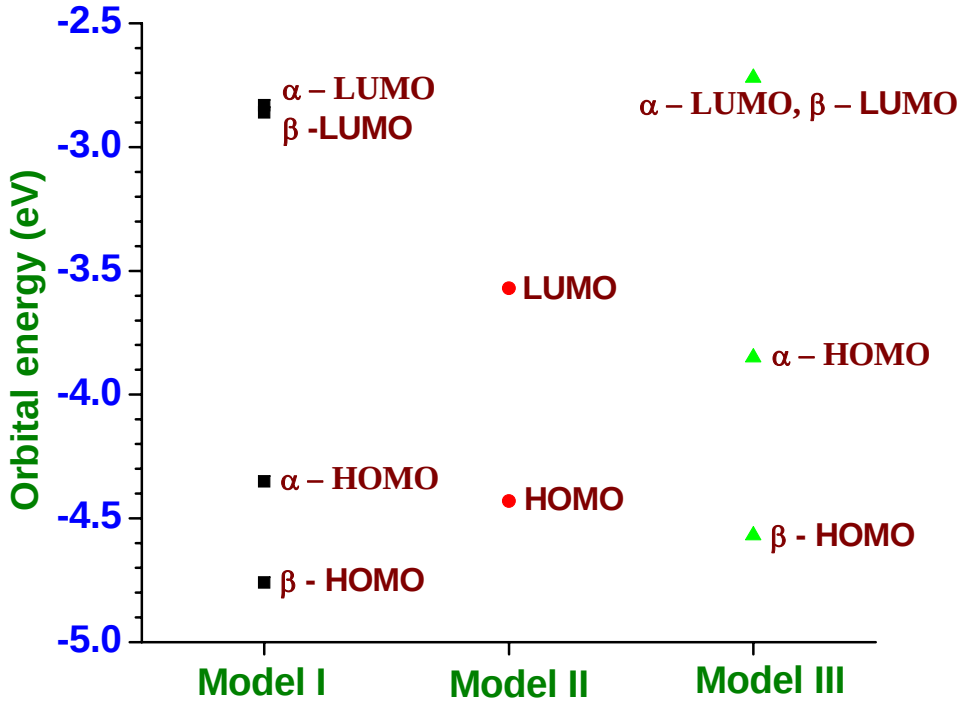


Relative energies of HOMO - LUMO orbitals of model - III

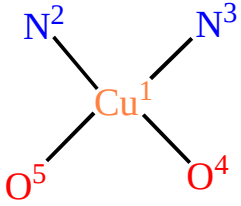


Comparison of HOMO-LUMO energy gap for the models I, II and III

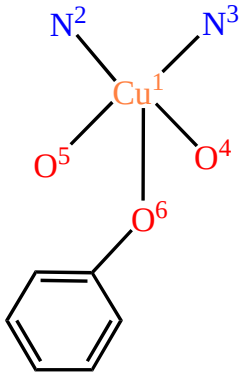
	HOMO (eV)	LUMO (eV)	ΔE (eV)
Model-I	-4.35 (α) -4.76 (β)	-2.83 (α) -2.86 (β)	1.52 1.90
Model-II	-4.43	-3.57	0.86
Model-III	-3.85 (α) -4.57 (β)	-2.72(α) -2.72(β)	1.13 1.85



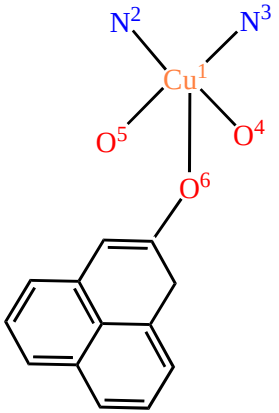
Comparison of atomic spin densities on Models I, II and III



Model-I



Model-II



Model-III

	Model - I	Model - II	Model - III
Cu1	0.457	-0.338	0.748
N2	-0.491	0.203	-0.531
N3	-0.498	0.071	-0.562
O4	-0.470	-0.267	-0.618
O5	-0.471	-0.133	-0.563
O6	-	-0.270	-0.647

Conclusion

The following results are obtained from DFT study upon anchoring the truncated models of galactose oxidase catalyst onto the hydroxyl functionalised carbon support,

- **The bond lengths of Cu-N decreases whereas Cu-O increases.**
- **Inplane ∠N-Cu-N increases and ∠N-Cu-O, ∠O-Cu-O decreases. But out of plane ∠O- Cu-O increases.**
- **Percentage of metal orbital contribution to HOMO and LUMO energy level is low when compared to ligand orbitals. Hence redox properties of the catalyst is mostly ligand based rather than metal.**
- **Shifting of HOMO energy to less negative value and decreasing HOMO-LUMO energy gap indicates that the reducing capacity of the catalyst is still reduced and the oxidising capacity of the catalyst is increased by increasing the number of fused carbon rings in the carbon support.**

References

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