

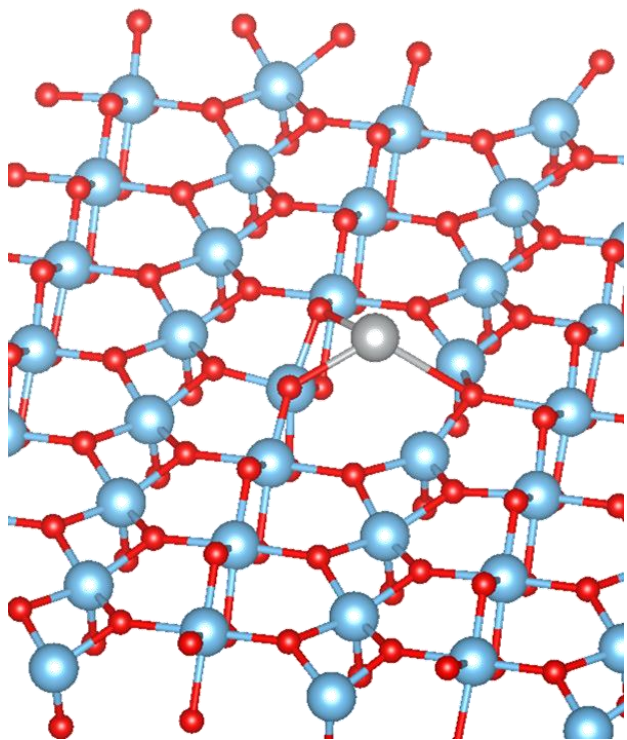


# 金属负载TiO<sub>2</sub>表面的结构与性质的理论研究

答辩人：刘喆

指导教师：田福平 樊红军

大连理工大学 大连化学物理研究所



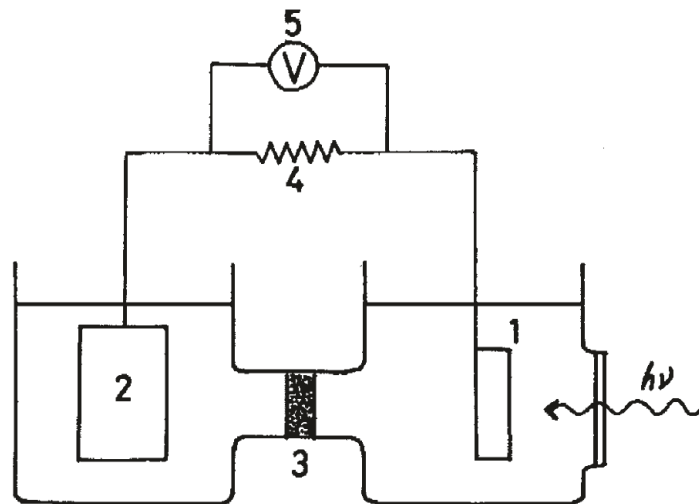
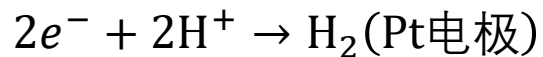
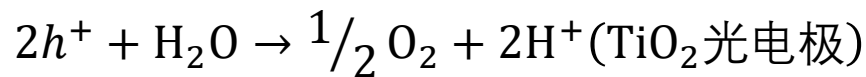
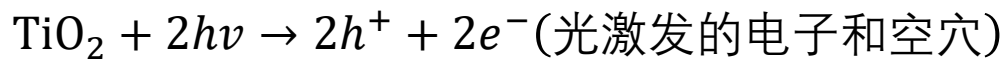
Ag原子在面氧空位上的吸附

## 金属负载TiO<sub>2</sub>表面的结构与性质的理论研究

- 文献综述
- 化学计量比TiO<sub>2</sub>表面和还原性TiO<sub>2</sub>表面
- 还原性TiO<sub>2</sub>表面的吸附
- 化学计量比TiO<sub>2</sub>表面的吸附

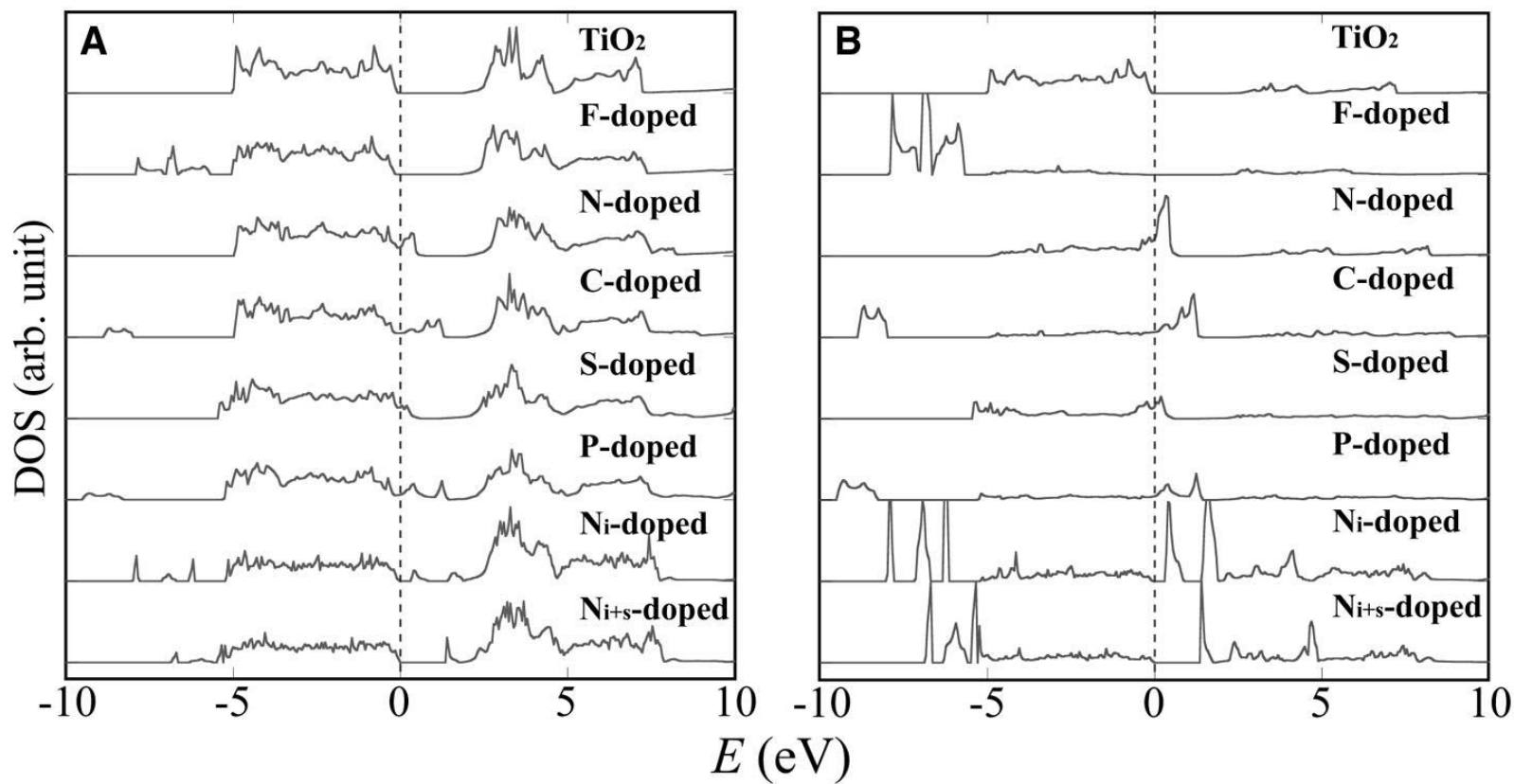
## 研究背景

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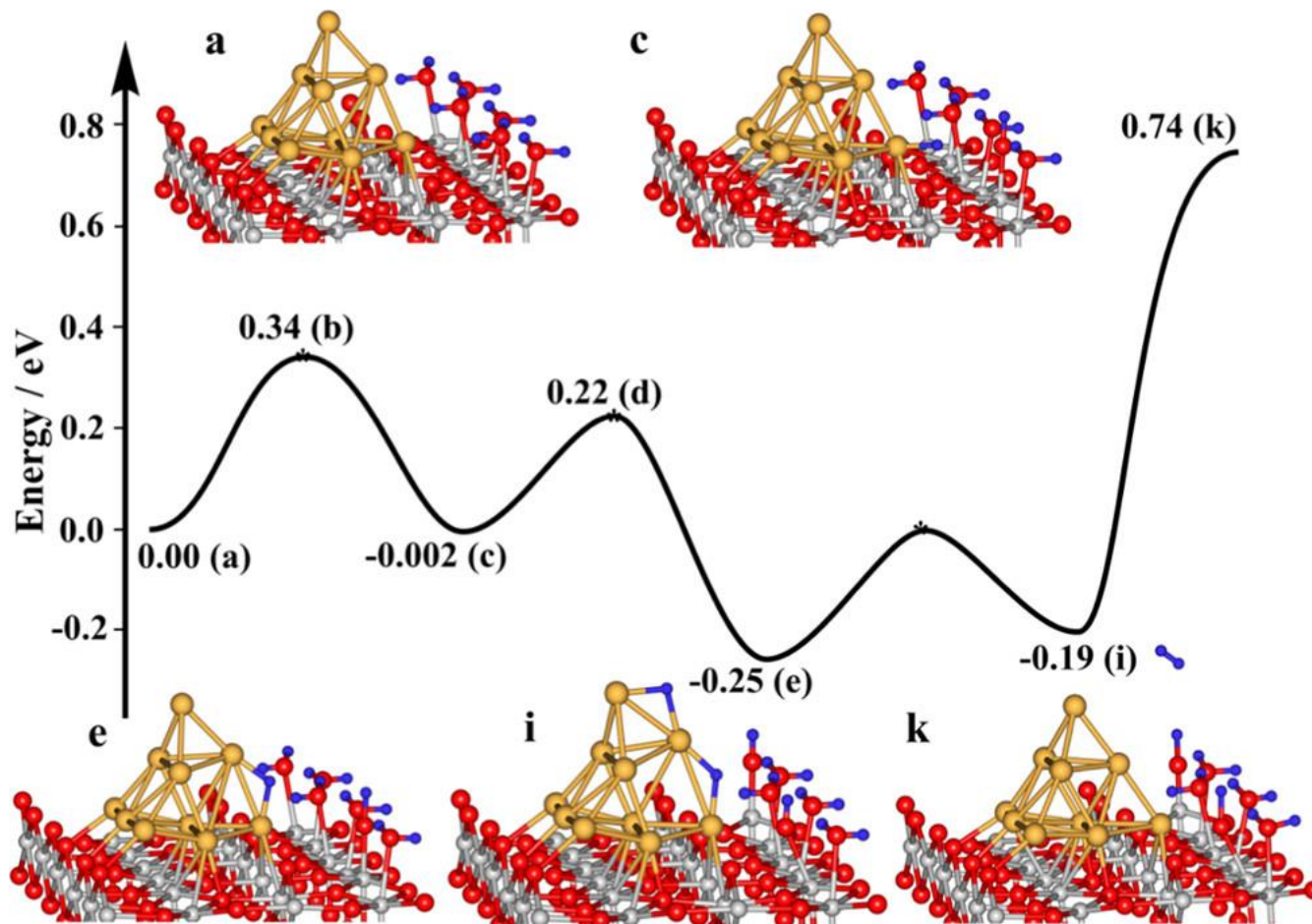
Fujishima A , Honda K . Electrochemical Photolysis of Water at a Semiconductor Electrode[J].  
Nature, 1972, 238(5358):37-38.

# 研究背景



Asahi, R. Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides[J]. Science, 2001, 293(5528):269-271.

# 研究背景

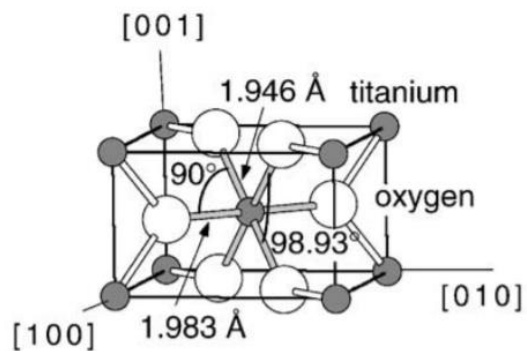


Geng Z , Jin X , Wang R , et al. Low-Temperature Hydrogen Production via Water Conversion on Pt/TiO<sub>2</sub>[J]. J. Phys. Chem. C, 2010, 101(136):695-708.

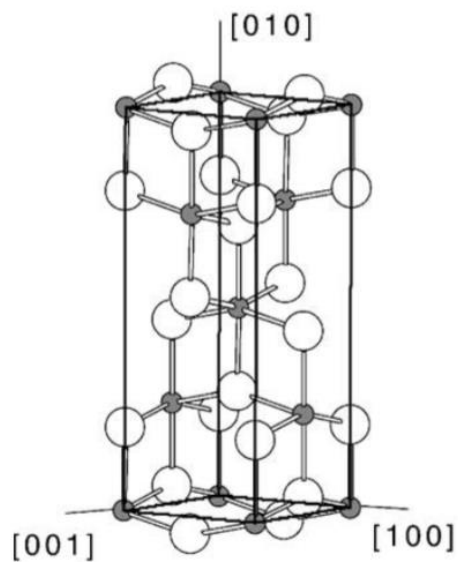
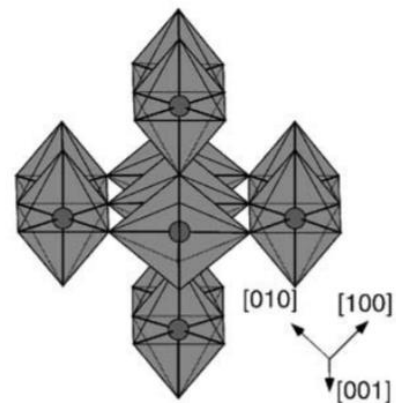
## 选题意义及创新点

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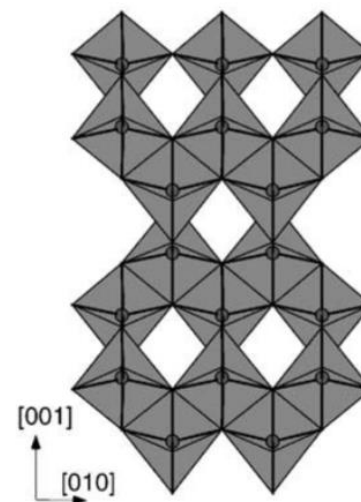
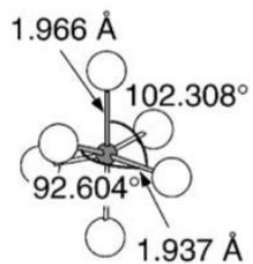
- 现有理论研究主要集中在 $\text{TiO}_2$ 表面的金属团簇，本文研究了 $\text{TiO}_2$ 表面的单原子吸附  
实验方法探究吸附后表面性质，成键情况，电子结构等存在诸多困难
- 现有实验和理论研究主要针对桥氧空位表面  
本文不仅讨论了桥氧空位表面，还涉及了面氧空位表面
- 现有理论研究主要讨论单一金属吸附后的性质  
本文研究了不同的过渡金属，并讨论了性质的递变规律



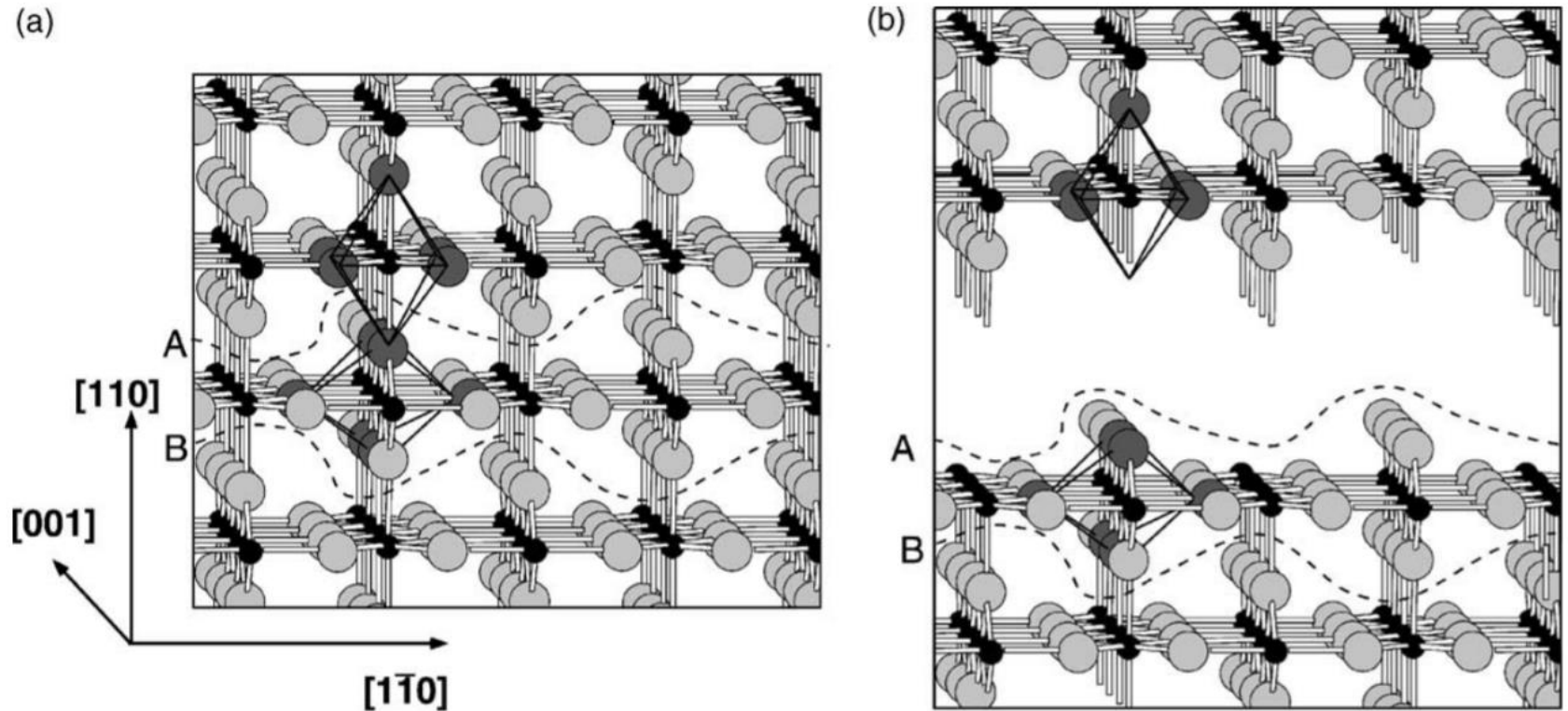
Rutile



Anatase



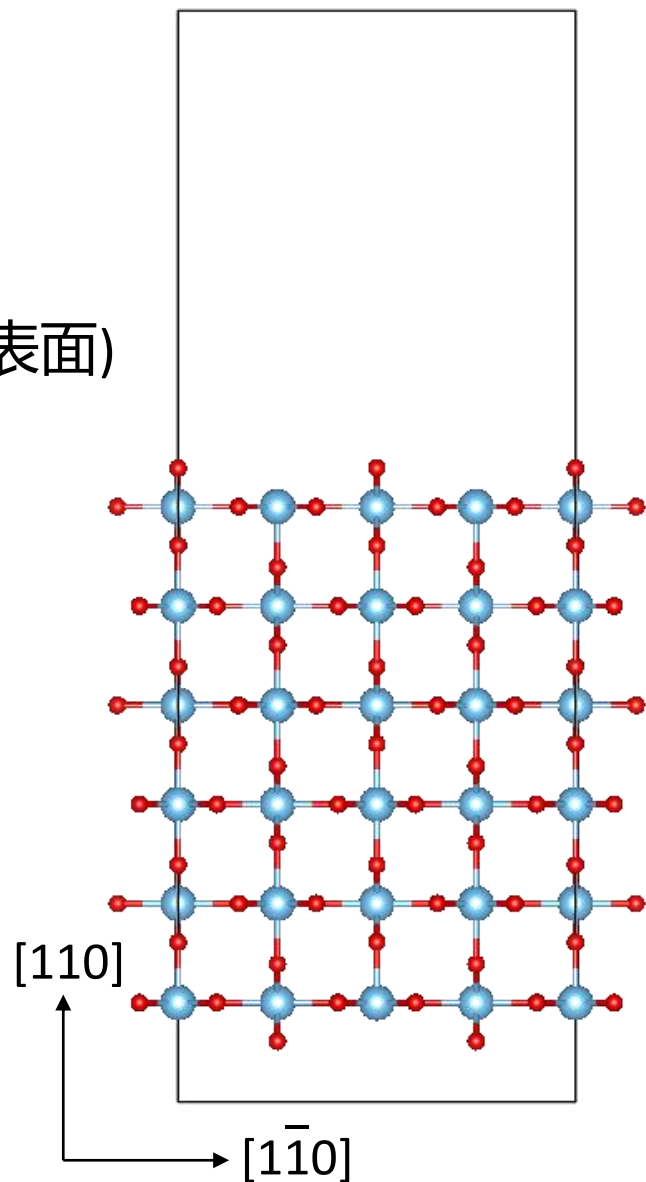
# 研究背景



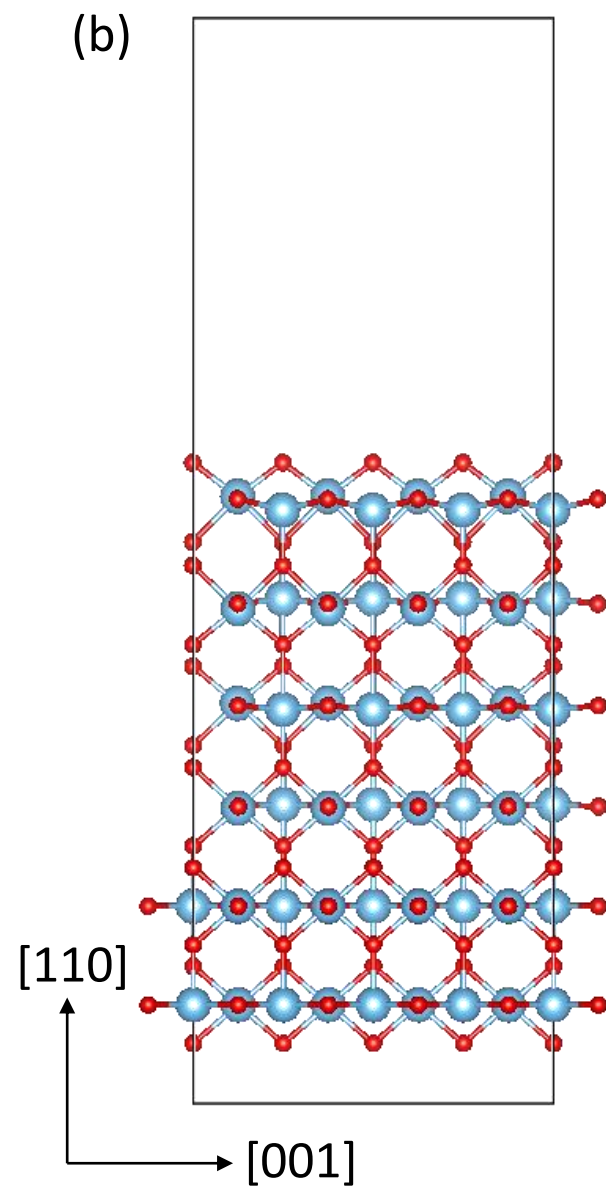
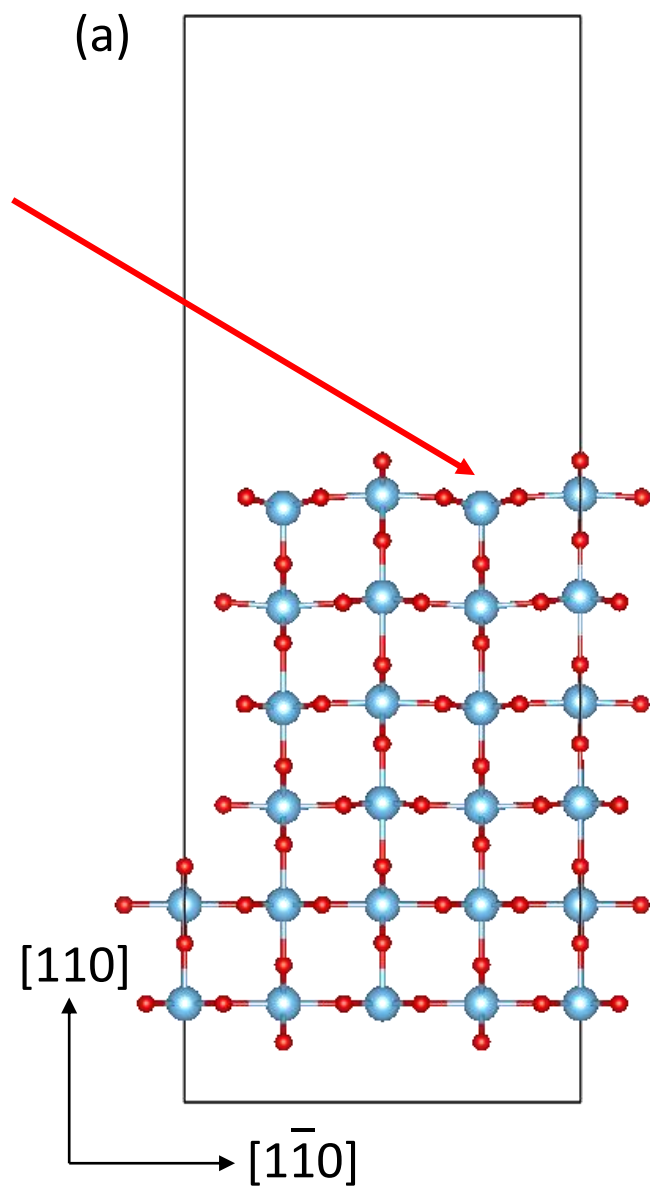
Diebold U . The Surface Science of Titanium Dioxide[J]. Surface Science Reports, 2003, 48(5):53-229.



- PAW-PBE
- $4 \times 4 \times 6$  (96) Ti; 192 O (化学计量比表面)
- Kinetic Cutoff: 400 eV
- Density Cutoff: 605.4 eV
- Monkhorst-Pack grid
- $(2 \times 1 \times 2)$  k-points

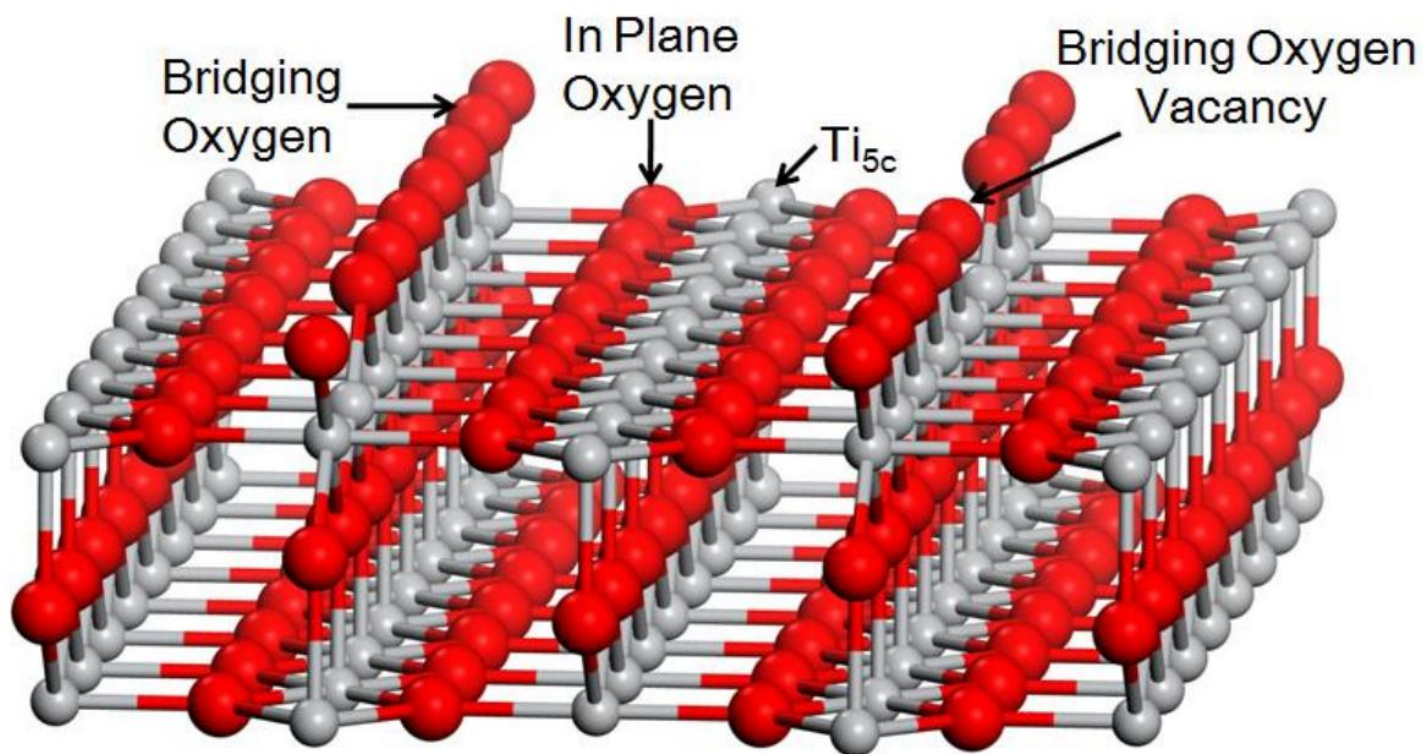


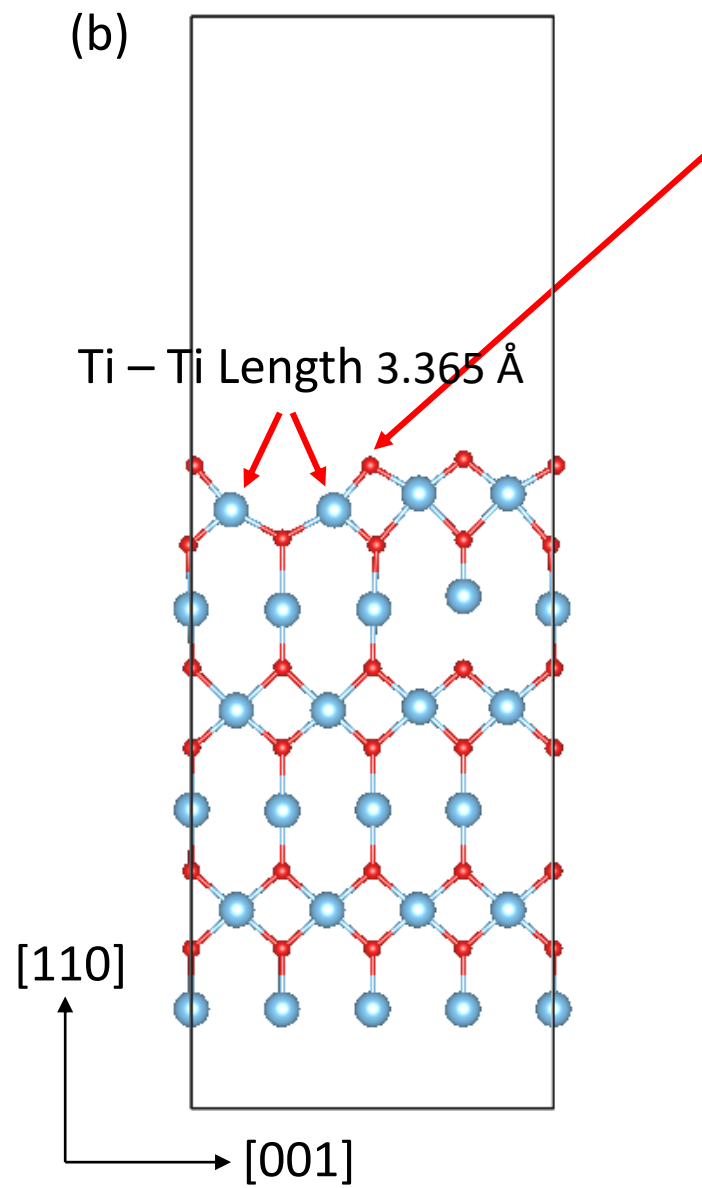
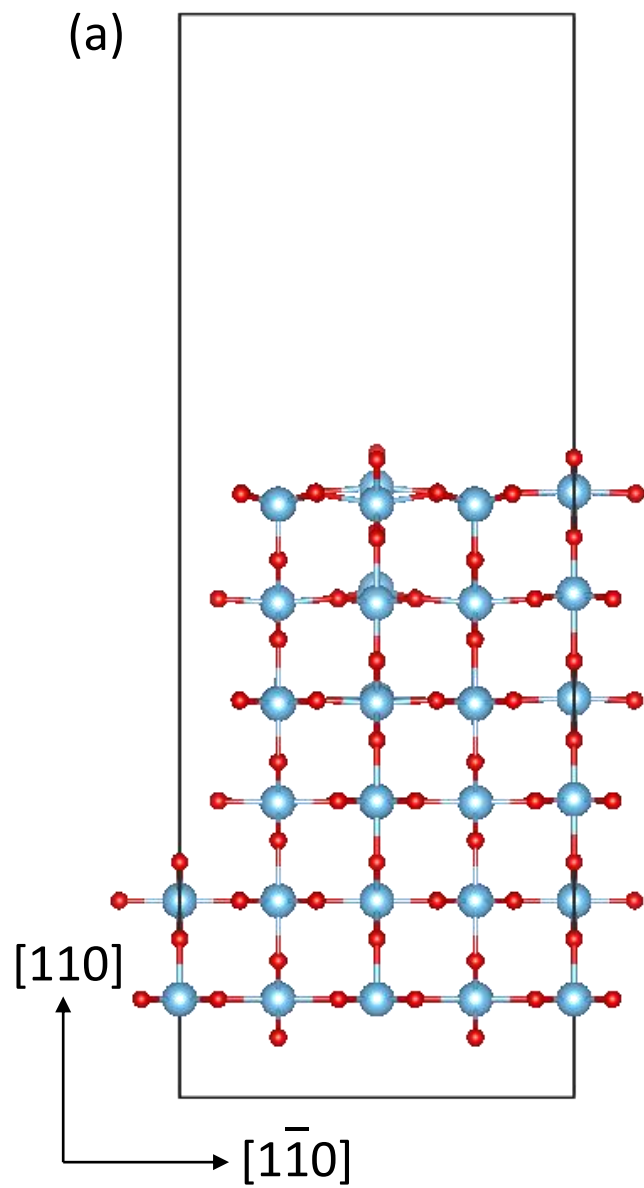
$a = 12.98880 \text{ \AA}$ ,  $b = 35.71898 \text{ \AA}$ ,  $c = 11.82960 \text{ \AA}$



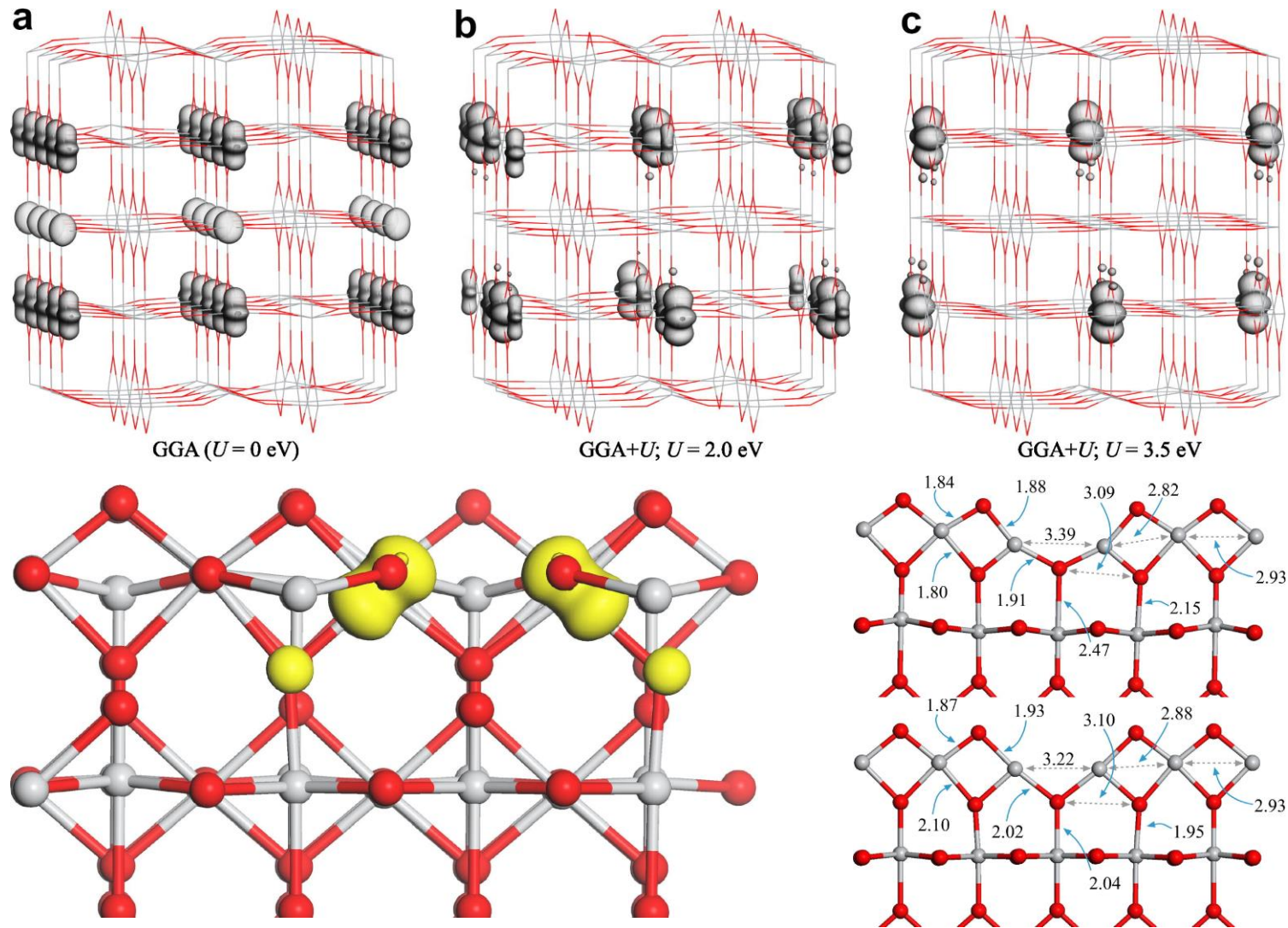
## 还原性表面

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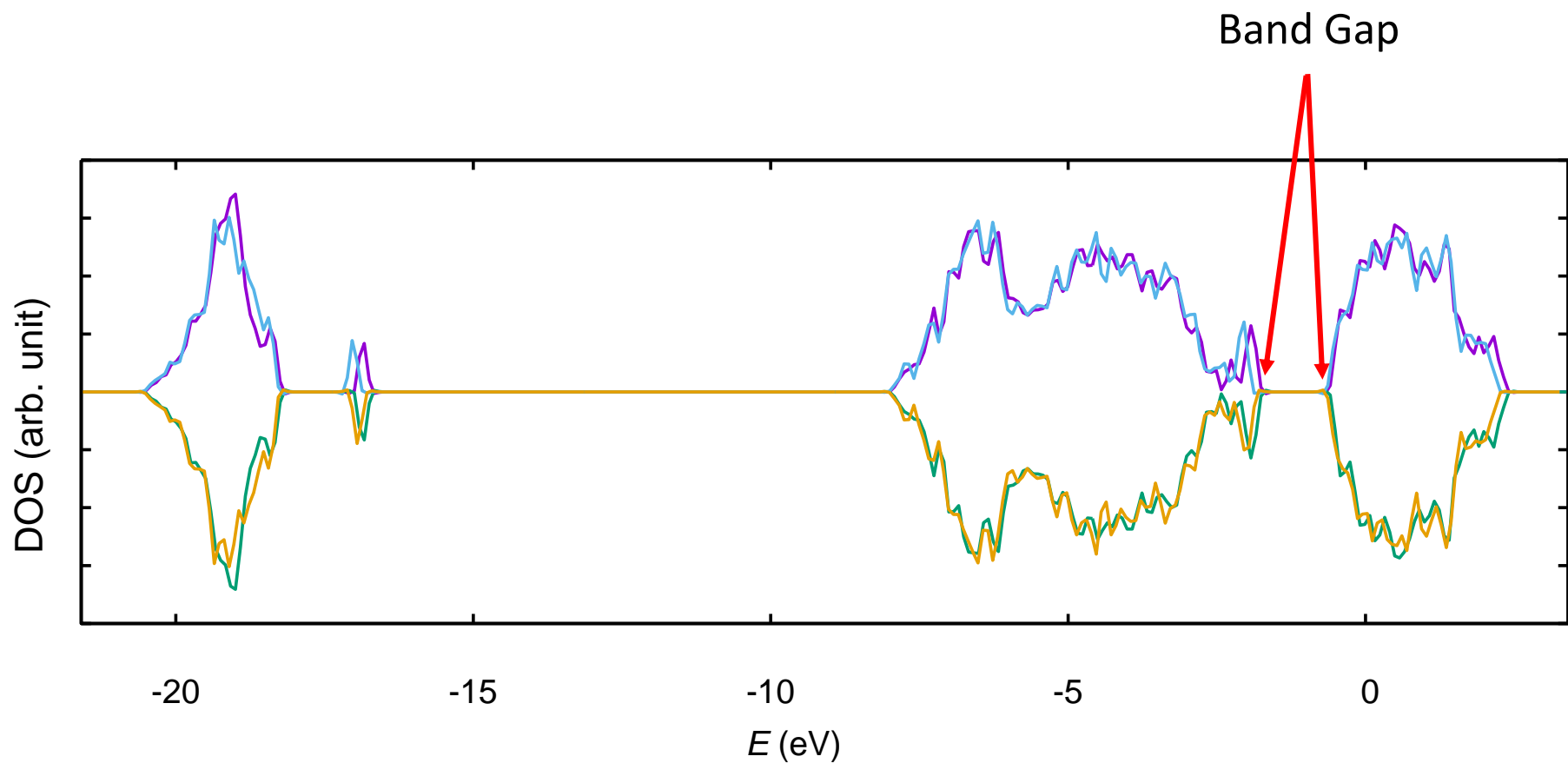




桥氧空位表面



Morgan B J , Watson G W . A DFT+ $U$  description of oxygen vacancies at the TiO<sub>2</sub> rutile (110) surface[J]. Surface Science, 2007, 601(21):5034-5041.

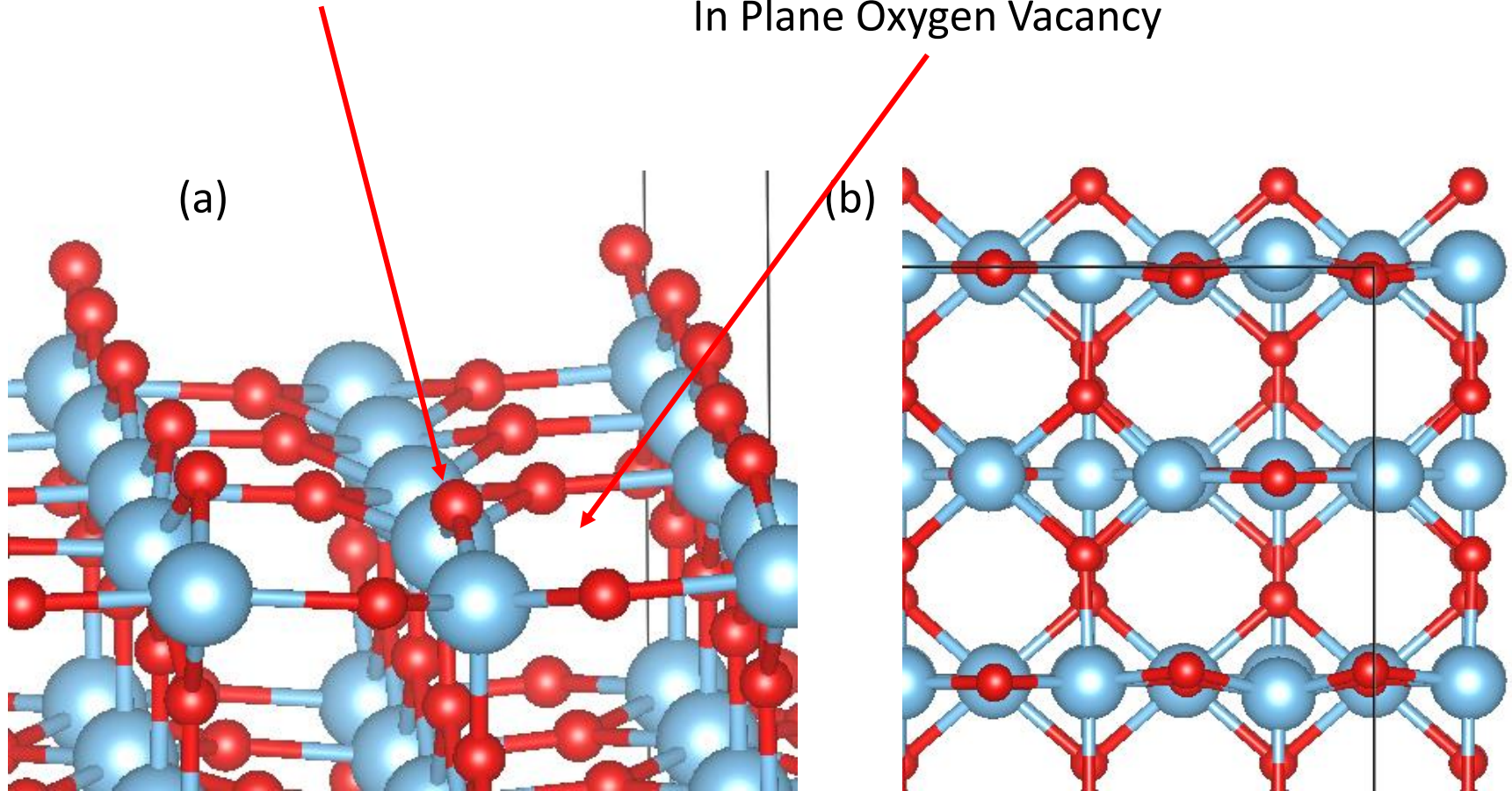


紫色：桥氧空位表面自旋向上电子。绿色：桥氧空位表面自旋向下电子。 $E_{\text{fermi}} = -0.5647$  eV

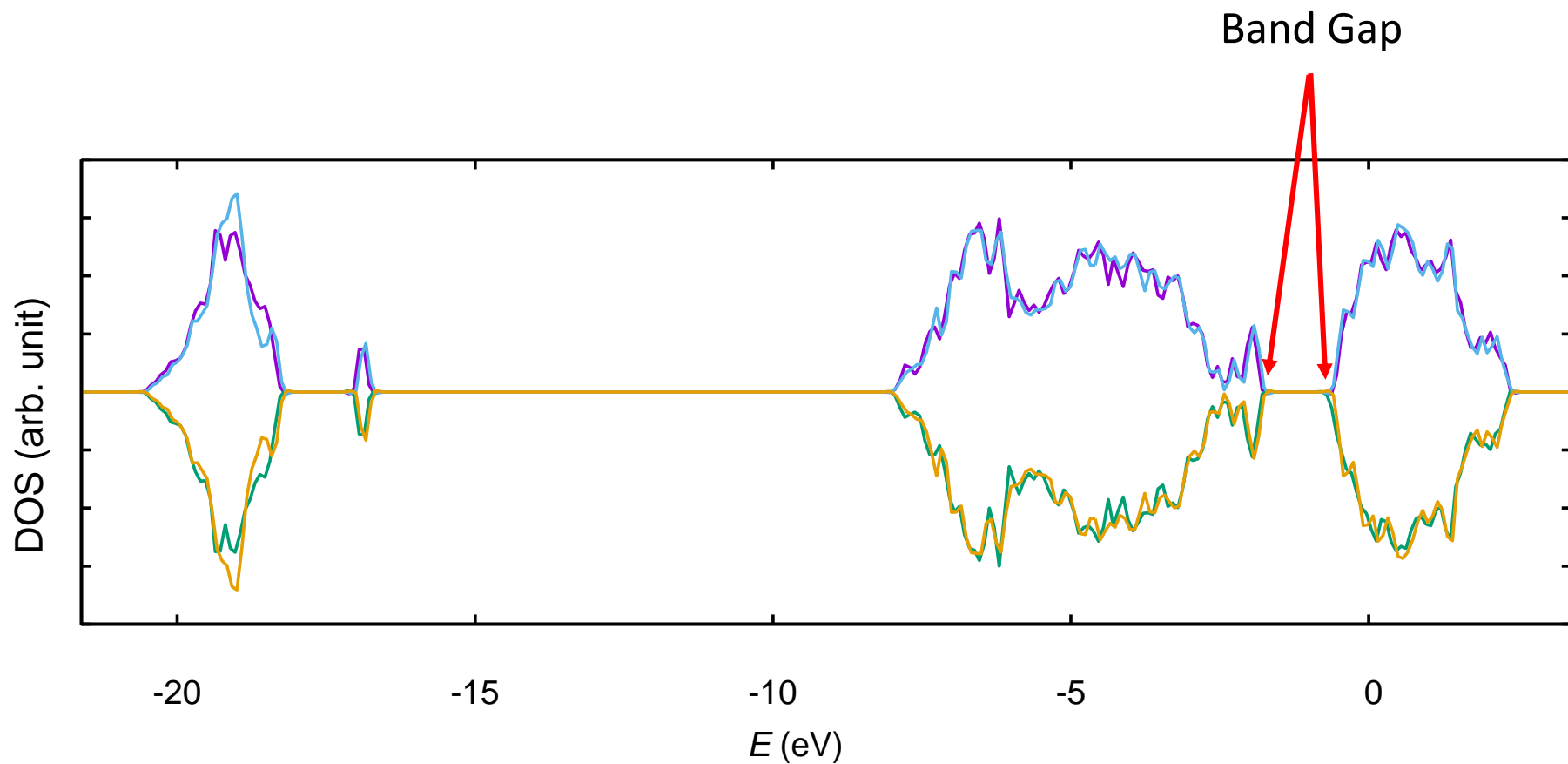
蓝色：化学计量比表面自旋向上电子。黄色：化学计量比表面自旋向下电子。 $E_{\text{fermi}} = -1.927$  eV



# In Plane Oxygen Vacancy



Ti – Ti length 3.379 Å

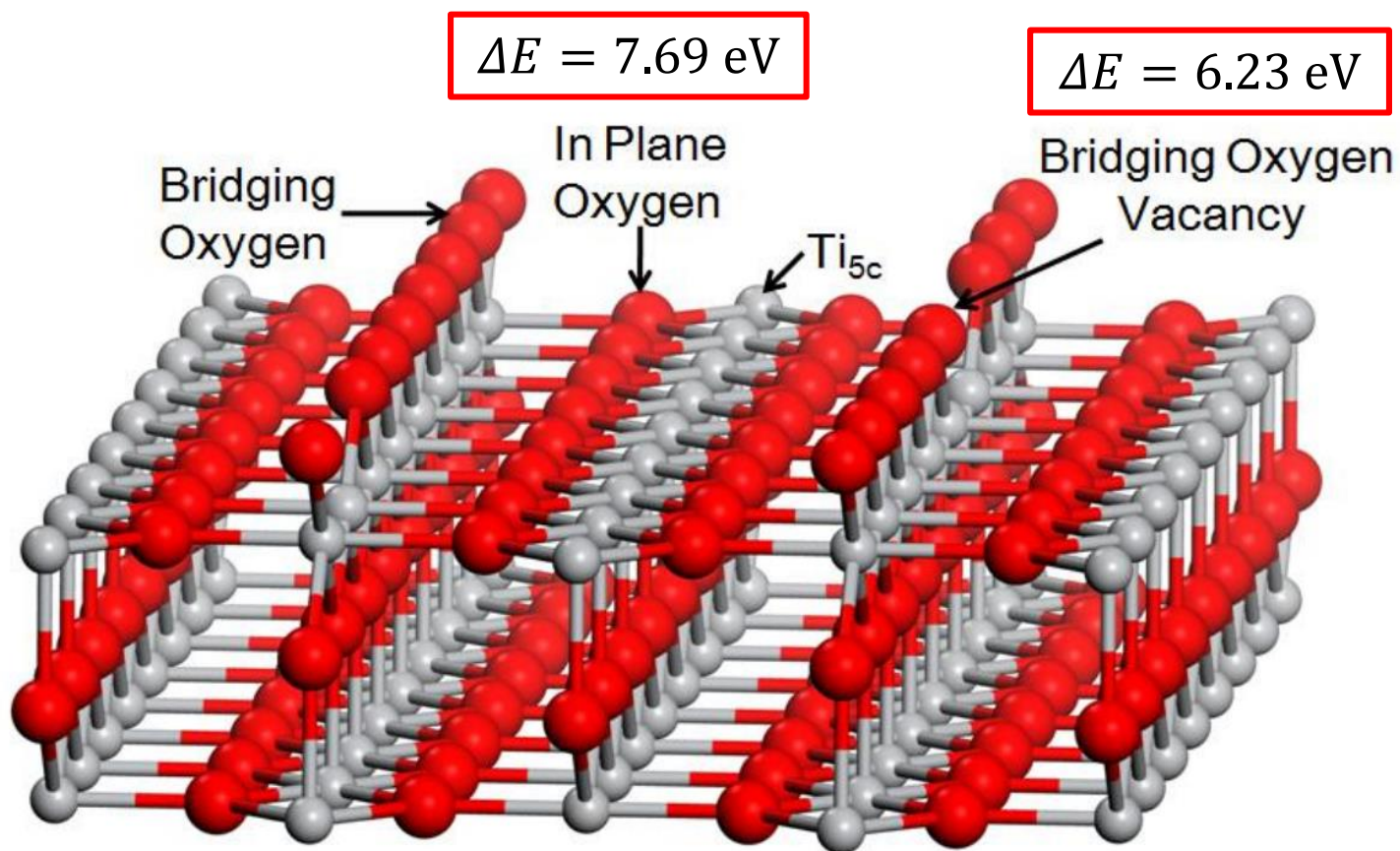


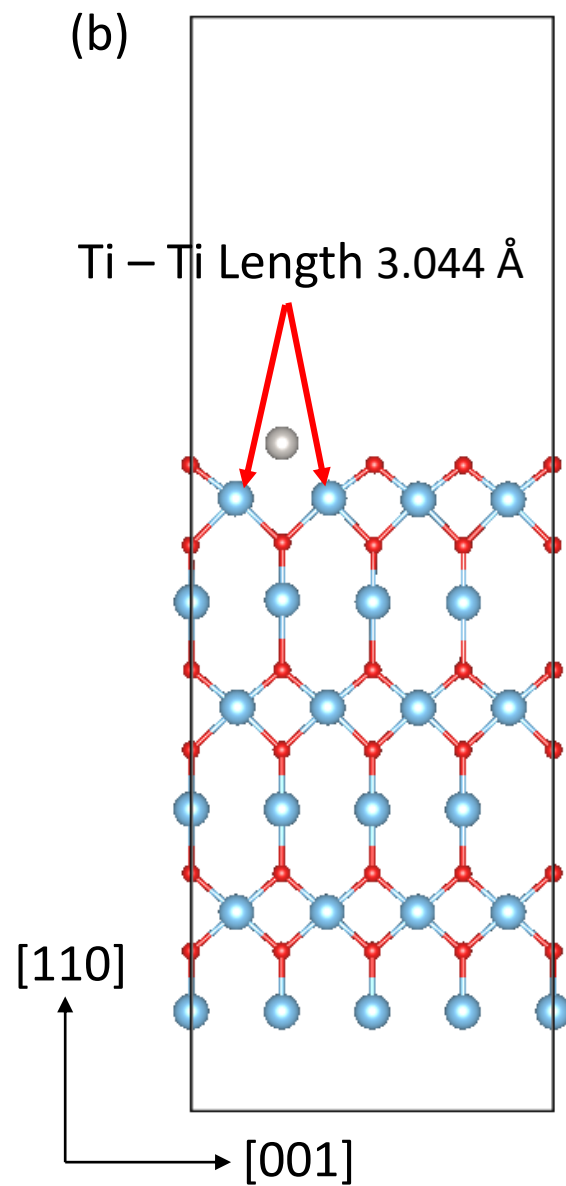
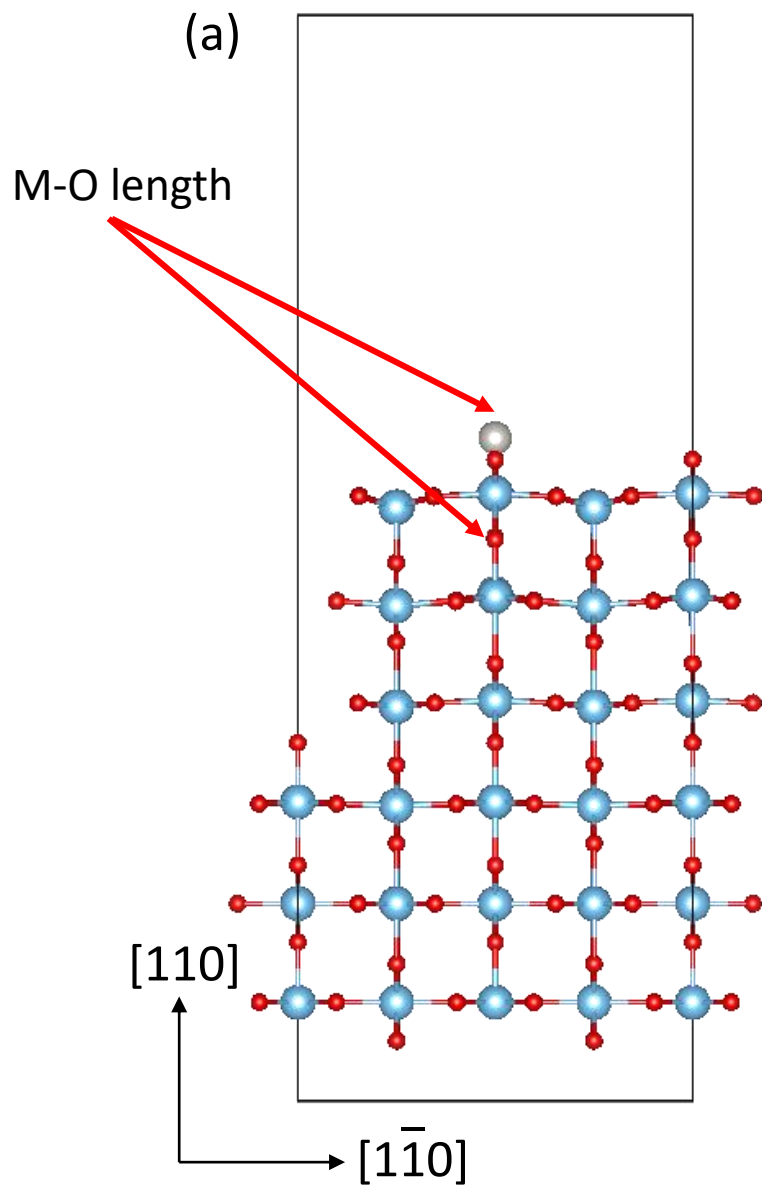
紫色：基层氧空位表面自旋向上电子。绿色：基层氧空位表面自旋向下电子。 $E_{\text{fermi}} = -0.6038$  eV

蓝色：桥氧空位表面自旋向上电子。黄色：桥氧空位表面自旋向下电子。 $E_{\text{fermi}} = -0.5647$  eV



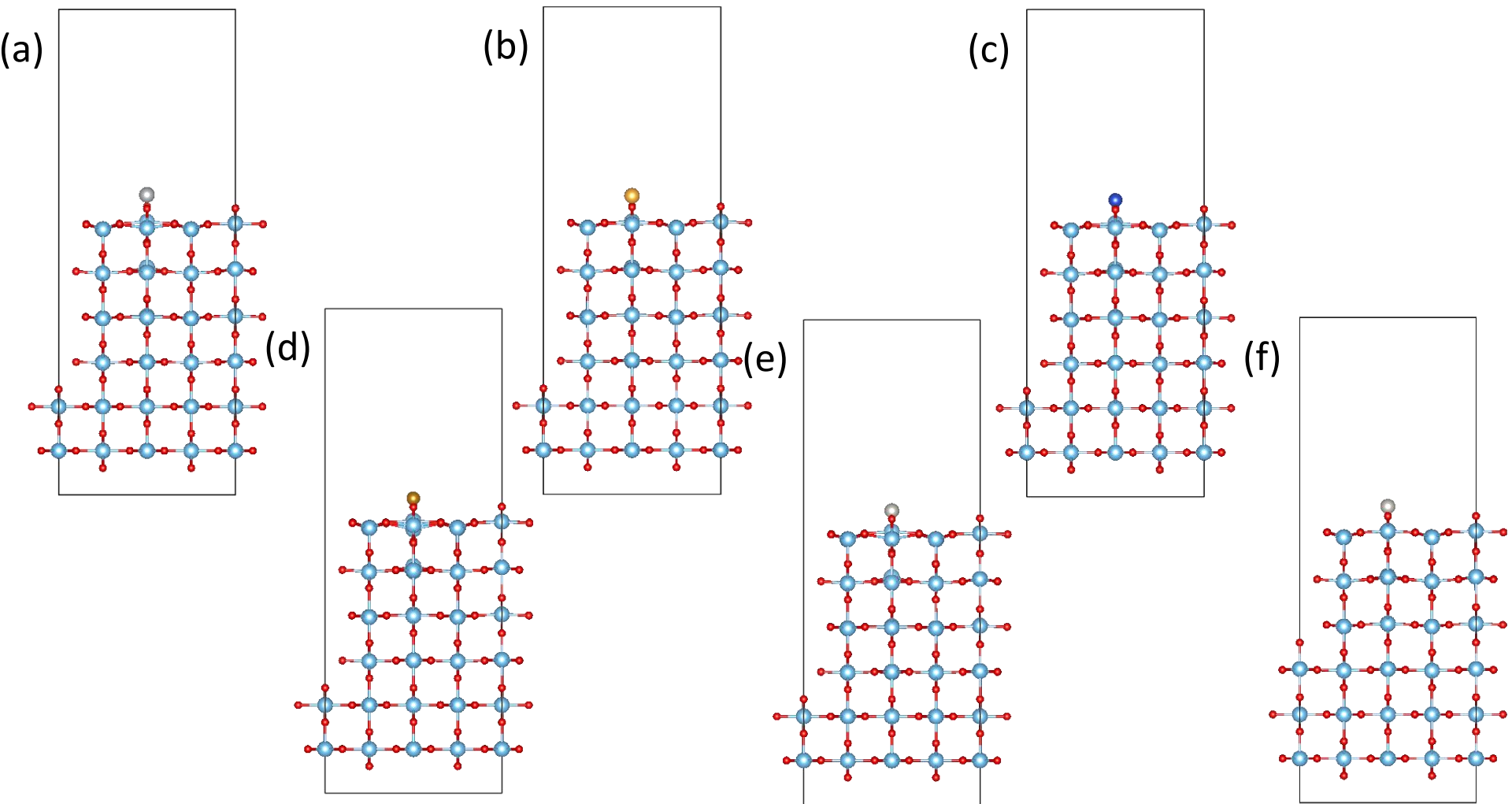
## 还原性表面





Pt在桥氧空位表面的吸附

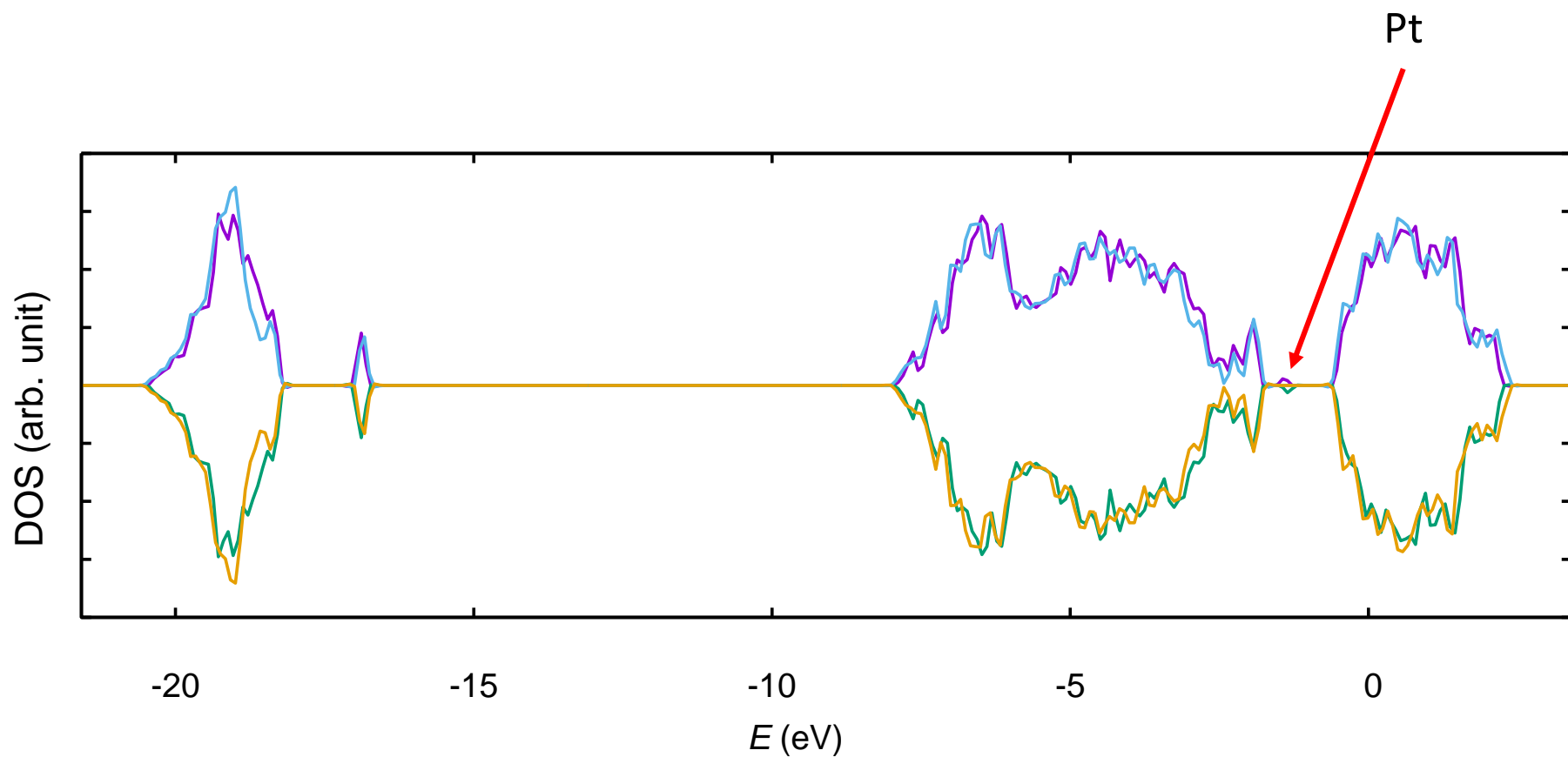
# 桥氧空位表面吸附



(a) : Ag, (b) : Au, (c) : Cu, (d) : Fe, (e) : Pd, (f) : Pt

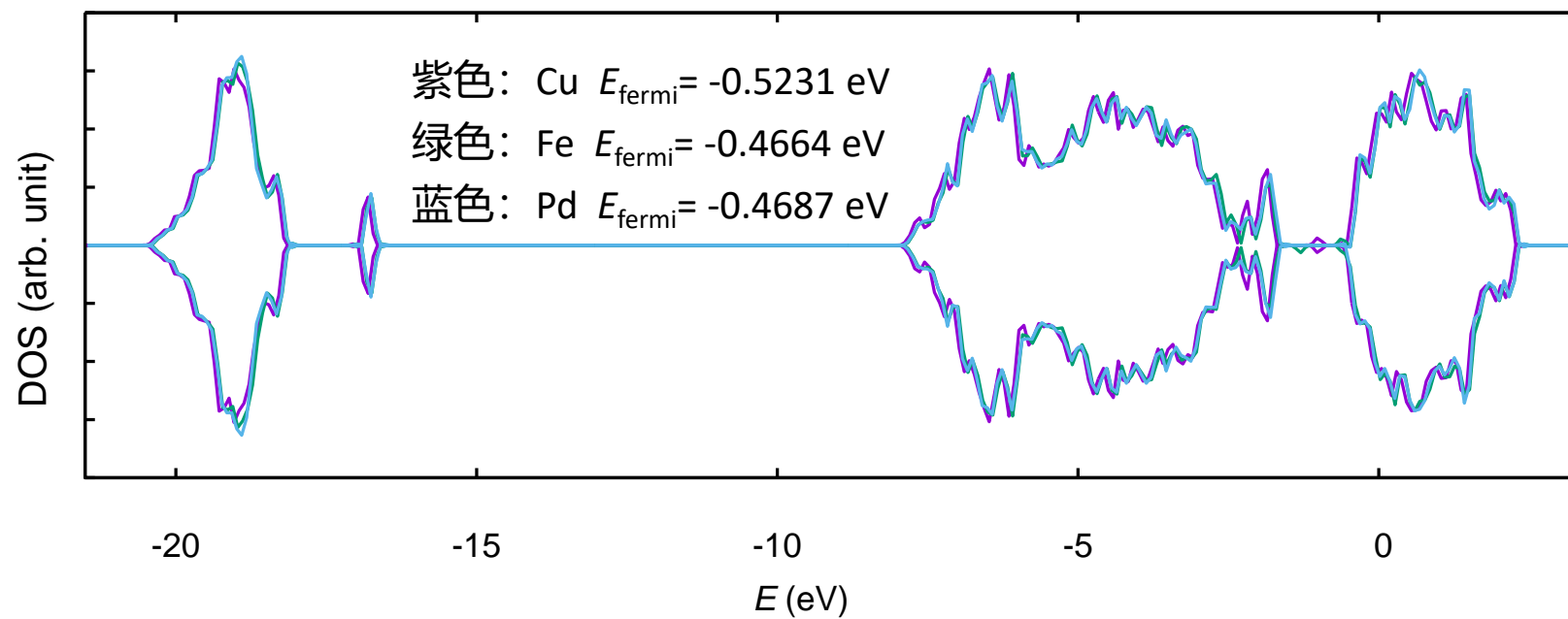
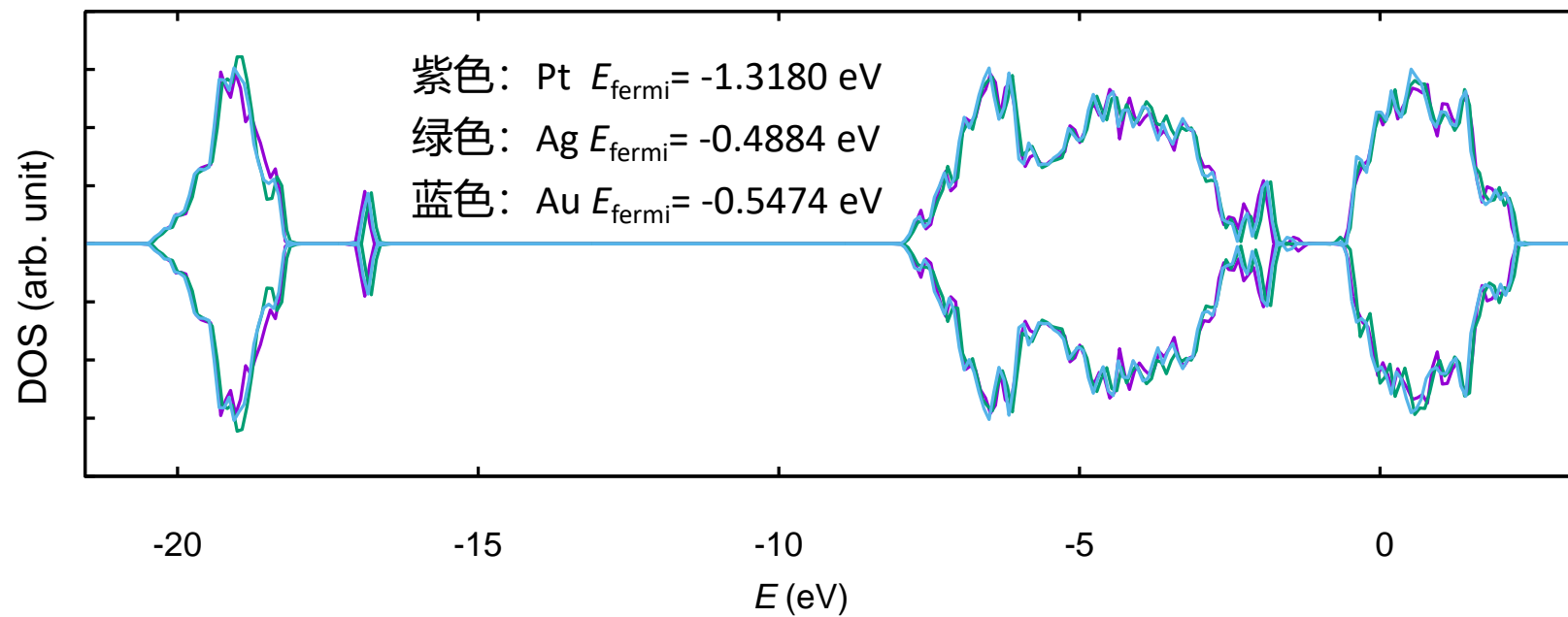
# 桥氧空位表面吸附

	Ag	Au	Cu	Fe	Pd	Pt
$\Delta E$ (eV)	-1.8149	-2.8867	-2.3634	-2.8560	-2.6997	-4.6519
Ti-Ti length	3.2376	3.2427	3.1540	3.1494	3.2263	3.0444
M-O length	3.5342	3.3652	3.2682	3.4909	3.1867	3.2471



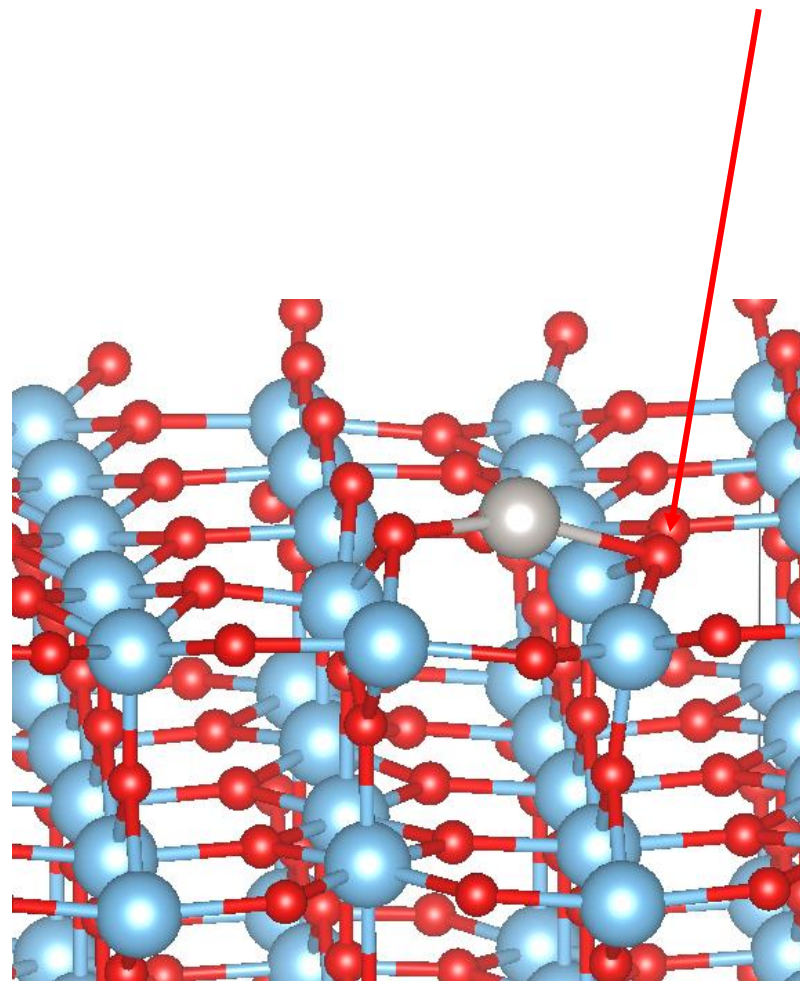
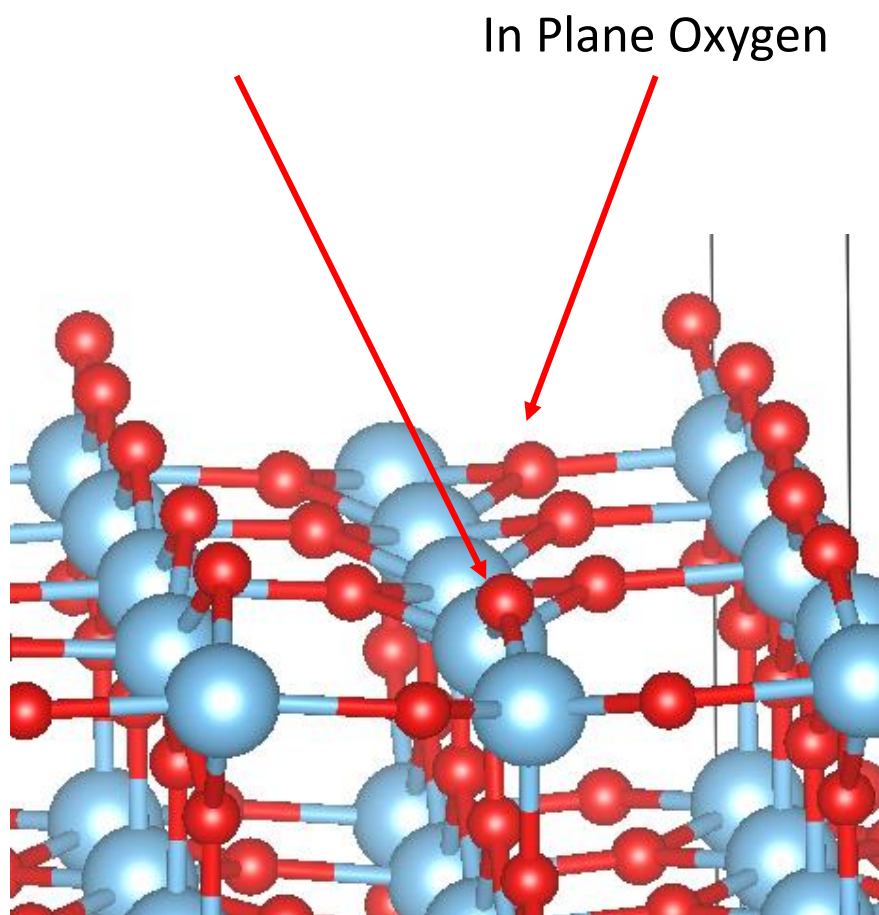
紫色：Pt原子吸附表面自旋向上电子。绿色：Pt原子吸附表面自旋向下电子。  $E_{\text{fermi}} = -1.3180$  eV

蓝色：桥氧空位表面自旋向上电子。黄色：桥氧空位表面自旋向下电子。  $E_{\text{fermi}} = -0.5647$  eV



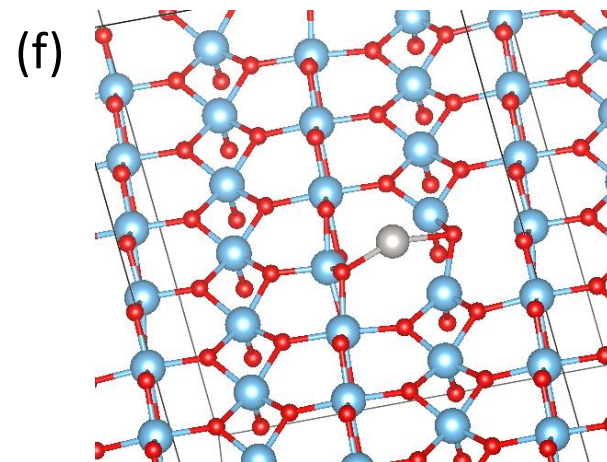
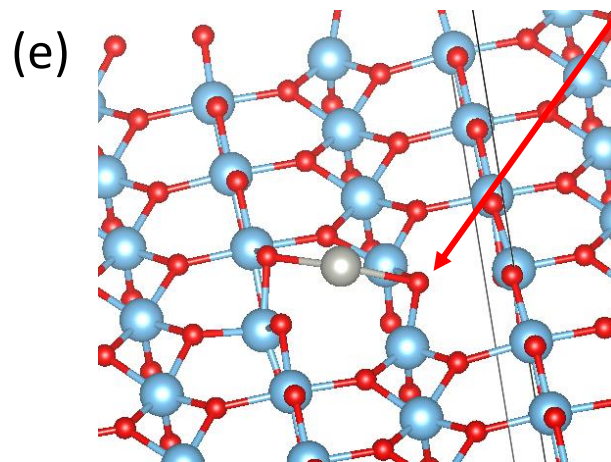
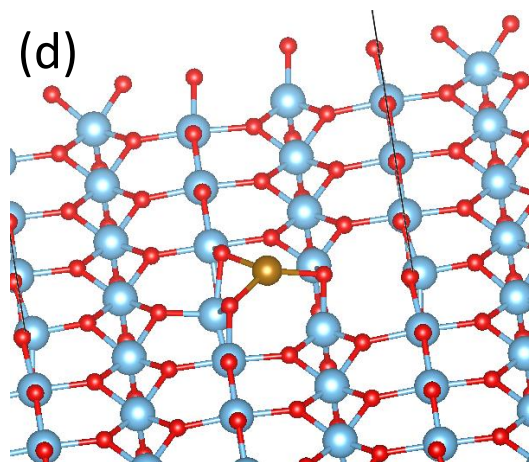
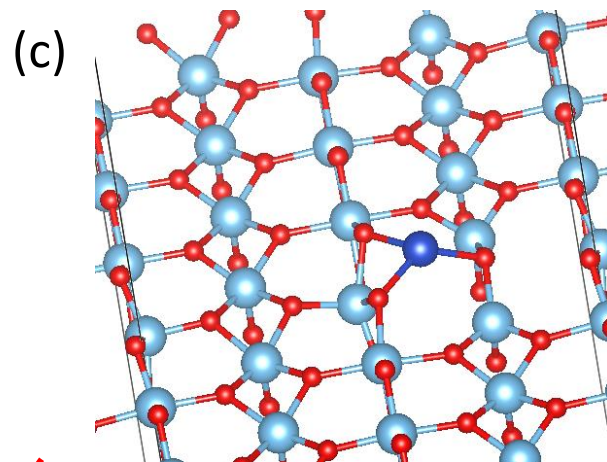
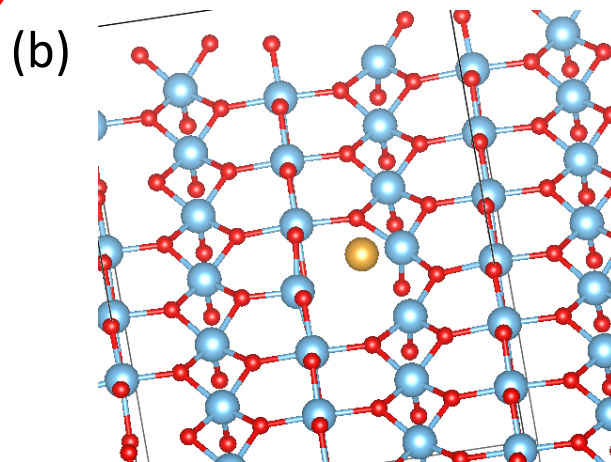
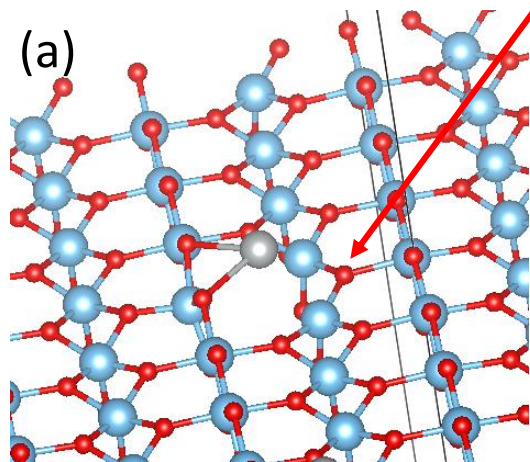
## 面氧空位表面吸附

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# 面氧空位表面吸附



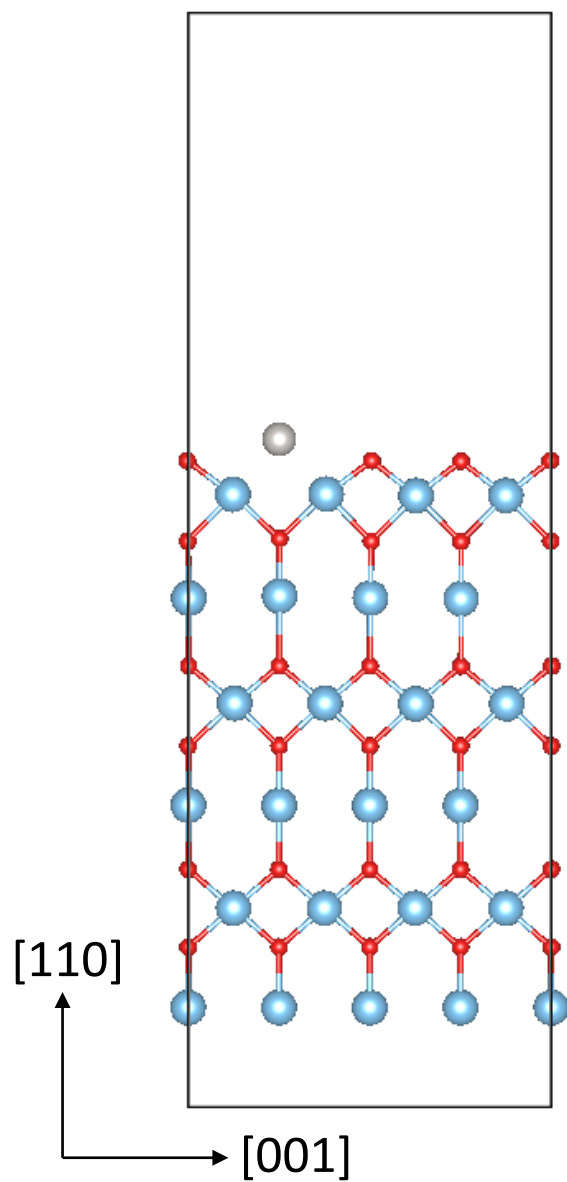
(a) : Ag, (b) : Au, (c) : Cu, (d) : Fe, (e) : Pd, (f) : Pt



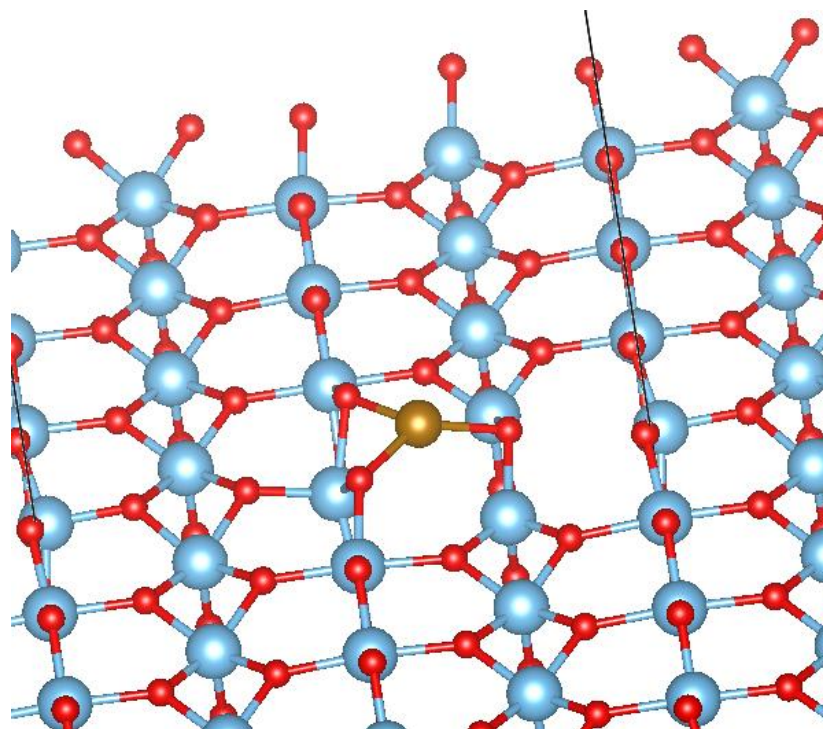
# 还原性表面吸附

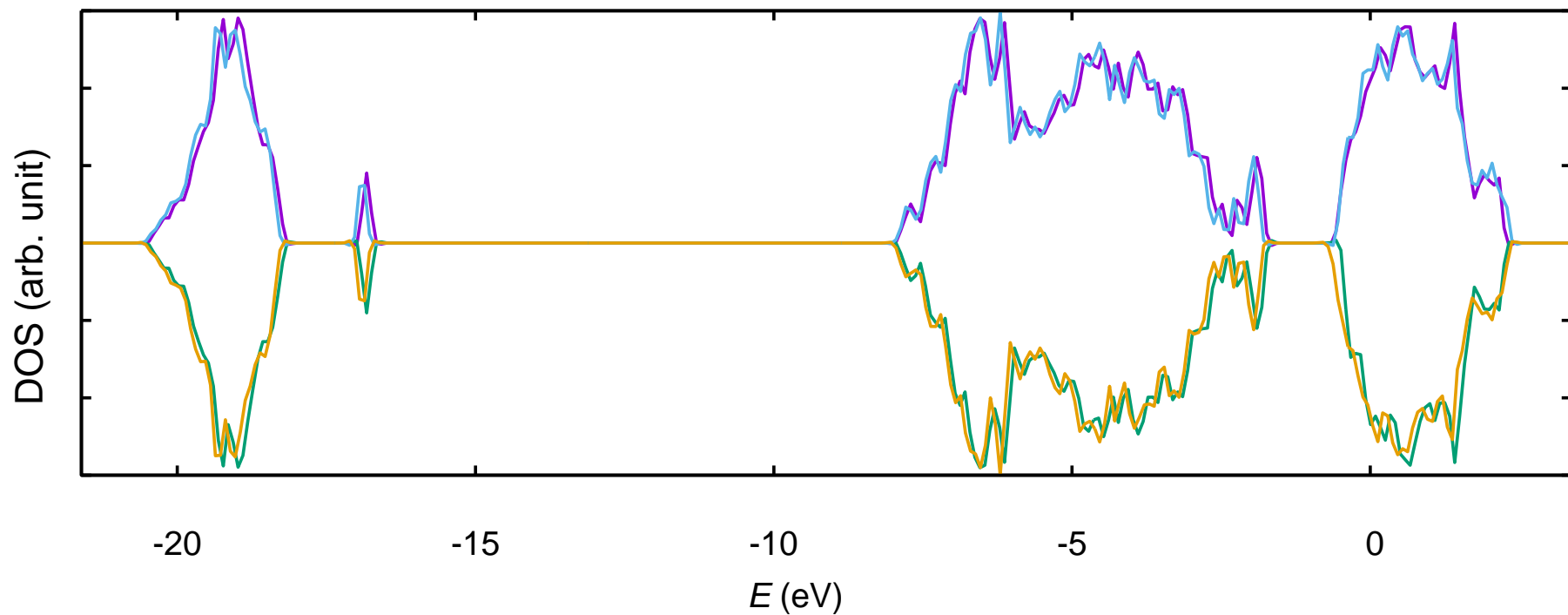
$\Delta E$ (eV)	Ag	Au	Cu	Fe	Pd	Pt
Bridge Oxygen Vacancy	-1.8149	-2.8867	-2.3634	-2.8560	-2.6997	-4.6519
In Plane Oxygen Vacancy	-1.1882	-2.0766	-2.1562	-3.6175	-2.6316	-3.9674

桥氧空位吸附



面氧空位吸附

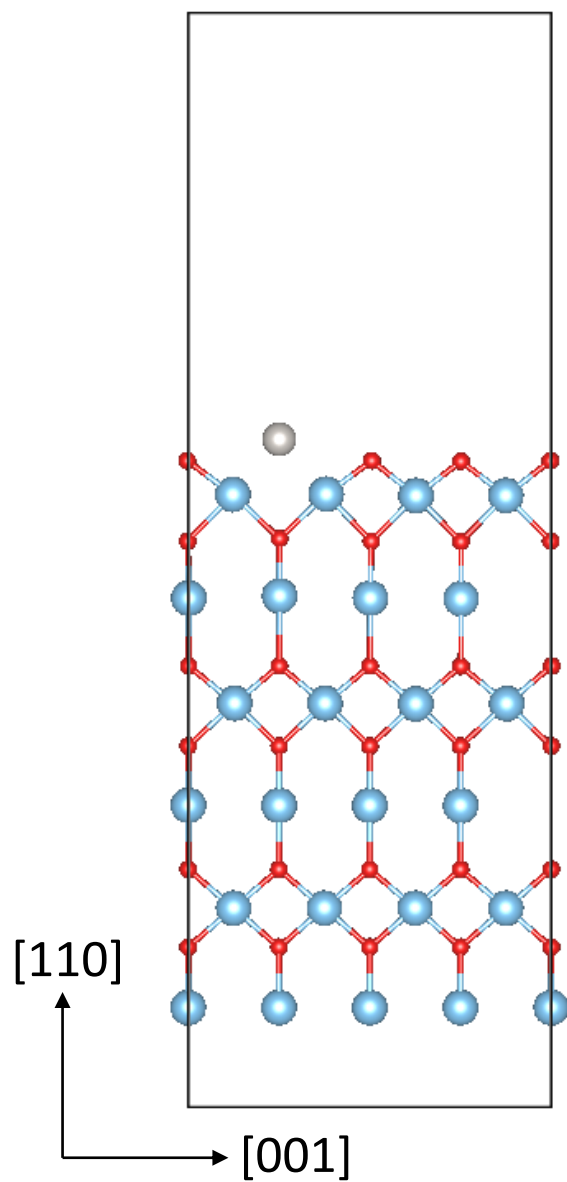




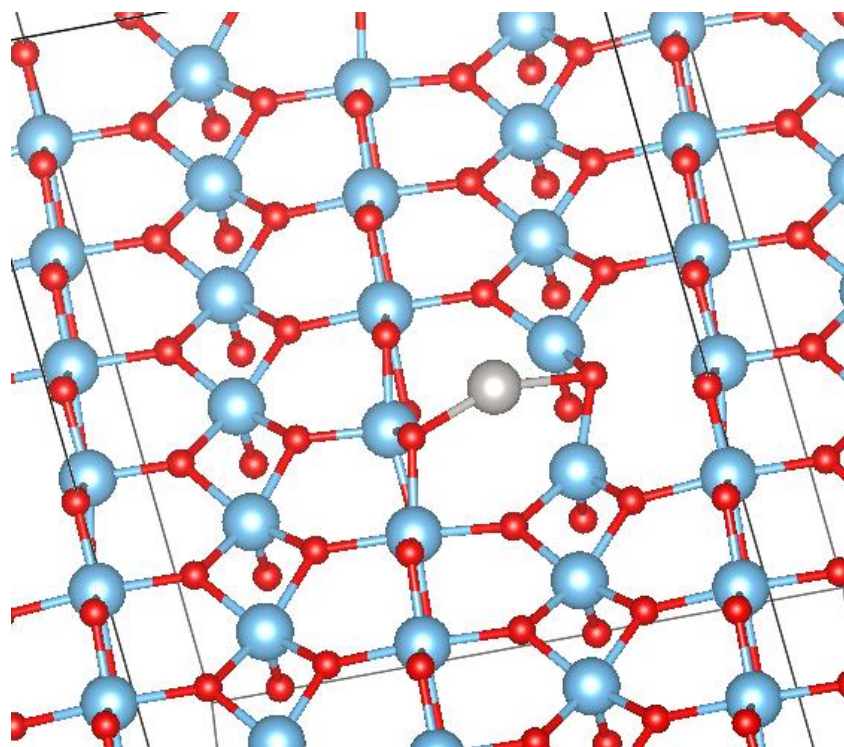
紫色：Pt原子吸附表面自旋向上电子。绿色：Pt原子吸附表面自旋向下电子。 $E_{\text{fermi}} = -0.5270$  eV

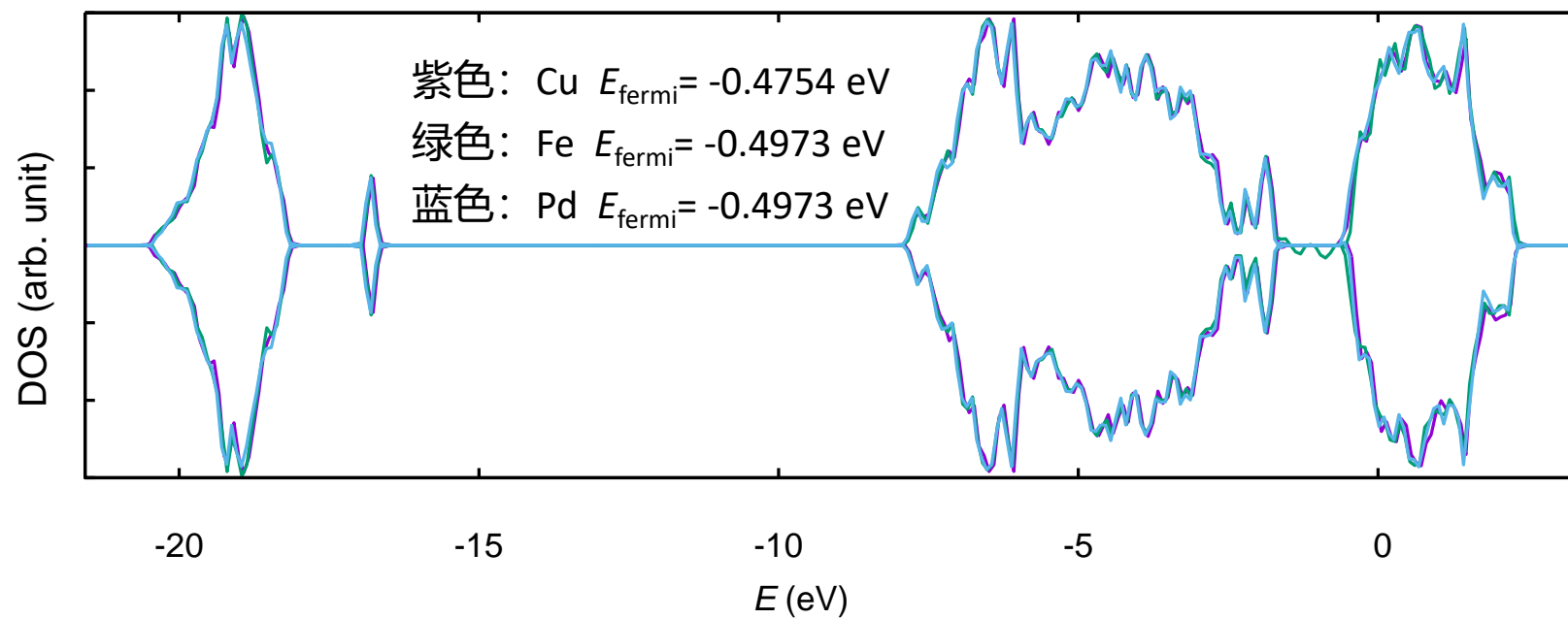
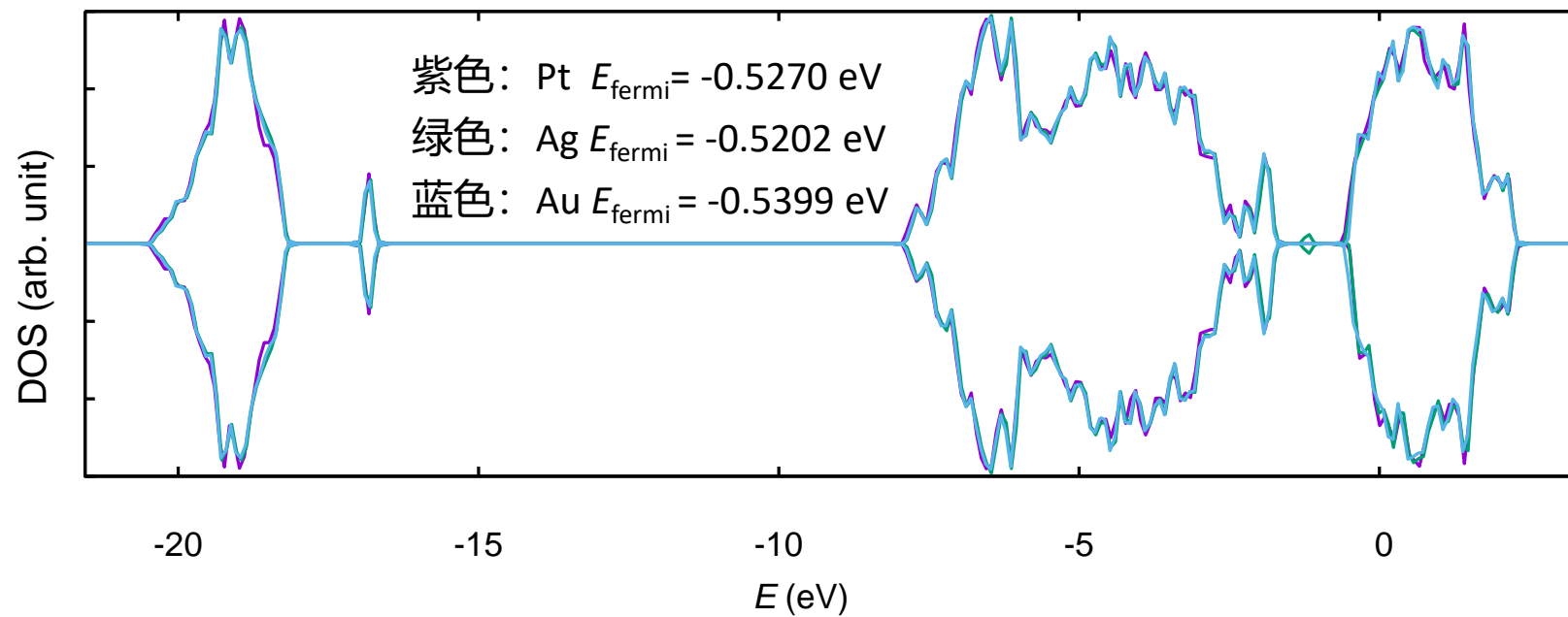
蓝色：面氧空位表面自旋向上电子。黄色：面氧空位表面自旋向下电子。 $E_{\text{fermi}} = -0.6038$  eV

桥氧空位吸附

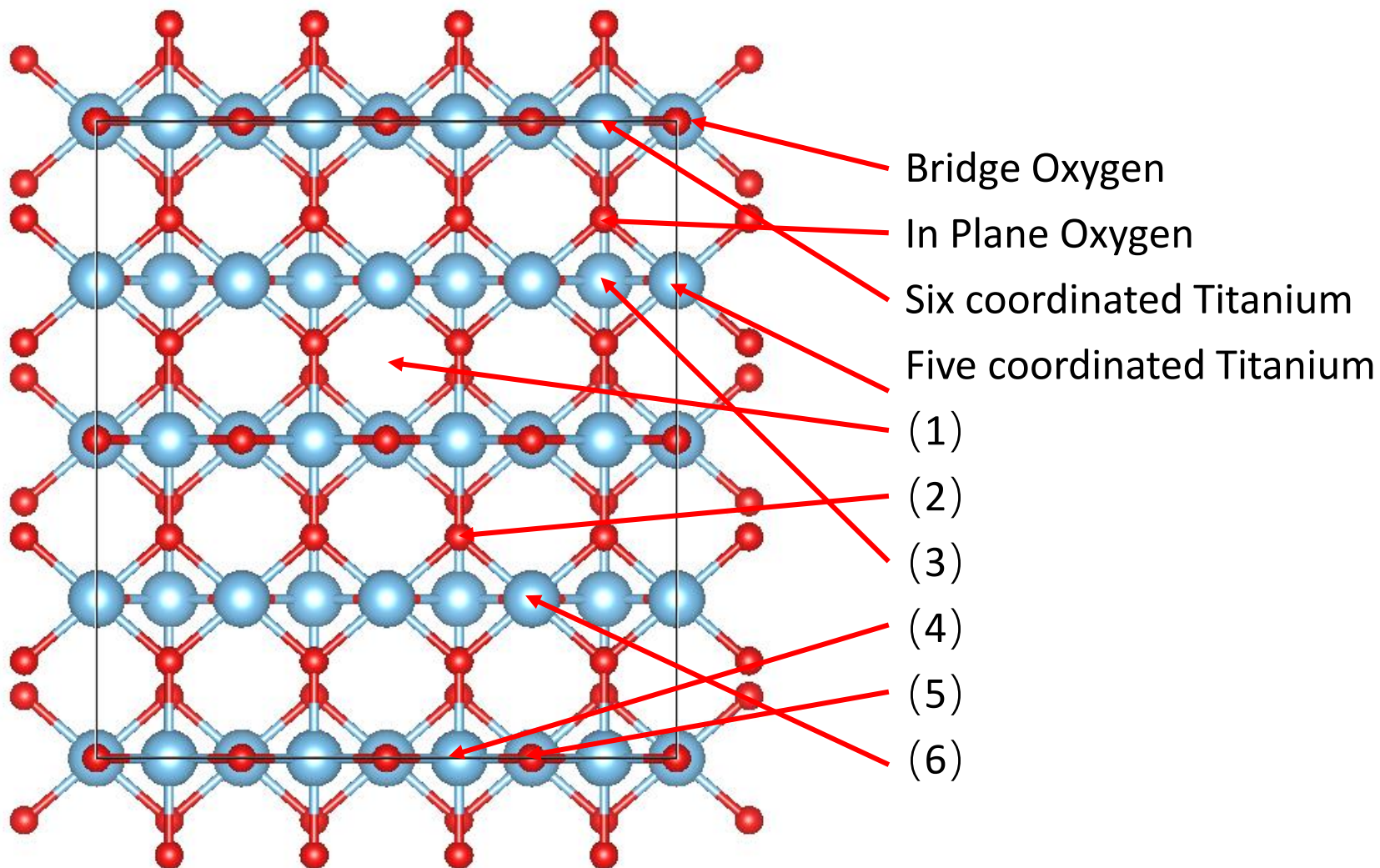


面氧空位吸附





# 化学计量比表面吸附

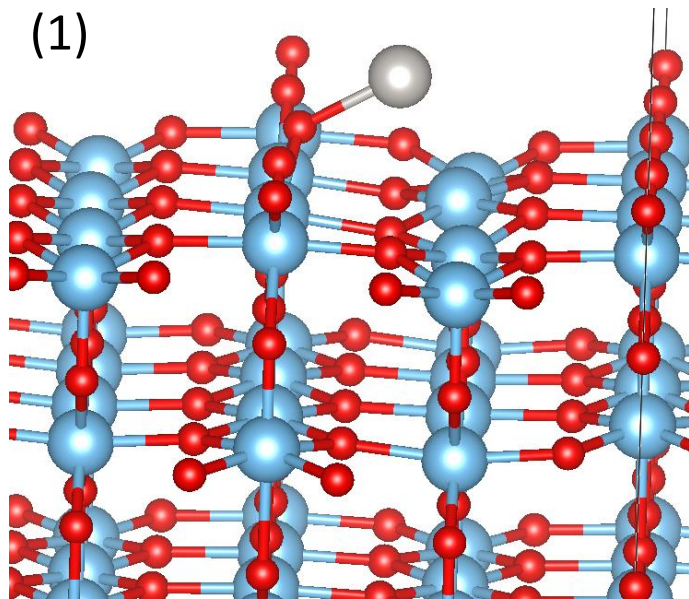


# 化学计量比表面吸附

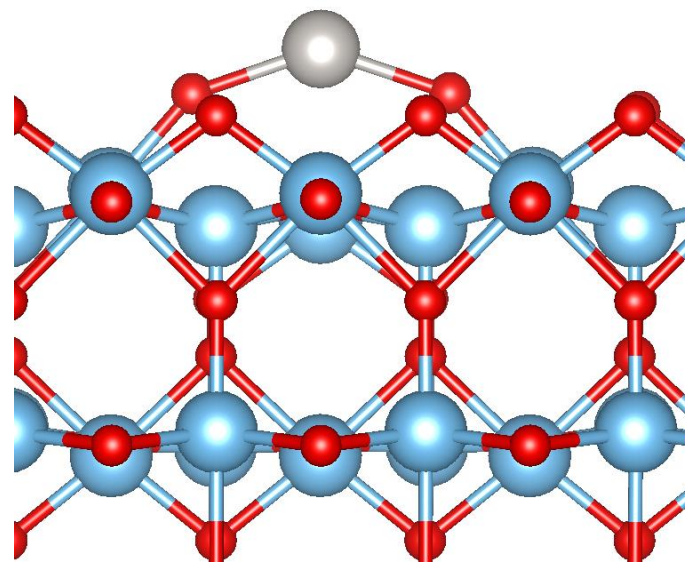
Adsorption Sites	1	2	3	4	5	6
Initial Structure	H1	topOba	H2	Ti6c	topObr	Ti5c
$\Delta E$ Cu	-1.35237	-	-0.71101	-1.92568	-1.26904	-0.4997
$\Delta E$ Pt	-2.47735	-	-	-2.23641	-1.70688	-1.37589



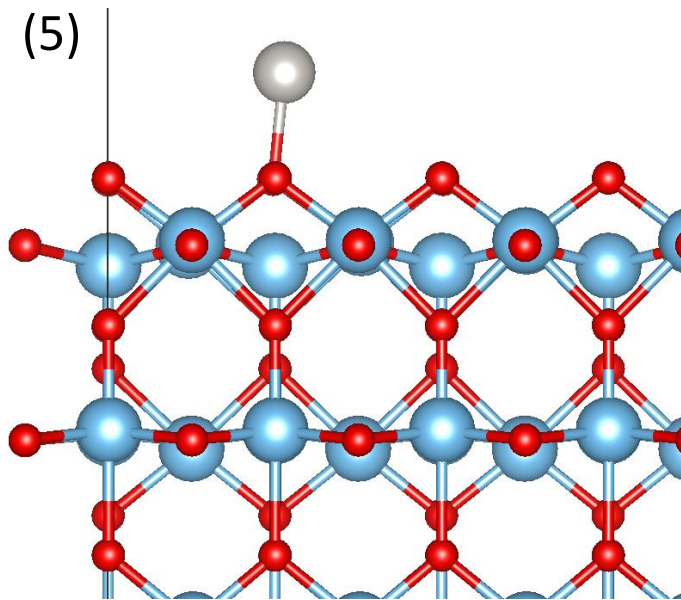
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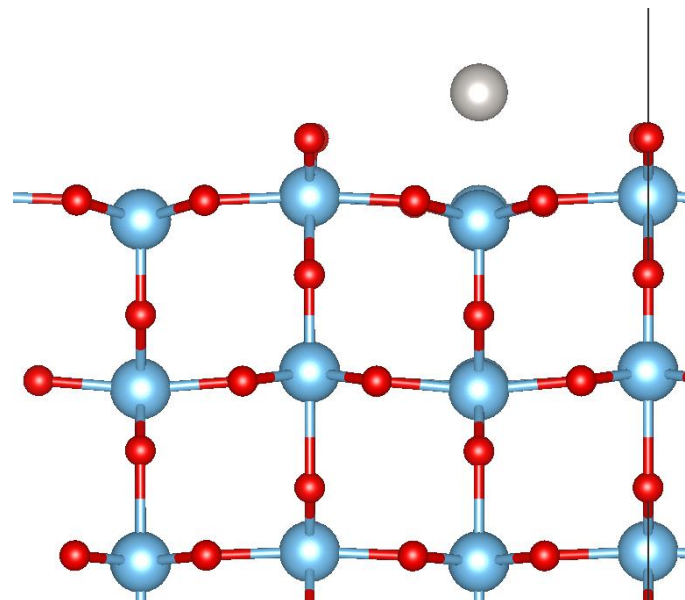
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(5)

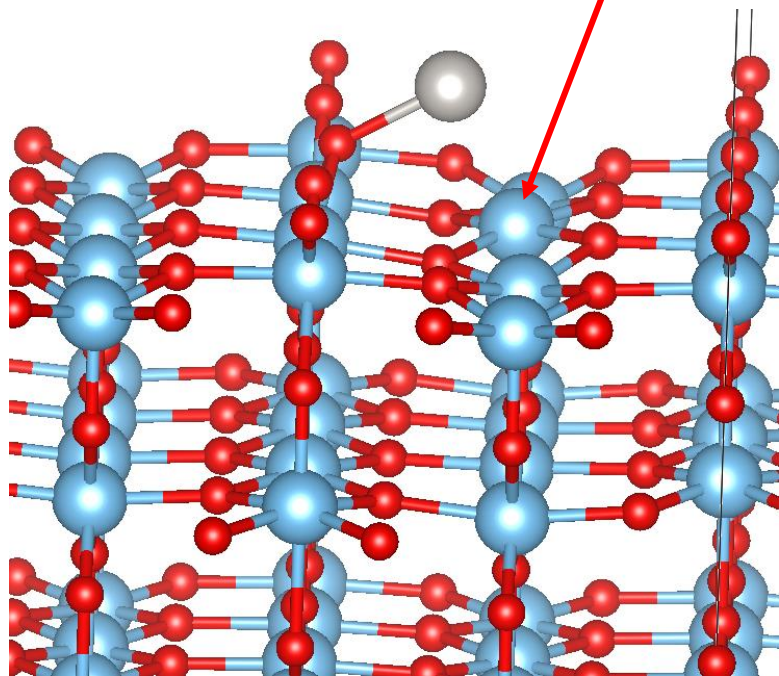


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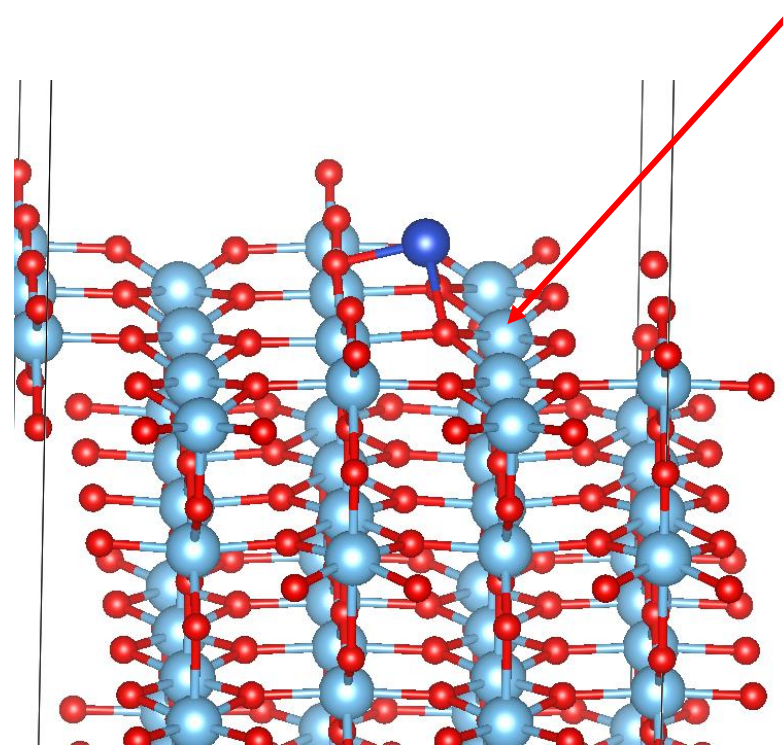




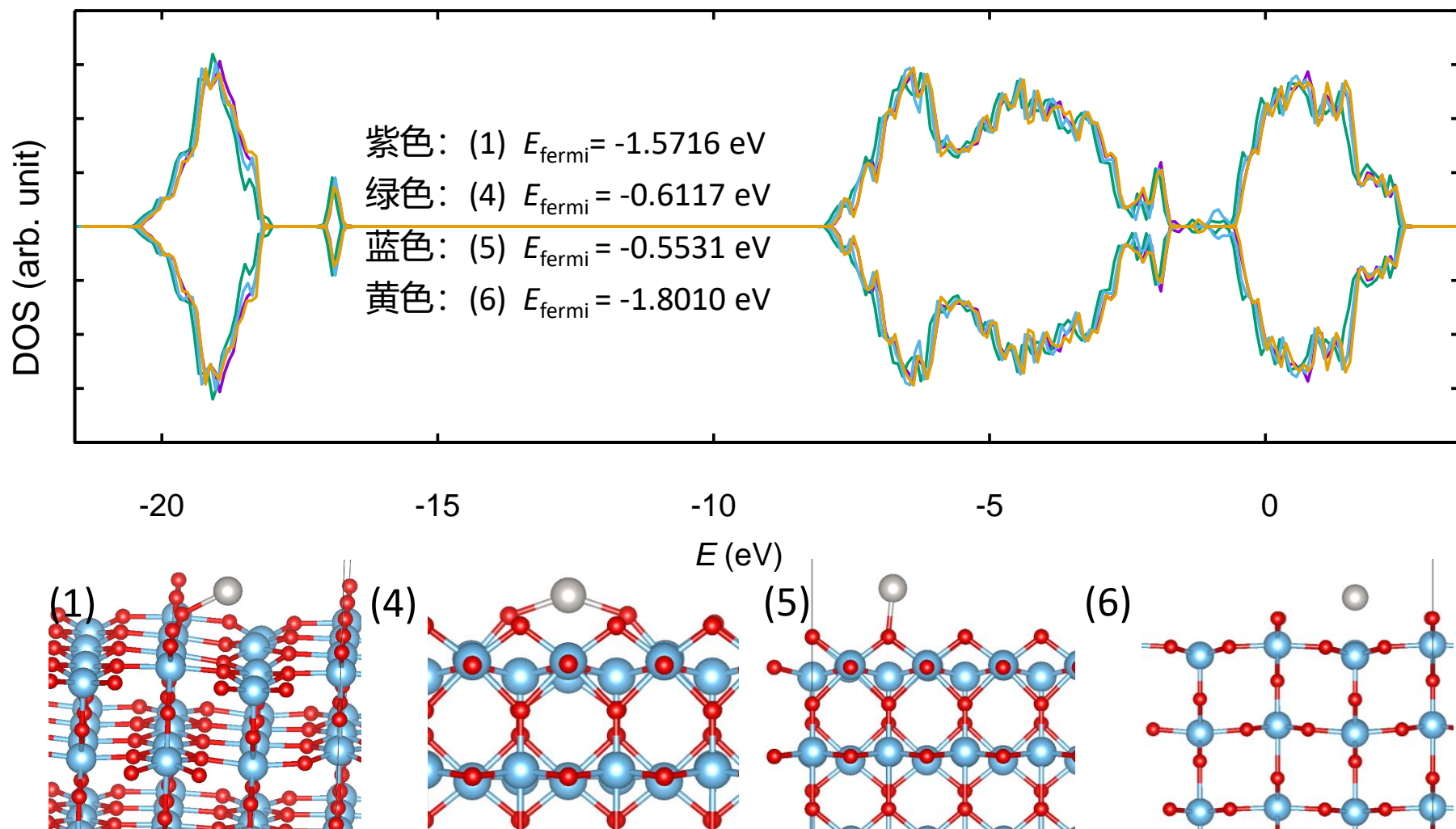
Pt吸附在化学计量比表面1号位置



Cu吸附在化学计量比表面1号位置



# Pt化学计量比表面吸附



THANK

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