生成润滑添加剂抗磨损膜的摩擦化学反应量子化学模拟

Mechanochemical Reactive Simulation of lubricant Additive Antiwear Film Formation by Quantum Chemics

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目录 Content

动机 Motivation

- 润滑抗磨添加剂用于控制摩擦部件的磨损以满足对发动机耐久性的需求

Lubricant antiwear additives are used to control the wear of rubbing parts and thus provide acceptable engine durability.

- 强化与柴油机排放法规有关的环保法规和研发替代抗磨添加剂的需求

Heightened environmental regulations relating to diesel emission regulations and interest in the development of alternative antiwear additives.

- 滑动接触时的多重因素，如热、剪切力和径向载荷，被认为是加速润滑添加剂抗磨损膜的生成

lubricant additive antiwear film formation is believed to be accelerated by multiple factors such as heat, load, and shear force in a sliding contact.

- 受限于试验方面无法观察到基本的摩擦化学反应途径，这些因素的各自贡献还不能完全理解

The individual contributions of these factors are not fully understood because the elementary reaction pathways cannot readily be observed experimentally.

- 量子尺度模拟能获取生成抗磨损膜的摩擦化学反应途径

The use of simulations at the quantum scale can capture reaction pathways leading to film formation.

方法 Methods

- 添加剂抗磨损膜的生成过程 Additive antiwear film formation progress

  异构化、分解、吸附、脱附、氧化、恢复、聚合反应

  isomerization, decomposition, adsorption, desorption, oxidation, restortion, and polymerization reactions

- 第一性原理的密度泛函理论及计算软件Materials Studio的DMol^3 模块

  First principles DFT and Materials Studio DMol^3 software

- 吸附能计算式 Adsorption energy formula

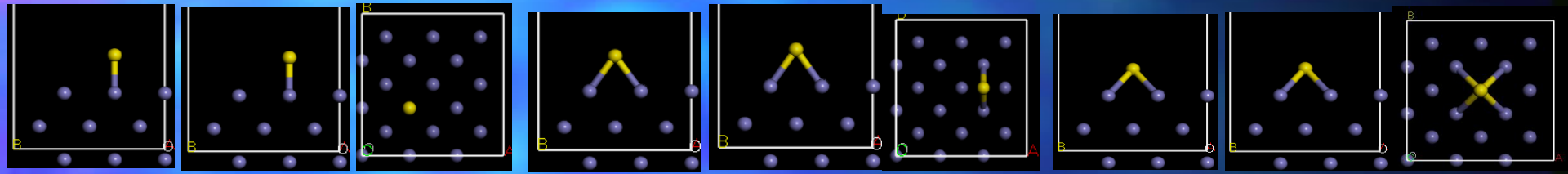
$$E_{ads} = E_{surface} + E_{adsorbate} - E_{total}$$

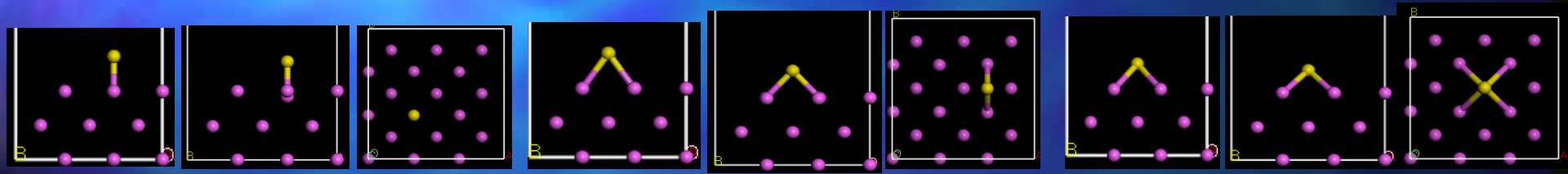
$E_{surface}$: 基底表面的总能 total energy of fundus surface; $E_{adsorbate}$: 自由吸附物在气相中的总能 total energy of free adsorbate in gas phase; E_{total} : 吸附物与基底表面的总能 total energy of free adsorbate & fundus surface

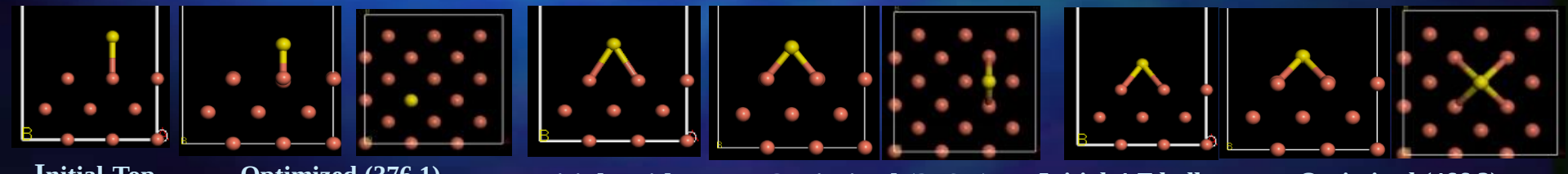
- 吸附能计算式 Adsorption energy formula

结果1 - 气相环境中S原子在Fe(100)、Al(100)和Cu(100)面的吸附构型和吸附能。黄色 - S，棕褐色 - Fe，橘黄色 - Cu，粉红色 - Al，括号内值是吸附能（单位：kJ·mol^{-1}）

Results 1 - Optimized adsorption configurations and energies of S atom on Fe(100) , Al(100) , Cu(100) surfaces in gas phase. Yellow - S, brown - Fe, orange - Cu, and pink - Al. Value in parenthesis is adsorption energy (unit: kJ·mol^{-1})







结果1的讨论 Discussion for results 1

- S原子吸附在 Top、Bridge或4F hollow位时，优化后还在Top、Bridge或4F hollow位置

  For S atom initially adsorpted at top, bridge and 4F hollow positions, optimized adsorption positions keep the same sites

- S原子在Top位的吸附能小于在Bridge和4F hollow位，S原子吸附在Top位最不稳定

  S adsorption energies are smallest in top, S is the most unstable at the top site

- S原子在Fe(100)面的吸附能比Cu(100)和Al(100)都大，S原子更易吸附在Fe(100)面

  S adsorption energies are biggest on Fe(100) surfaces, S is more easily adsorbed on the Fe(100) surfaces

- S原子在Cu(100)面的吸附能最小，在Fe(100)面的吸附能最大。相应的最稳定的吸附表面的顺序是：Fe(100)面、Al(100)面、Cu(100)面

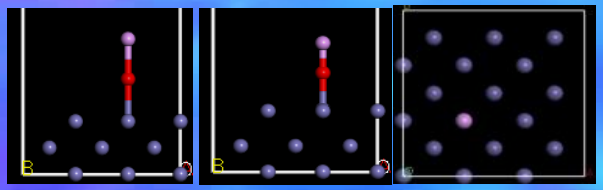
  S adsorption energies are smallest on Cu(100), biggest on Fe(100) surfaces, corresponding to the most stable adsorption surface order: Fe(100), Al(100), Cu(100)

- 结构优化后的键长伸长

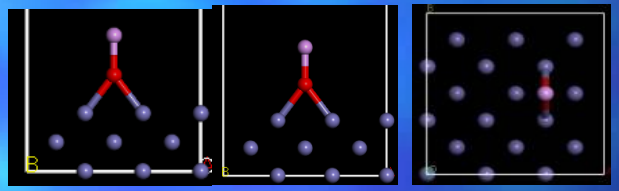
  Bond lengthes are longer after adsorption (optimized structures)

结果2 - 气相环境中PO 分子在Fe(100)、Al(100)和Cu(100)面的吸附构型和吸附能。黄色 - S，棕褐色 - Fe，橘黄色 - Cu，粉红色 - Al，括号内值是吸附能（单位：unit: kJ·mol^{-1}）

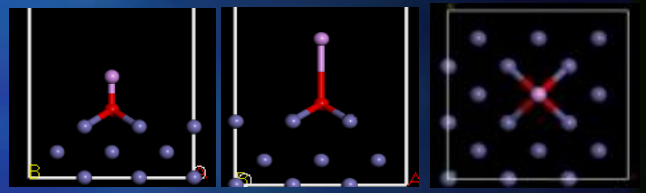
Results 2 - Optimized adsorption configurations and energies (unit: kJ·mol^{-1}) of PO molecule at top, bridge, and hollow sites on Fe(100) , Al(100) and Cu(100) surfaces in gas phase. Red - O, cmyk - P, brown - Fe, orange - Cu, pink - Al.



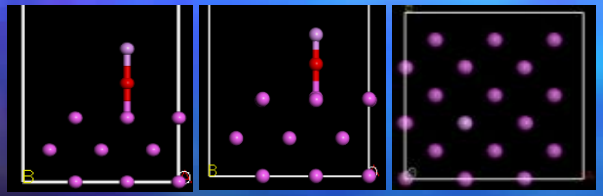
Initial-Top Optimized (283.65)



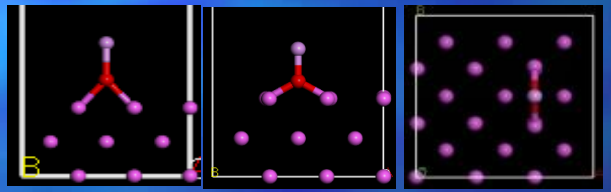
Initial-Bridge Optimized (4963.32)



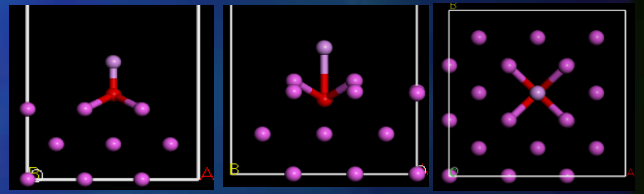
Initial-4F hollow Optimized (10035.6)



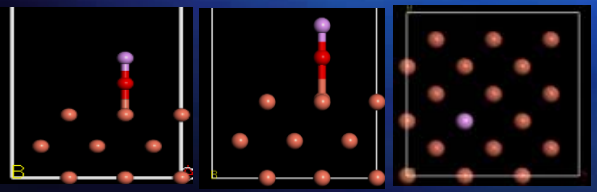
Initial-Top Optimized (279.5)



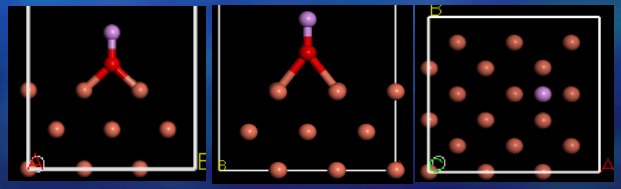
Initial-Bridge Optimized (-23.8)



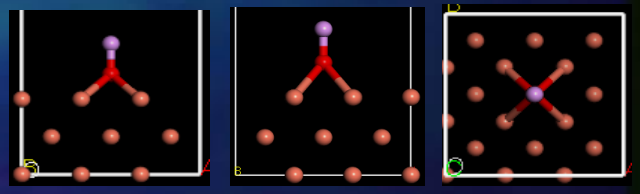
Initial-4-F hollow Optimized (107.8)



Initial-Top Optimized (-44.8)



Initial-Bridge Optimized (-49.6)



Initial-4-F hollow Optimized (-59.3)

结果2的讨论 Discussion for results 2

- PO 分子初始以Fe-O-P 180^{0}夹角吸附在Fe(100) 面的top, bridge和4-F hollow位置时，优化后PO 分子还是以Fe-O-P 180^{0}夹角吸附在原来的位置

  For PO molecule initially adsorpted at top, bridge and 4-F hollow positions on Fe(100) surface in Fe-O-P 180^0 angle, optimized positions keep the same sites and angle

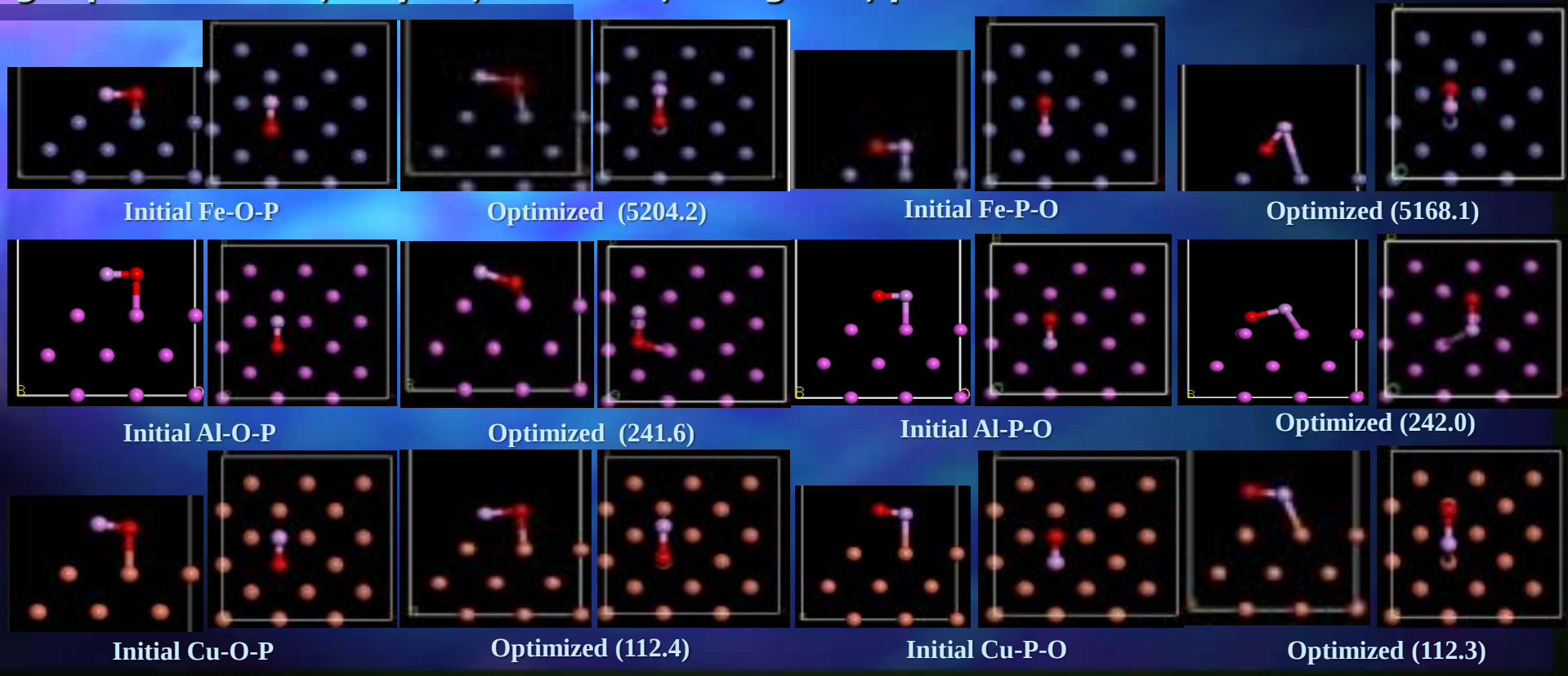
- 对Fe(100) 面，PO 分子的吸附能(正值)在top位置时最小，在4-F hollow位置时最大，相应的最稳定的位置顺序是：hollow, bridge, top

  For Fe(100) surface, PO adsorption energy (positive value) is smallest at top position, biggest in 4-F hollow position, corresponding to the most stable adsorption site order: hollow, bridge, top

- PO 分子初始吸附在Al(100)面的top, bridge和4-F hollow位置时，优化后PO 分子在bridge位置的吸附状态不稳定。PO 分子初始吸附在Cu(100)面时，优化后PO 分子在Cu(100)面的吸附状态很不稳定

结果3 - 气相环境中PO 分子以相同的初始角度在top位置的Fe(100)、Al(100)和Cu(100)面的吸附构型 和 吸附能。黄色-S ， 棕褐色-Fe，橘黄色-Cu，粉红色-Al，括号内值是吸附能（kJ·mol^{-1}）

Results 3 - Optimized adsorption configurations and energies (unit: kJ·mol^{-1}) of PO molecular at top sites on Fe, Al and Cu(100) surfaces with same initial angle in gas phase. Red-O, cmyk-P, brown-Fe, orange-Cu, pink-Al



结果3的讨论 Discussion for results 3

- 吸附在Fe(100) 面的top位置时，吸附能在Fe-O-P 180^0 夹角时小于Fe-O-P 90^0 夹角

  For at top site on Fe(100) surface, adsorption energy is smaller with Fe-O-P 180^0 angle than with 90^0 angle no matter Fe-O-P or Fe-P-O

- 吸附在Cu(100)和Al(100)面的top位置时，吸附能在Cu-O-P和Cu-P-O夹角90^0时几乎相同，这个趋势在 Al-O-P 和Al-P-O夹角90^0 时相同

  For at top site on Cu(100) and Al(100) surfaces, adsorption energies are almost same with 90^0 angle of Cu-O-P and Cu-P-O. Same trend is for with 90^0 angle of Al-O-P or Al-P-O

- 对于90^0夹角，PO 分子的吸附能在Cu(100)面最小，在Fe(100)面最大，相应的最稳定的(100)面顺序是：Fe(100), Al(100), Cu(100)

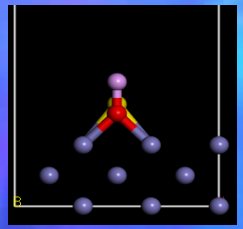
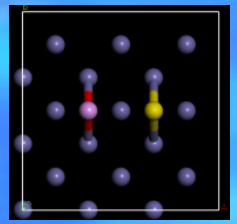
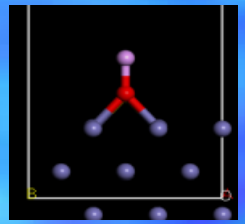
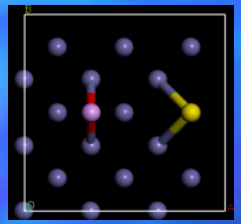
  For with 90^0 angle, PO adsorption energies are smallest on Cu(100), biggest on Fe(100) surfaces, corresponding to the most stable adsorption surface order: Fe(100), Al(100), Cu(100)

- Cu-O-P或Al-O-P的夹角小于180^0时，PO 分子能吸附在Cu(100)和Al(100)面的top位置

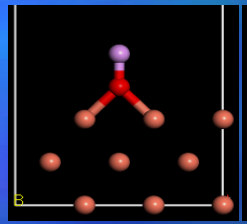
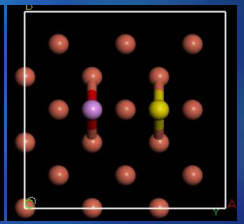
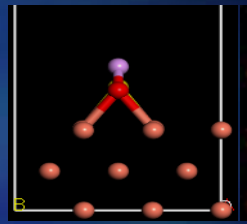
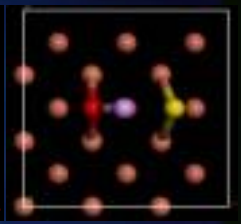
  For at top Cu(100) and Al(100) surfaces with angles of Cu-O-P or Al-O-P less than 180^0, PO can be adsorpted on Cu(100) and Al(100)

结果4 - 气相环境中S原子和PO分子在Fe(100), Al(100)和Cu(100)面的吸附构型和吸附能。黄色- S，红色 - O， Cu棕褐色 - Fe，橘黄色 - Cu，粉红色 - Al，括号内值是吸附能（单位：kJ·mol^{-1}）

Results 4 - Optimized adsorption configurations and energies (unit: kJ·mol^{-1}) of S atom and PO molecule on Fe(100) , Al(100) and Cu(100) surface in gas phase. Brown - Fe, red - O, cmyk - P, orange - Cu, pink - Al.

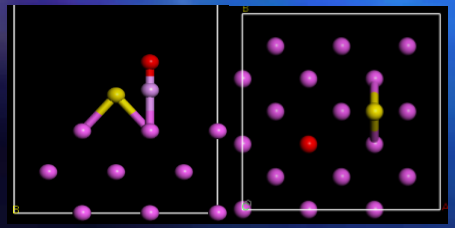
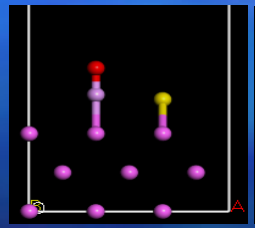
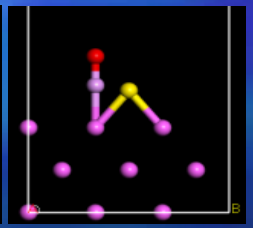
Initial　　Optimized (5775.1)

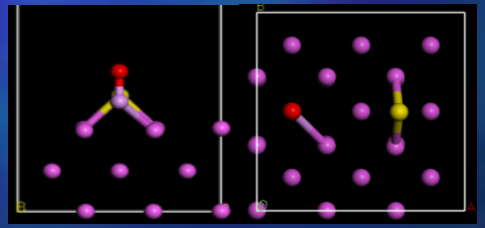
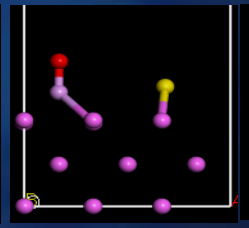
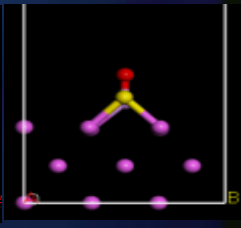
Initial　　Optimized (651.8)

Fe-O-P and Fe-S

Cu-O-P and Cu-S

Initial

Optimized (598.0)

Al-P-O and Al-S

结果4的讨论 Discussion for results 4

- S原子和PO分子间的横向排斥作用使S-Fe键, S-Cu键, and S-Al键发生倾斜

  Lateral repulsion between S atom and PO molecule makes S-Fe, S-Cu, and S-Al bond tilting

- 优化后，在bridge位置的垂直模型P-O键在Fe(100)面还保持相同的垂直状态，而在Cu(100)面P-O键发生倾斜

  After optimization, vertical mode of P-O bond at bridge site keeps same on Fe(100) surface and tilting on Cu(100) surface, respectively

- S原子和PO分子在Fe(100)面上的吸附能比在Cu(100)面上的大

  Adsorption energy of S atom and PO molecule is bigger on Fe(100) surface than on Cu(100) surface

- 优化后和在Al(100)面，Al-P键由垂直发生倾斜，而P-O还保持垂直状态

  After optimization and on Al(100) surface, vertical mode of Al-P bond becomes tilting, while vertical mode of P-O bond keeps same

结论 Conclusion

- S原子能在Fe(100), Al(100)和Cu(100)面上化学吸附

  Chemisorption of S atom can occur on Fe(100), Al(100), and Cu(100) surfaces
- PO分子能在Fe(100)面上无条件化学吸附，而在Al(100)和Cu(100)面上是有条件化学吸附

  Chemisorption of PO molecule can occur on Fe(100) surface undonditionally, and on Al(100) and Cu(100) surfaces conditionally.
- S原子和PO分子最稳定的化学吸附面顺序是：Fe(100), Al(100), and Cu(100)面

  The most stable S atom and PO molecule Chemisorption surface order: Fe, Al, Cu
- S原子最稳定的化学吸附位置顺序是：hollow, bridge和top位

  The most stable adsorption site of S atom order: hollow, bridge, top
- PO分子在Fe(100)面最稳定的化学吸附位置顺序是：hollow, bridge, top

  The most stable adsorption site of PO molecule on Fe(100) surface order: hollow, bridge, top
- 分子键角影响化学吸附的构型和吸附能

  Molecule bond angle influes adsorption configurations and energies

结论 Conclusion

- S原子和PO分子间在(100)面上的横向排斥影响化学吸附的构型和吸附能

Lateral repulsion among atoms and molecules on (100) surfaces influes adsorption configurations and energies

- ZDDP生成抗磨损膜中的其它原子和分子的化学吸附的构型和吸附能也能用目前的方法预测

Adsorption configurations and energies of other atoms and molecules of atiwear film from ZDDP can be predicted by the present simulation approach

- 本研究的结果可以帮助我们深入了解各种理论机理的的相对重要性

The results of this study should provide insight on the relative significance of the various theoretical mechanisms that are believed to be at work. This approach can be a useful tool to design tribopairs, lubricants and additives

感谢聆听 Thank You for Attention

欢迎提问 Questions