

# Simple Methods for Photo Reaction Modeling

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Umberto Martinez  
Bjørk Hammer

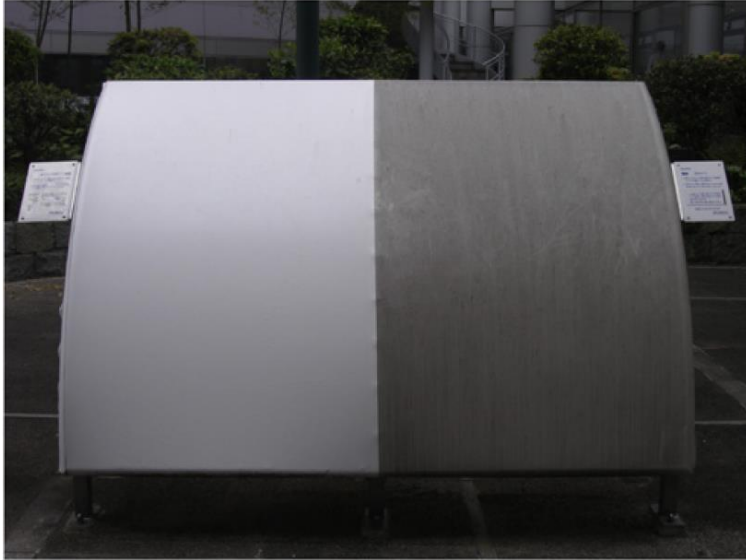
Aarhus University, Denmark

# TiO<sub>2</sub> Self-Cleaning

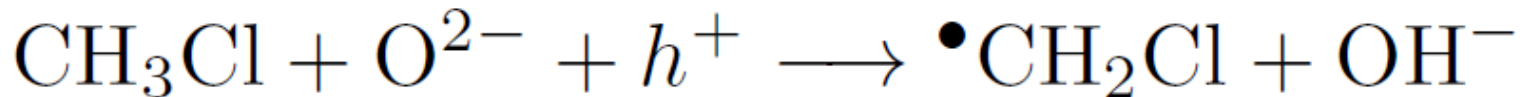
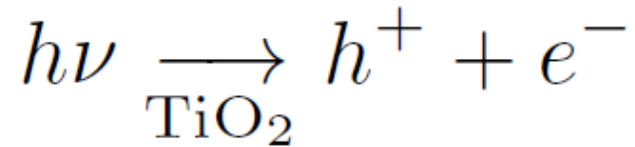


A. Fujishima et al, Surface Science Reports 63, (2008) 515-582

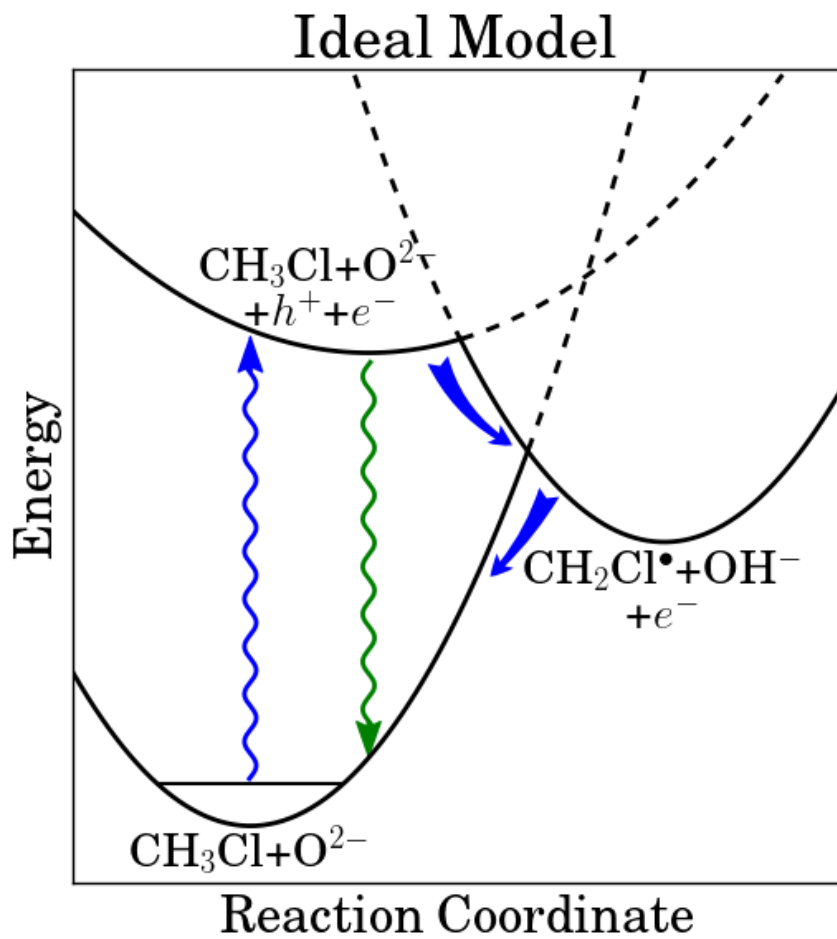
# TiO<sub>2</sub> Self-Cleaning



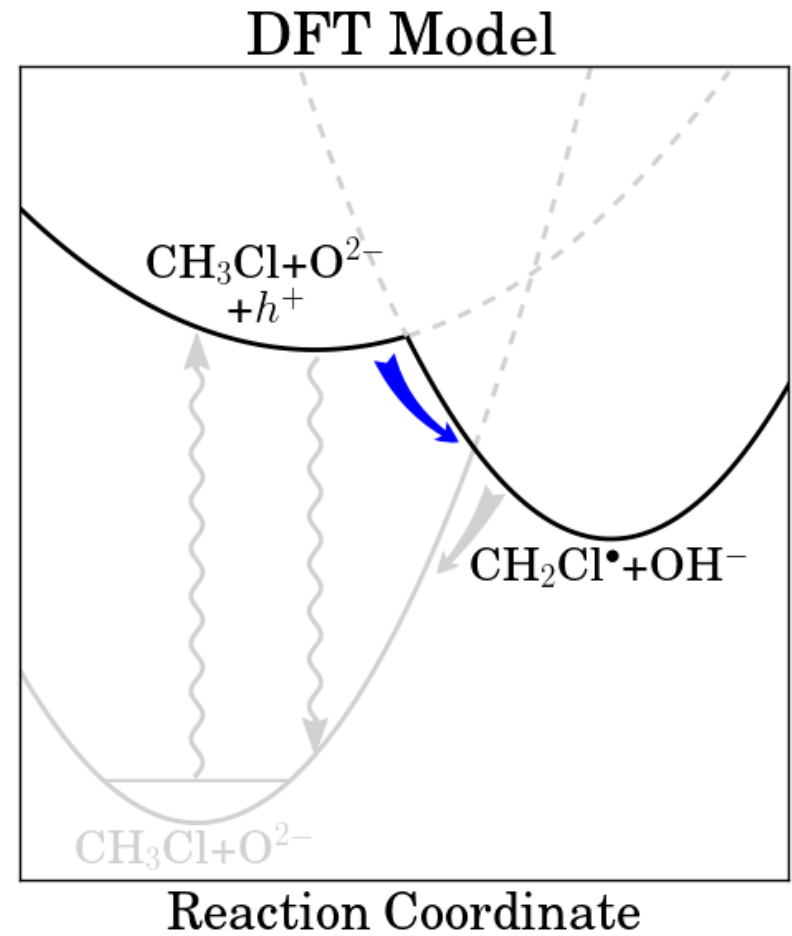
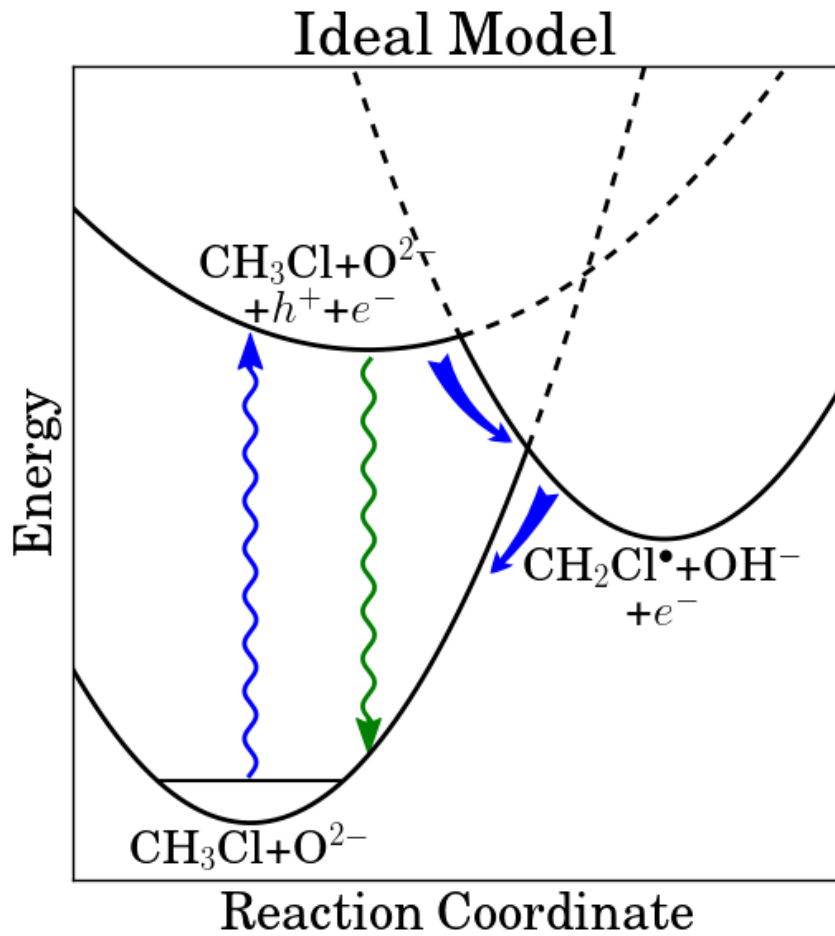
A. Fujishima et al, Surface Science Reports 63, (2008) 515-582



# DFT Approach



# DFT Approach

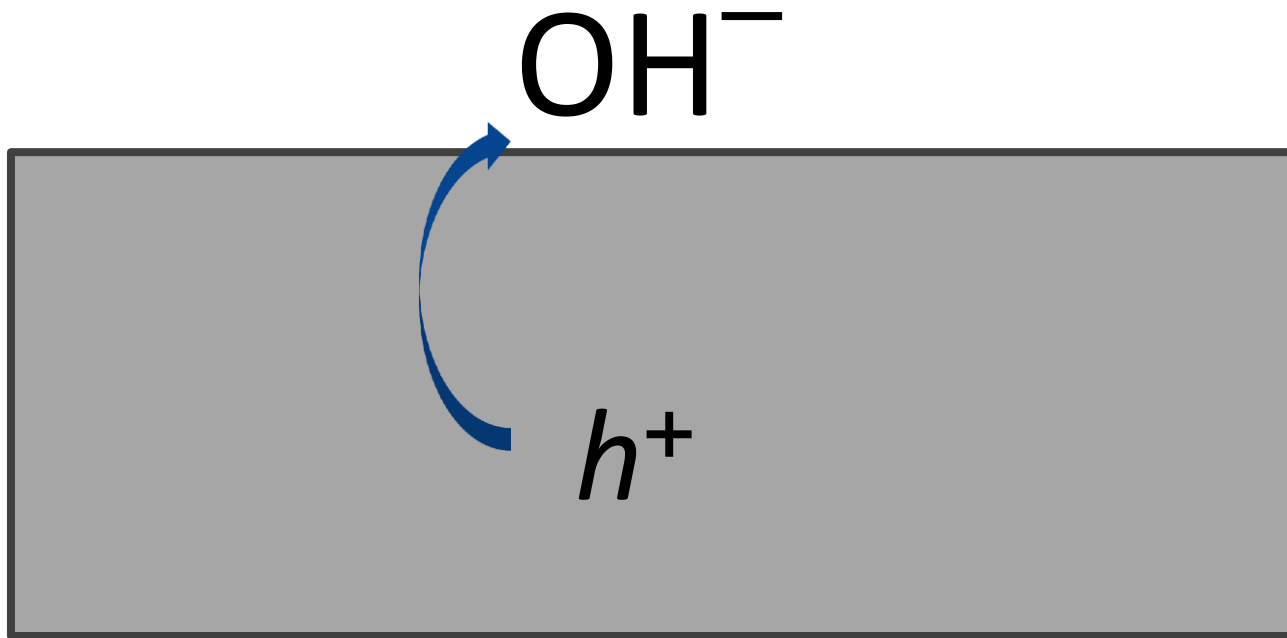


# Hole Creation

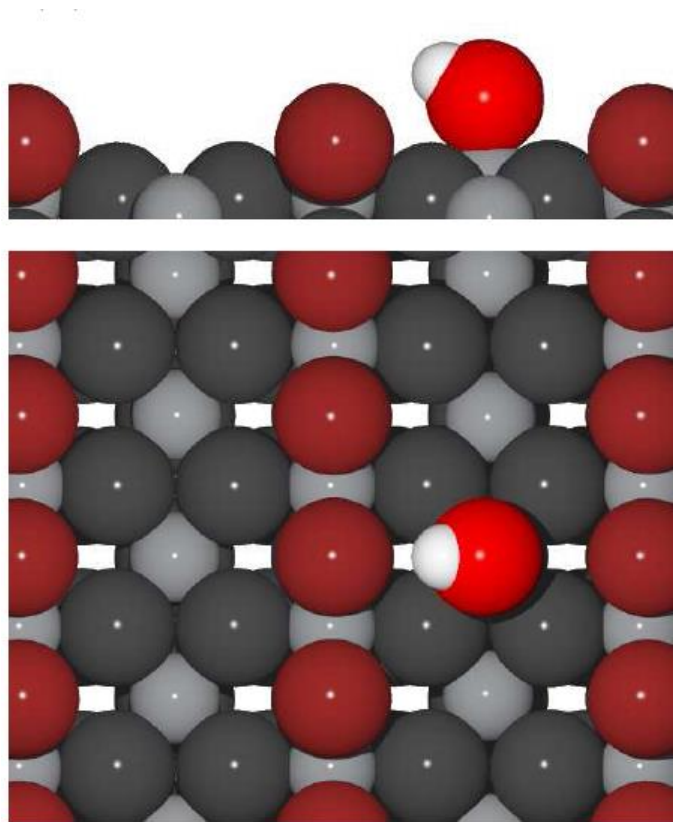
OH



# Hole Creation

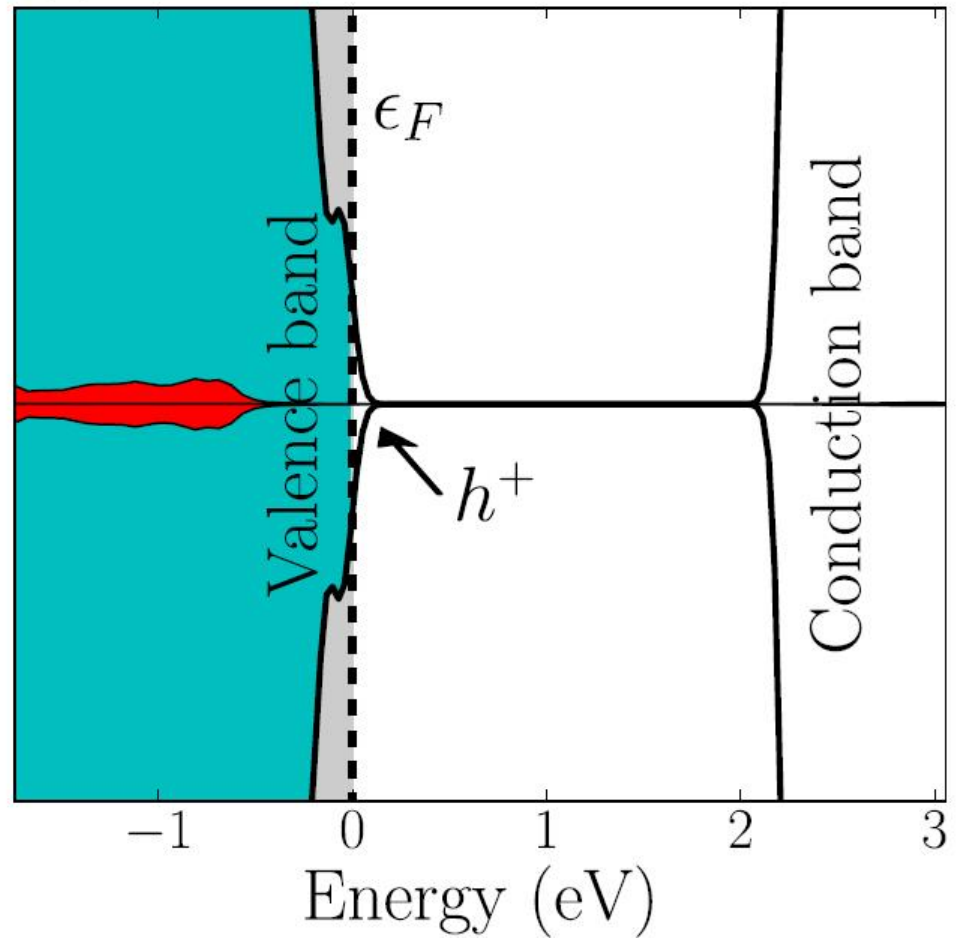
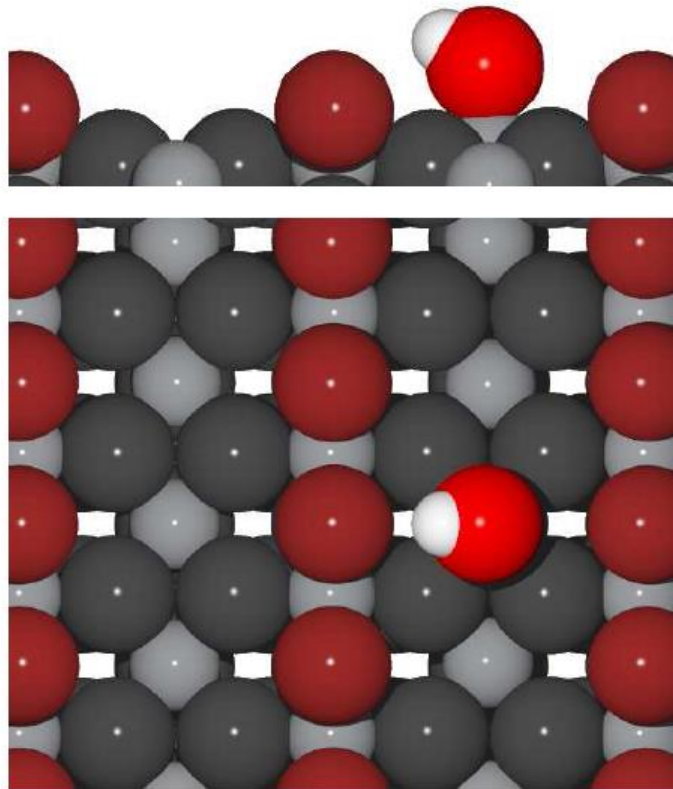


# Hole Creation



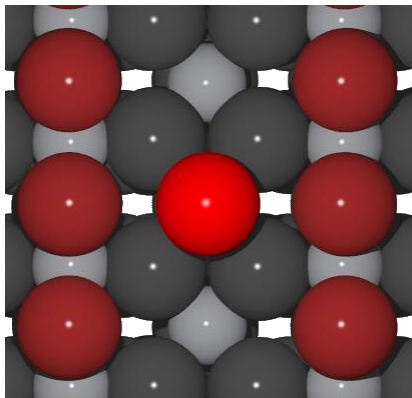
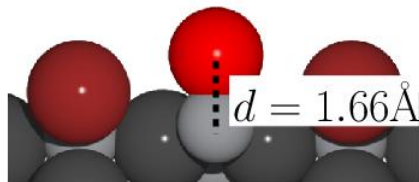
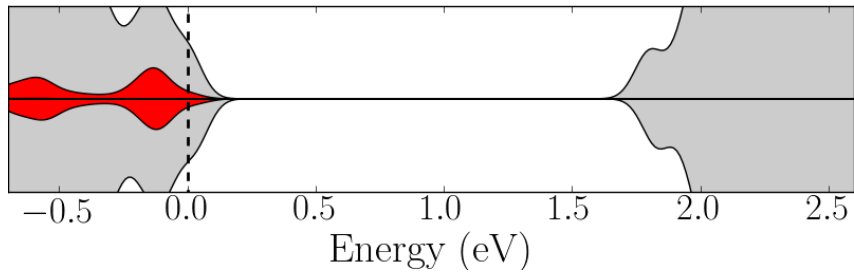


# Hole Creation

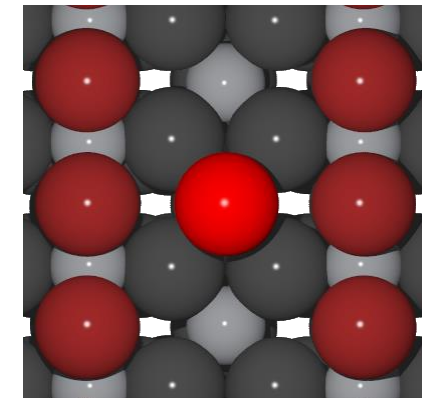
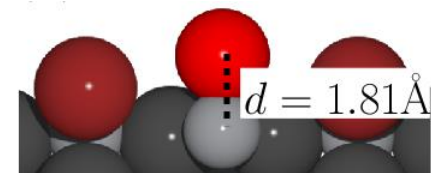
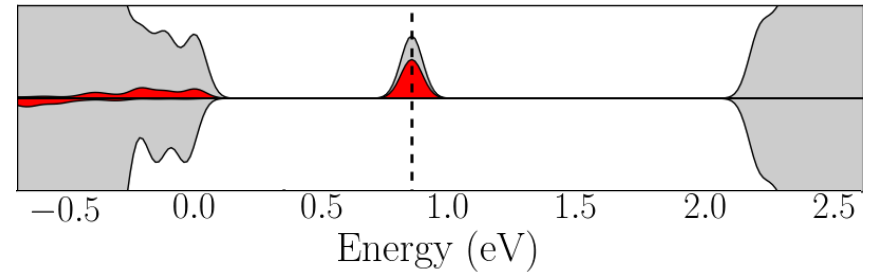


# Hole localization

PBE

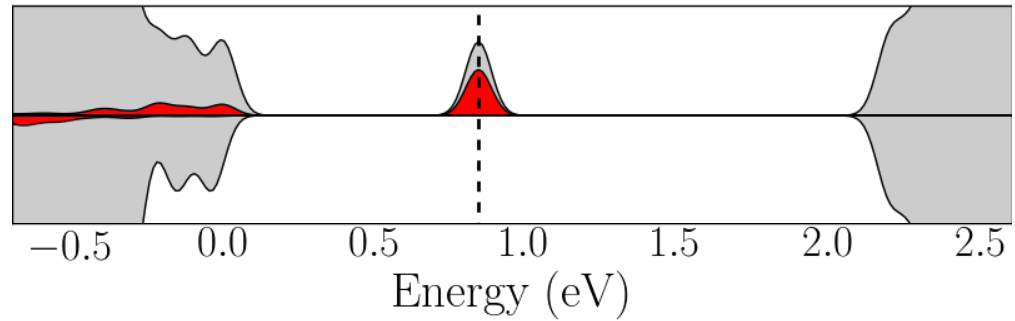
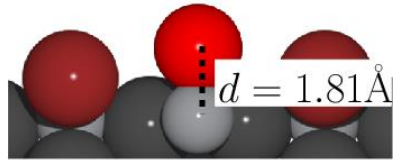


PBE+U



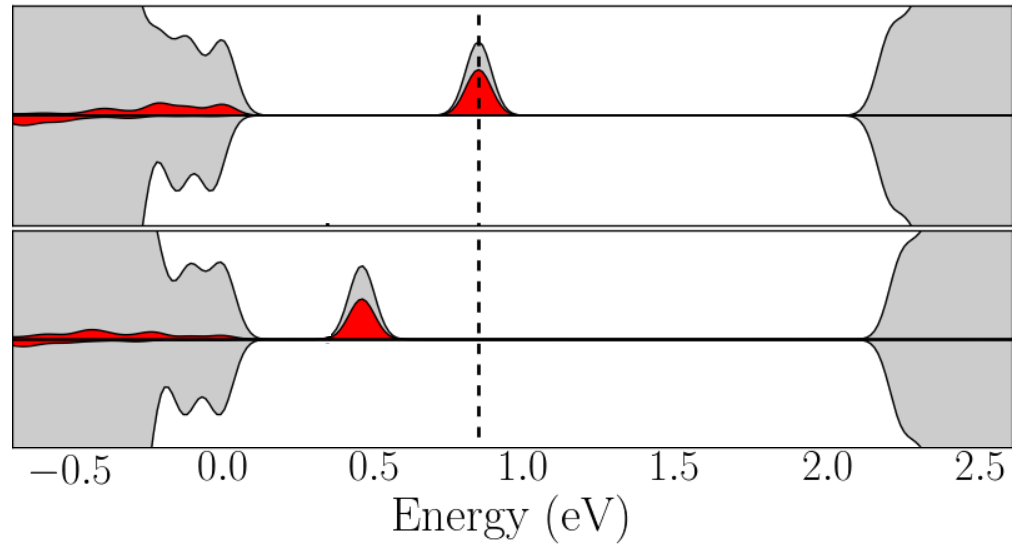
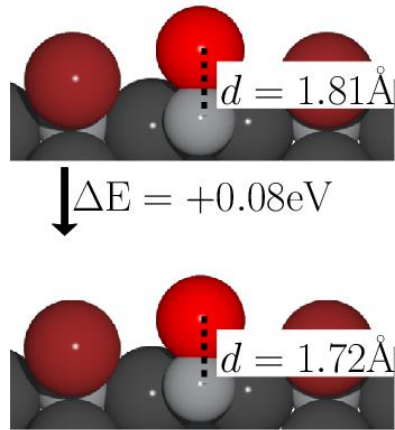
# Hole localization

PBE+U



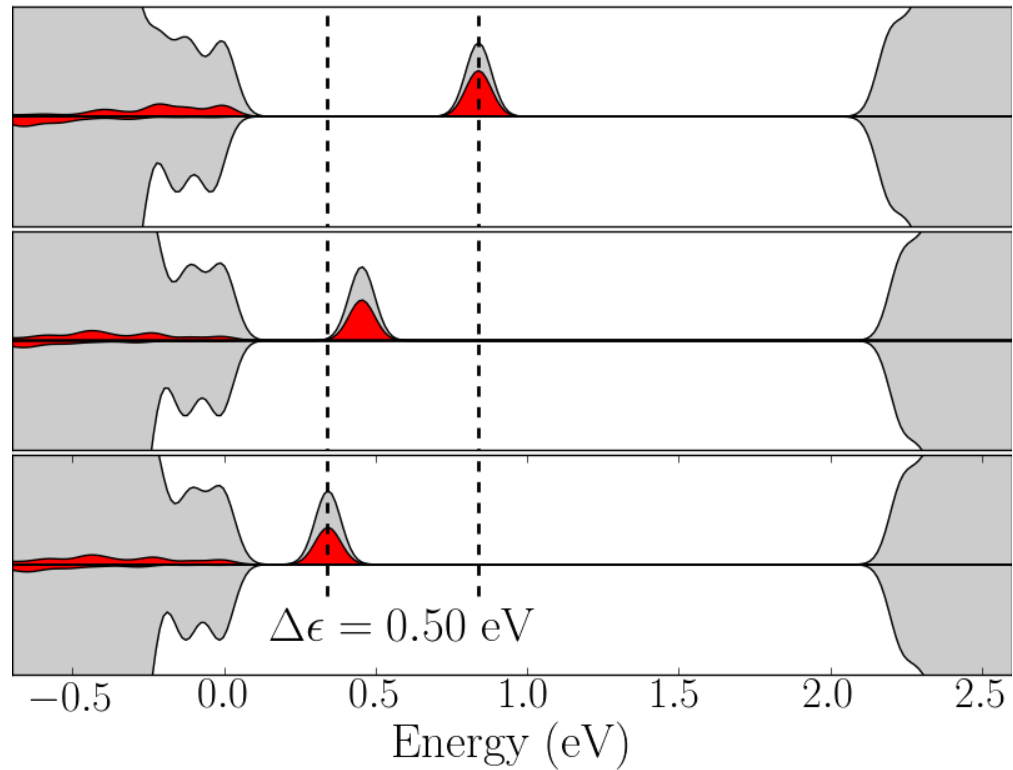
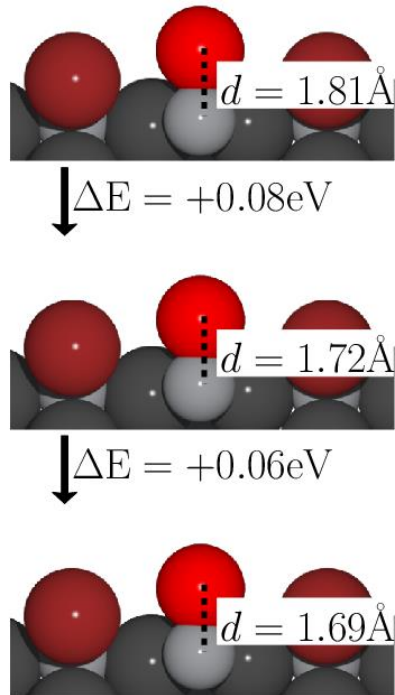
# Hole localization

PBE+U

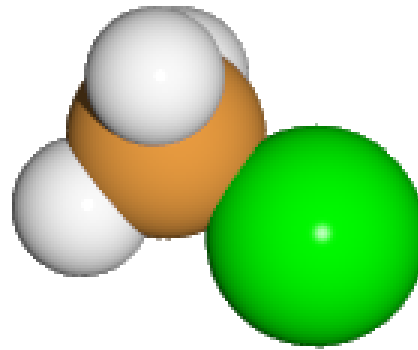


# Hole localization

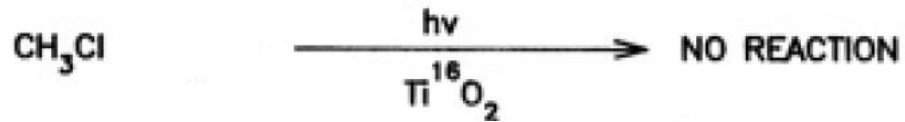
## PBE+U



# Photo-Oxidation of CH<sub>3</sub>Cl

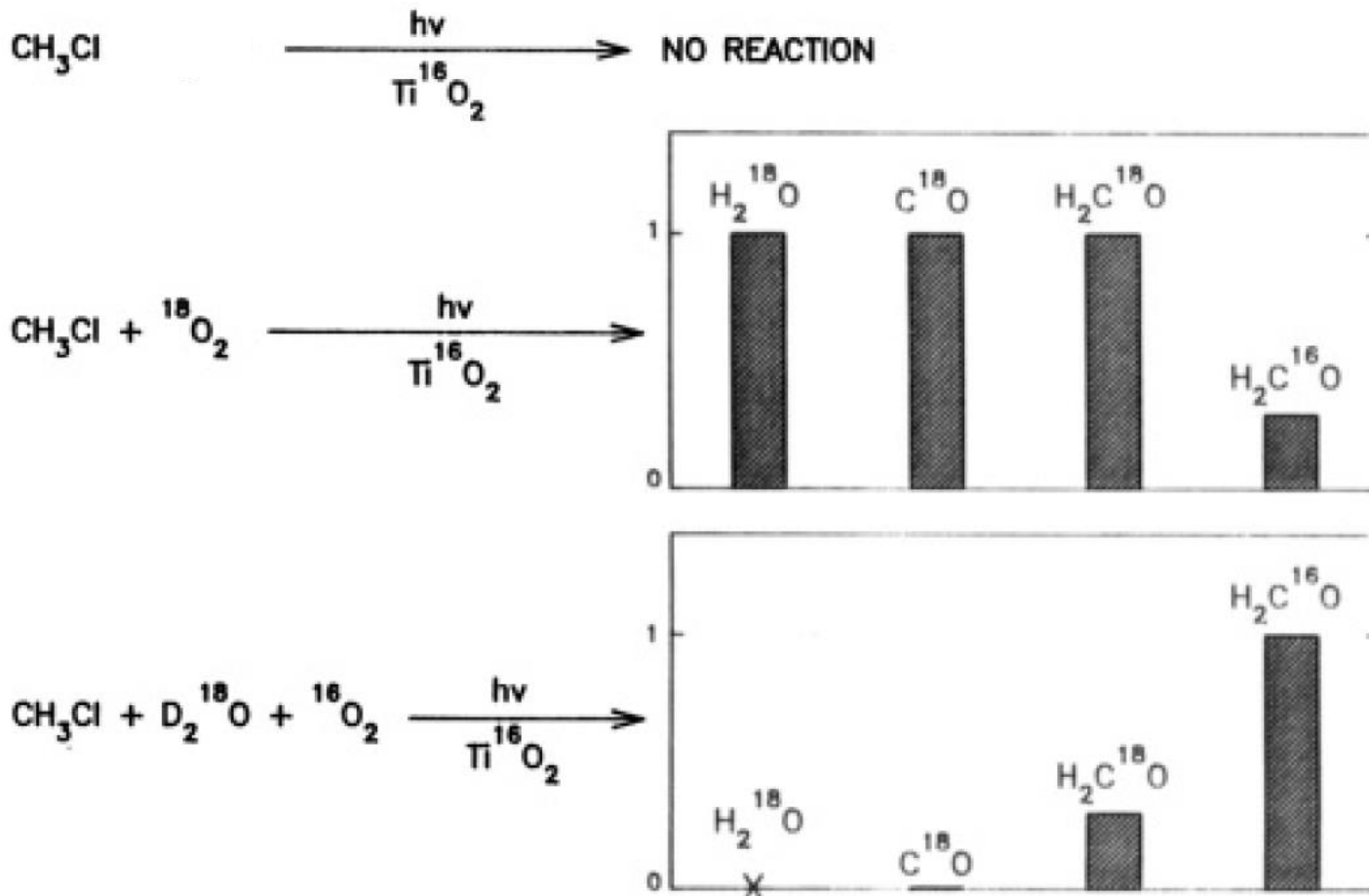


# Photo-Oxidation of CH<sub>3</sub>Cl



G. Lu et al, J. Phys. Chem. 99, (1995) 7626-7631

# Photo-Oxidation of CH<sub>3</sub>Cl

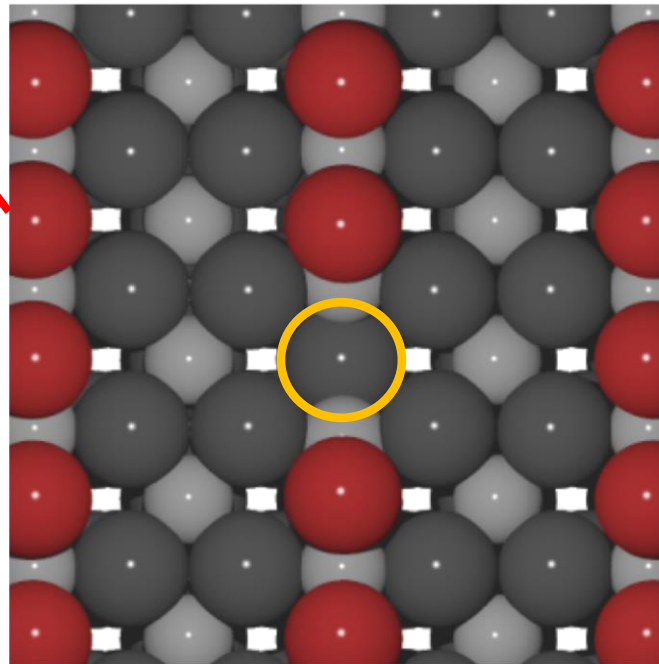


G. Lu et al, J. Phys. Chem. 99, (1995) 7626-7631



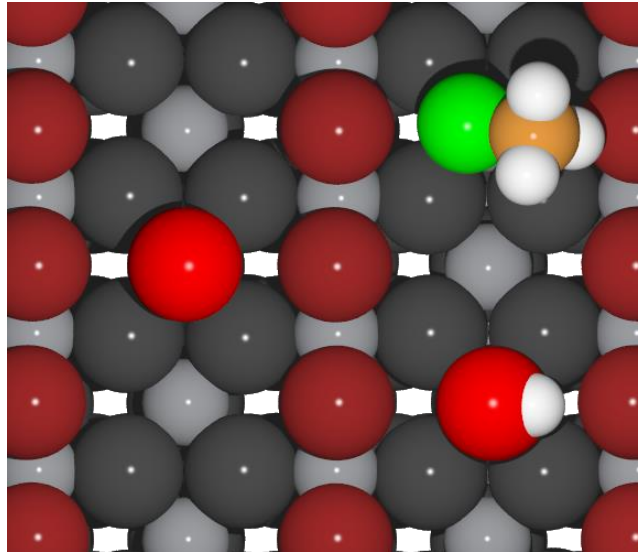
# Photo-Oxidation of CH<sub>3</sub>Cl

CH<sub>3</sub>Cl ON ANNEALED TiO<sub>2</sub>(110)

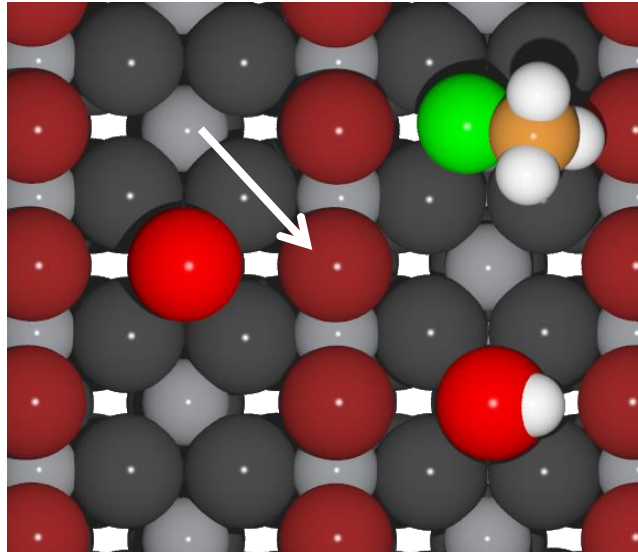


G. Lu et al, J. Phys. Chem. 99, (1995) 7626-7631

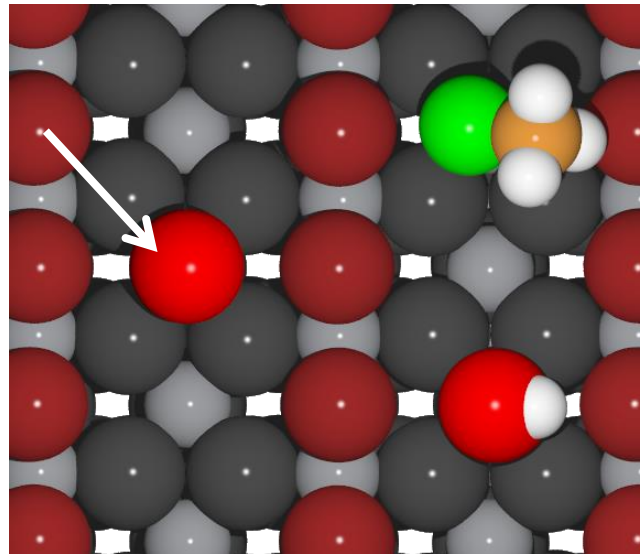
# Possible Surface Species



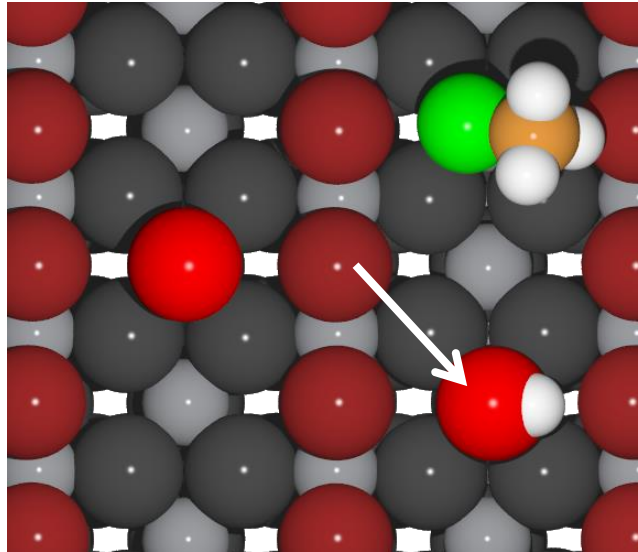
# Possible Surface Species



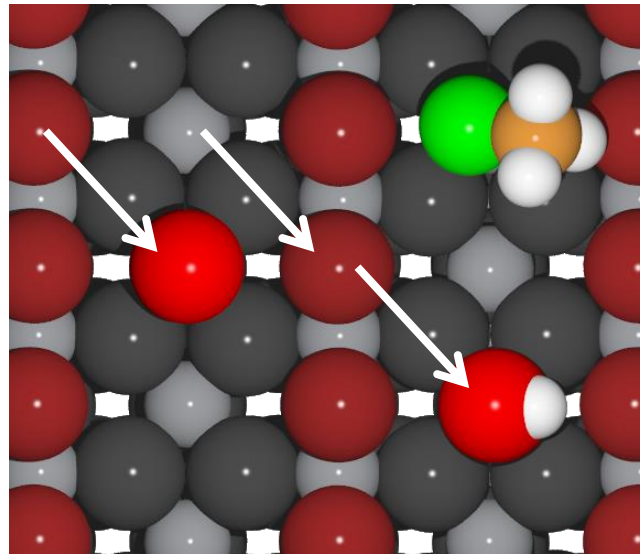
# Possible Surface Species



# Possible Surface Species

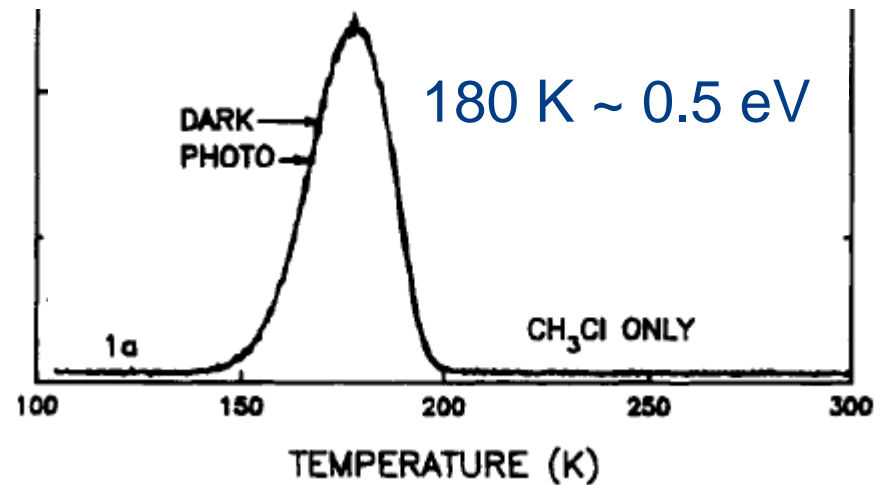
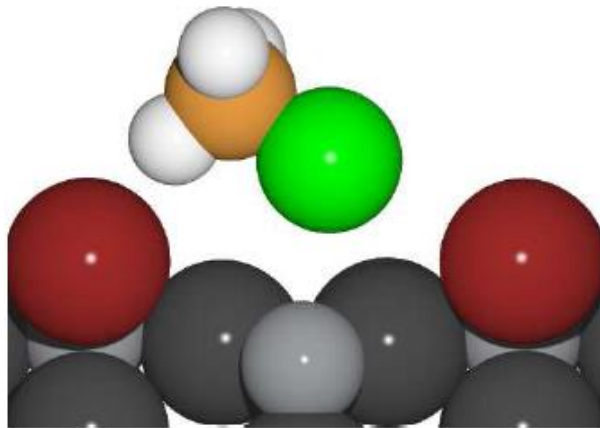


# Proton Acceptors

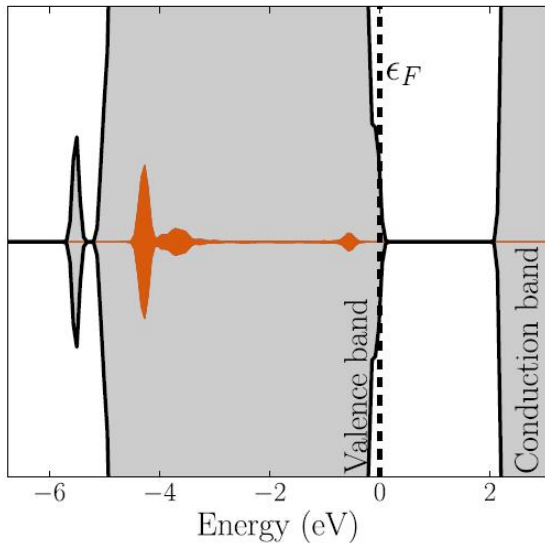


# CH<sub>3</sub>Cl Adsorption

XC	PBE	M06-L	BEEF-vdW
Adsorption energy	-0.25 eV	-0.55 eV	-0.42 eV



# Photo-Oxidation with $O_{br}$



GPAW:

BEEF-vdW

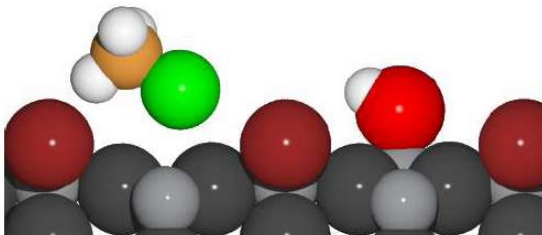
2x2 k-points

< 0.18 Å grid  
spacing

Computational Cell:

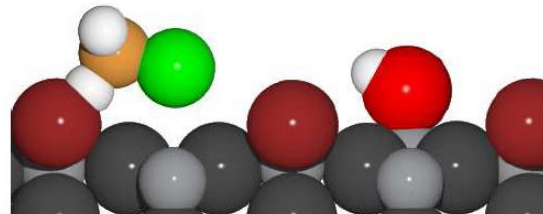
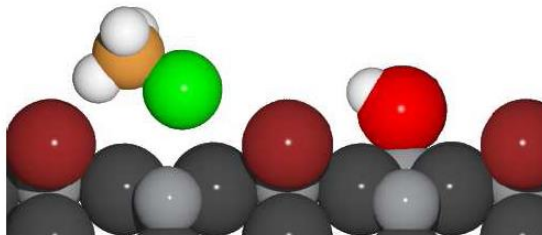
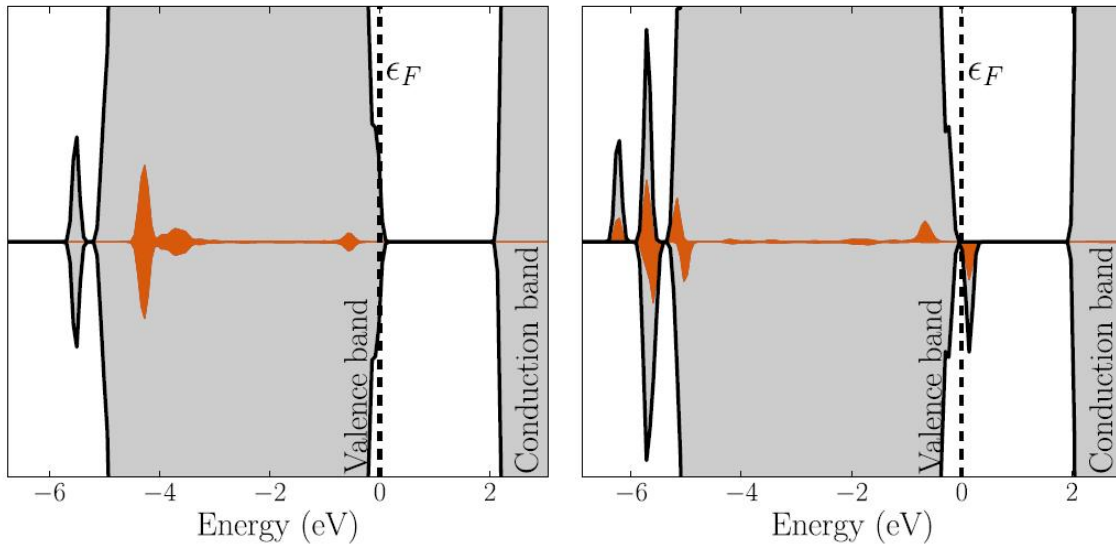
p(4x2)

Four tri-layers  
thickness

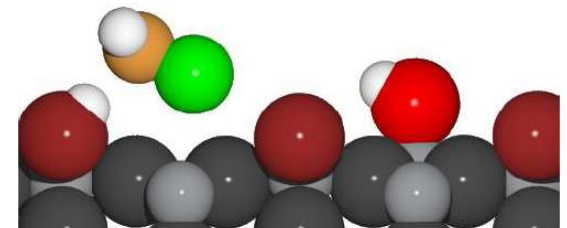
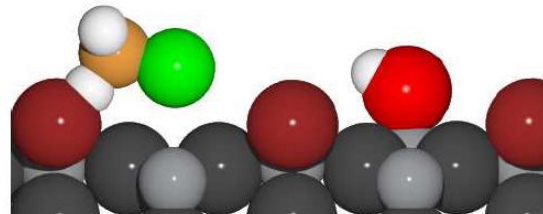
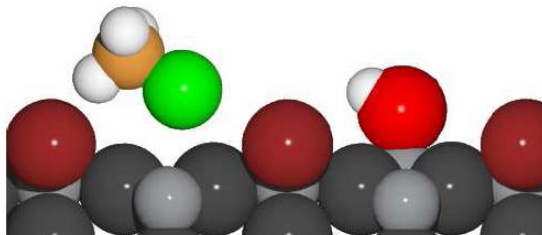
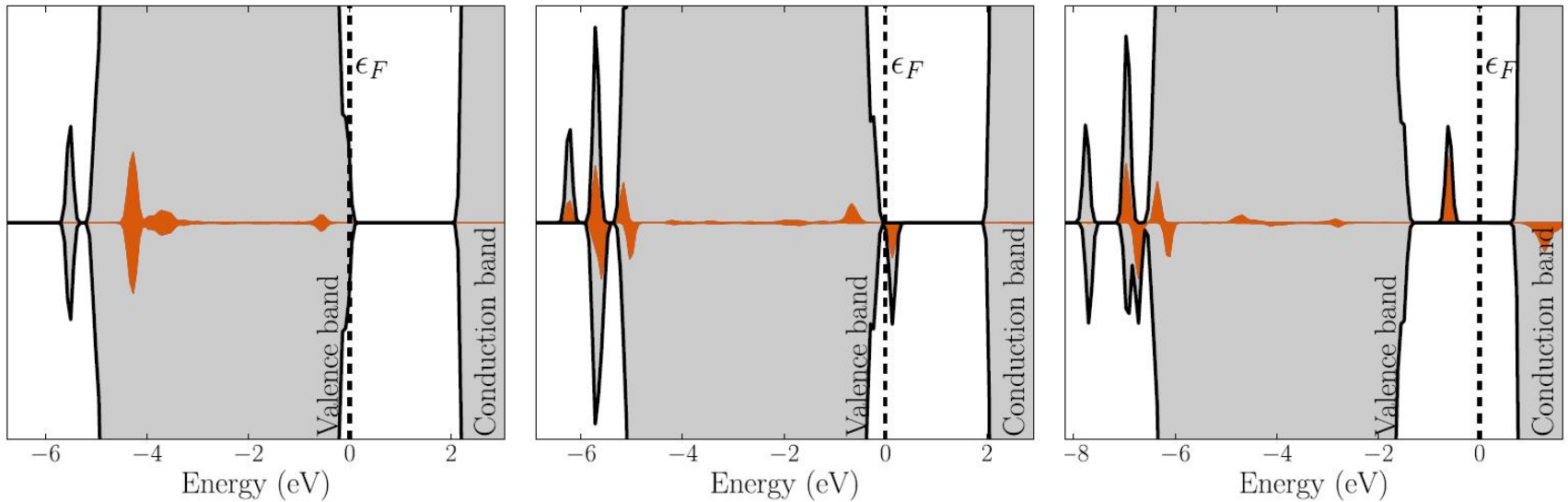




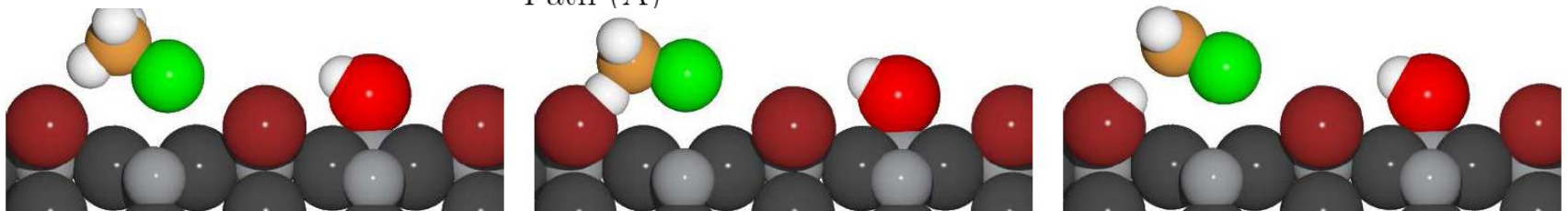
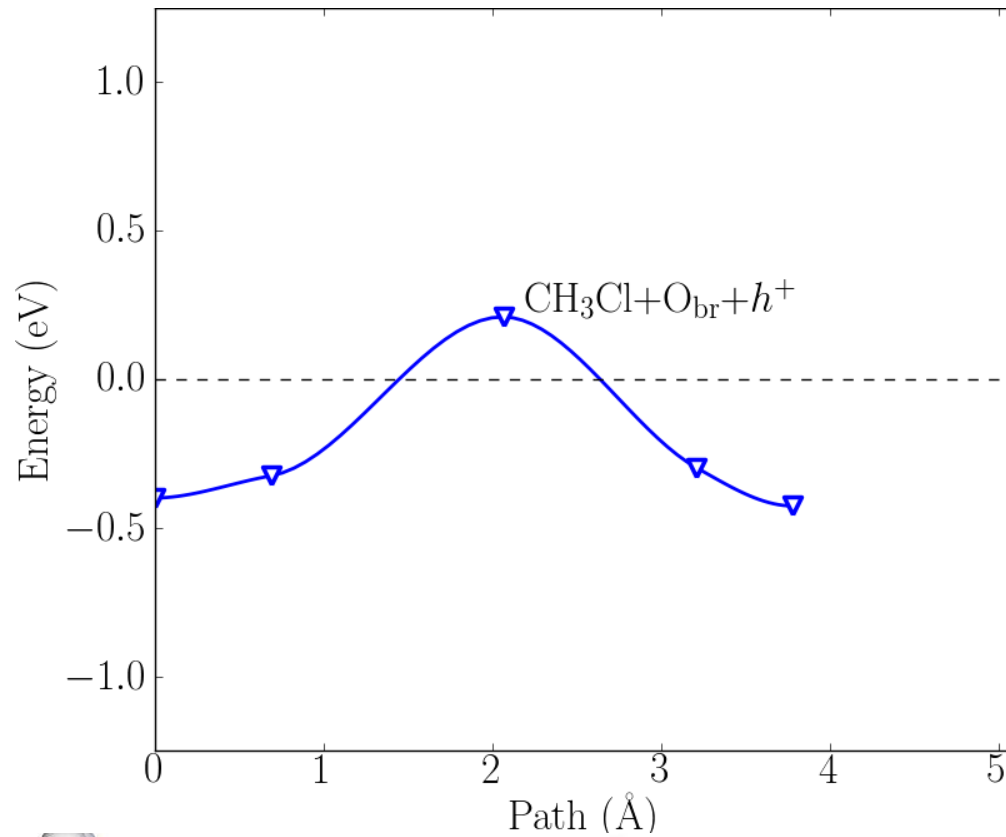
# Photo-Oxidation with $O_{br}$



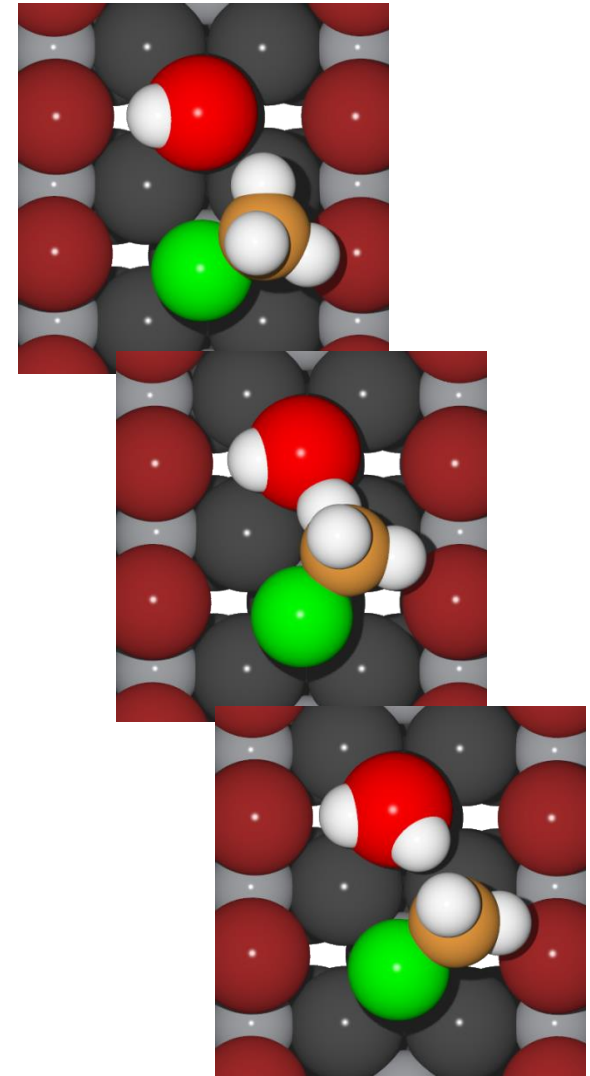
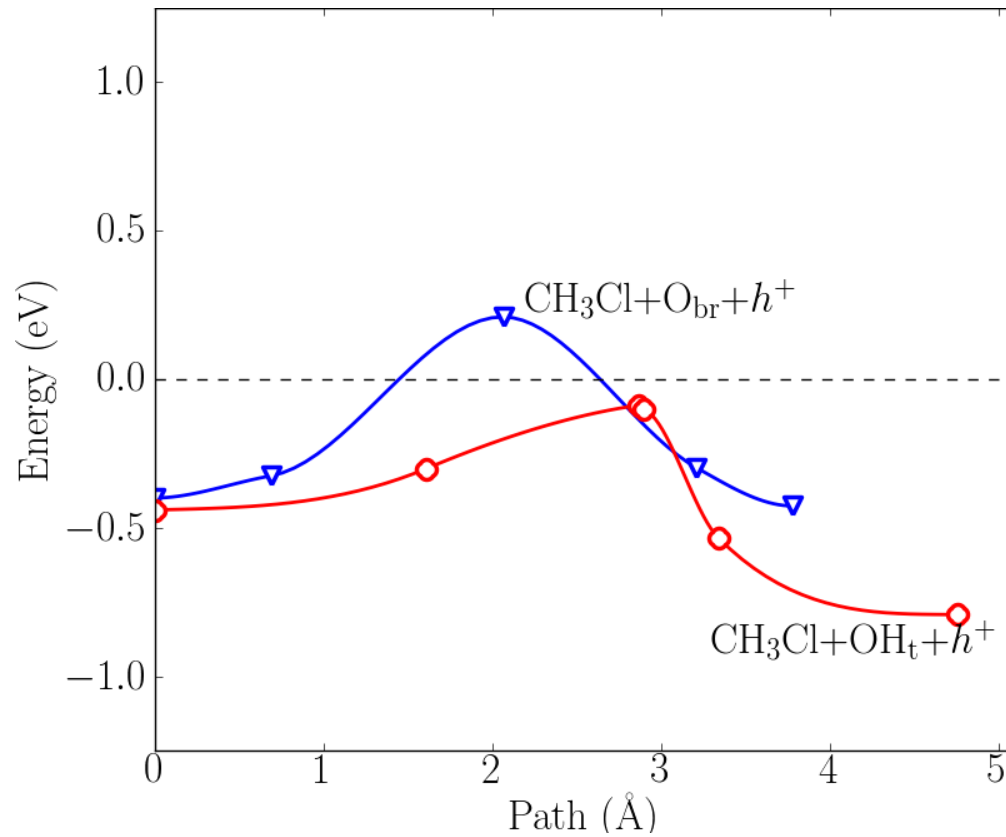
# Photo-Oxidation with $O_{br}$



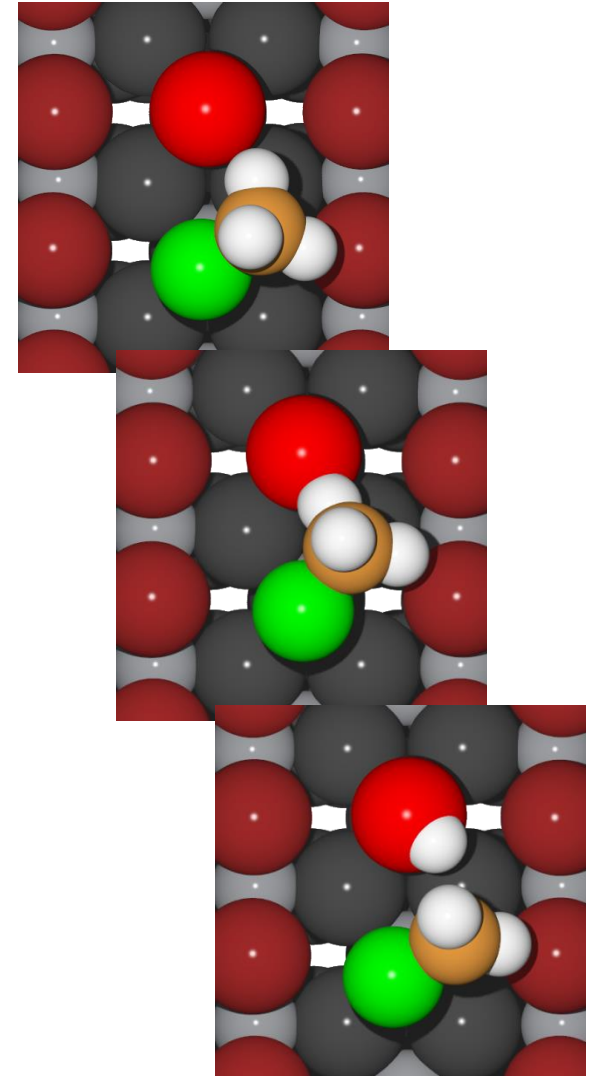
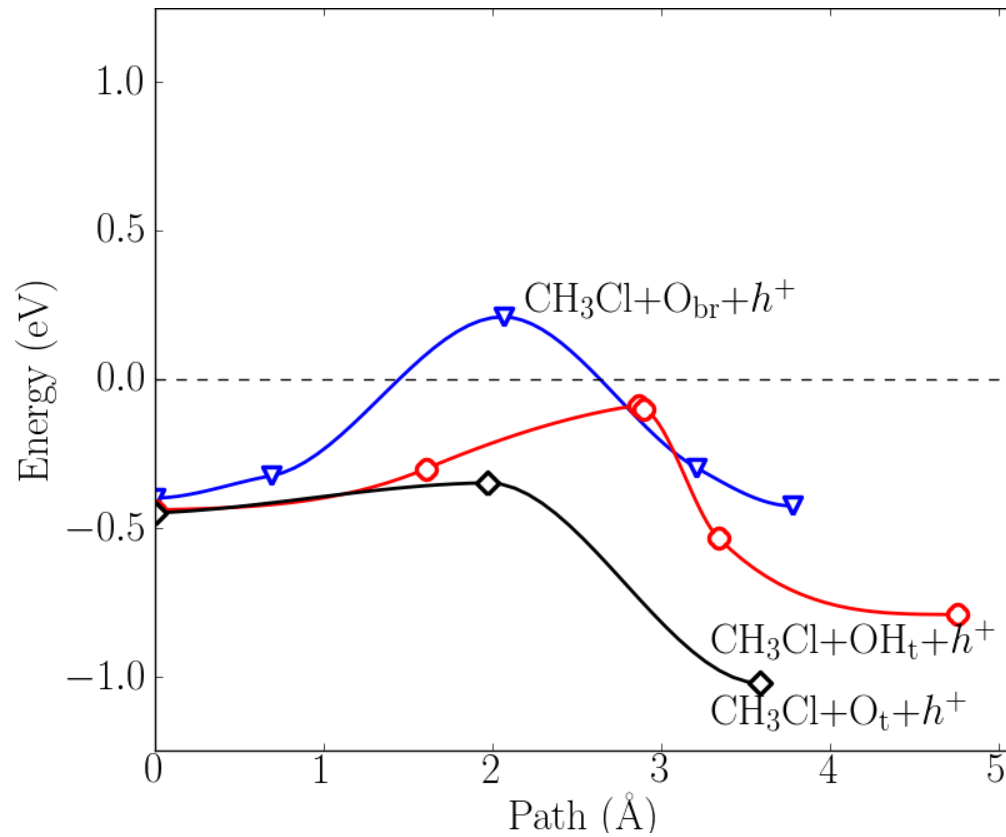
# Photo-Oxidation with $O_{br}$



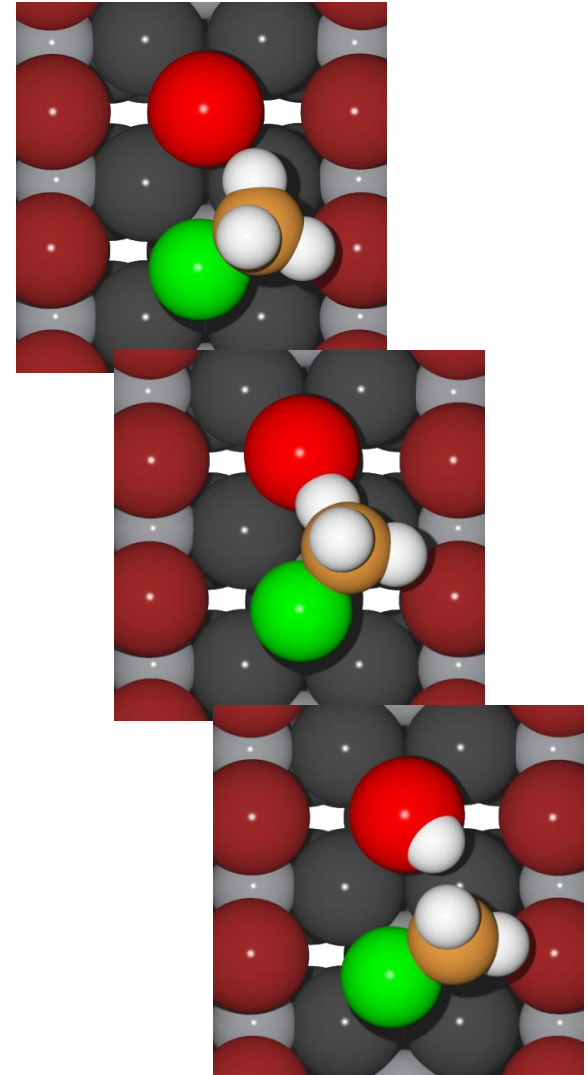
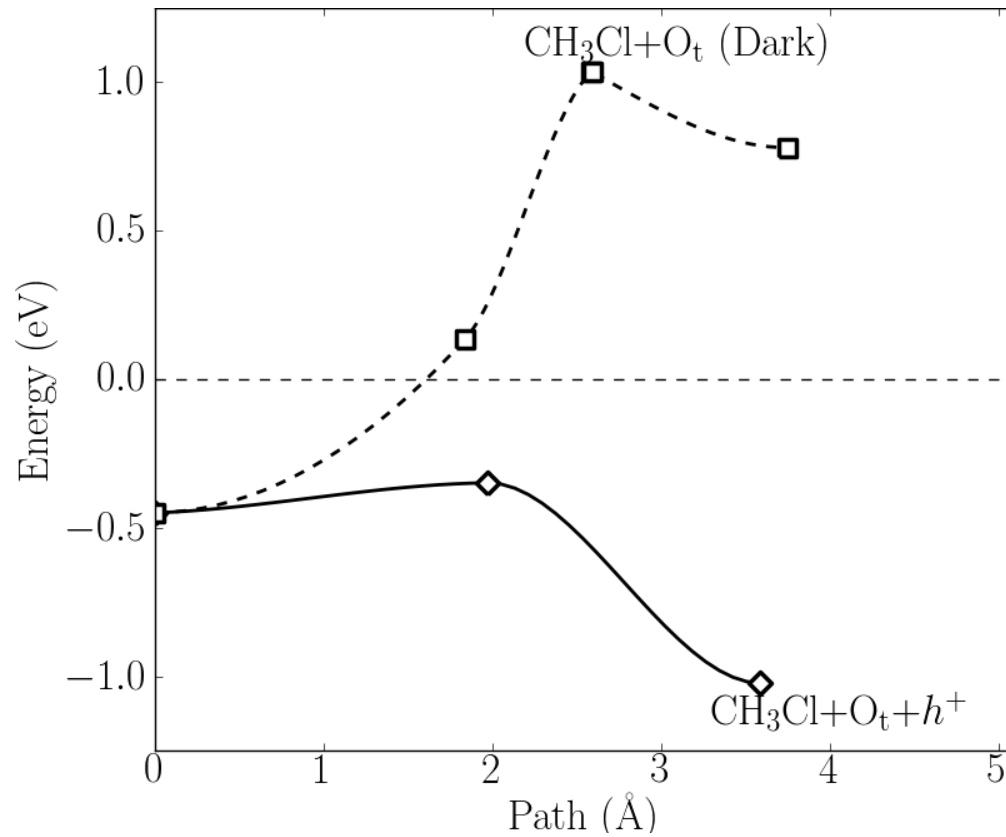
# Photo-Oxidation with $\text{OH}_t$



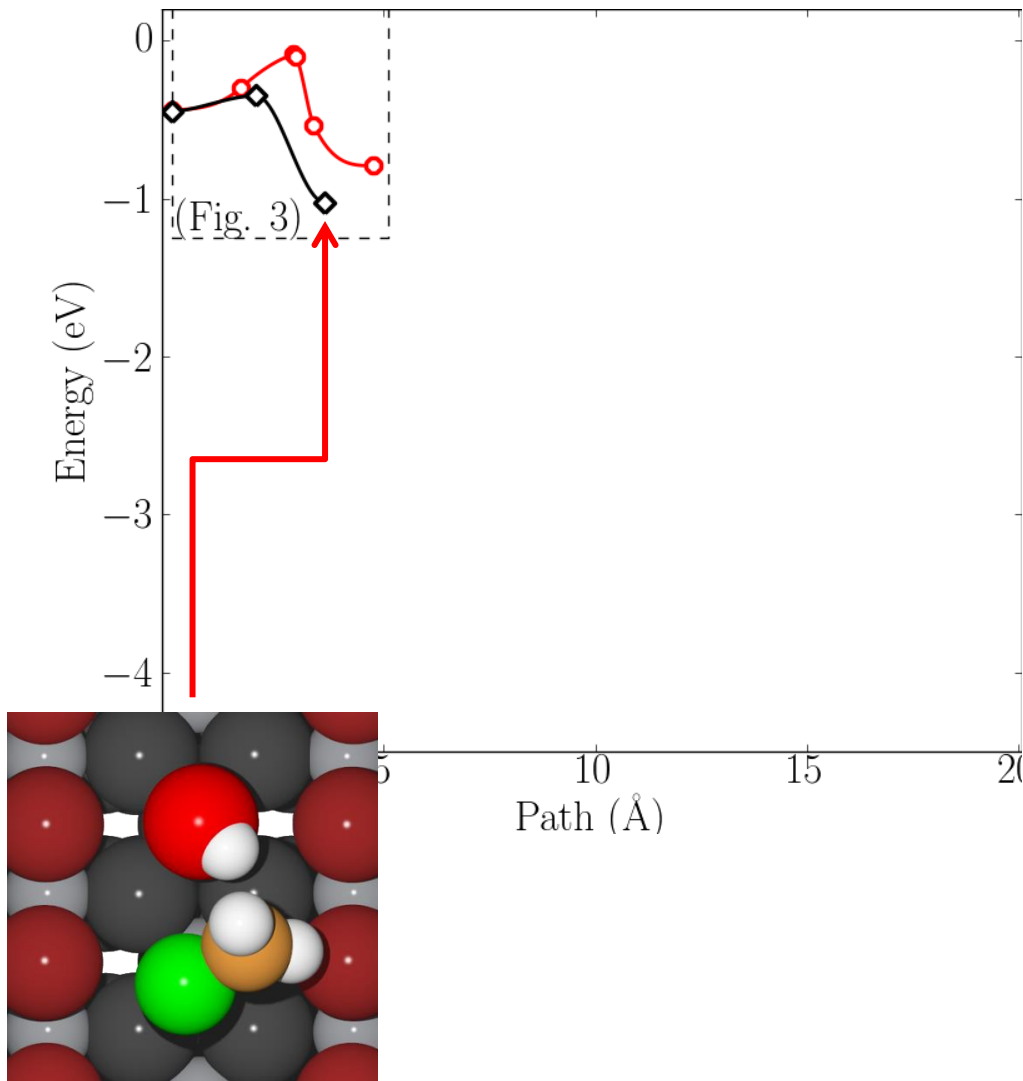
# Photo-Oxidation with $O_t$



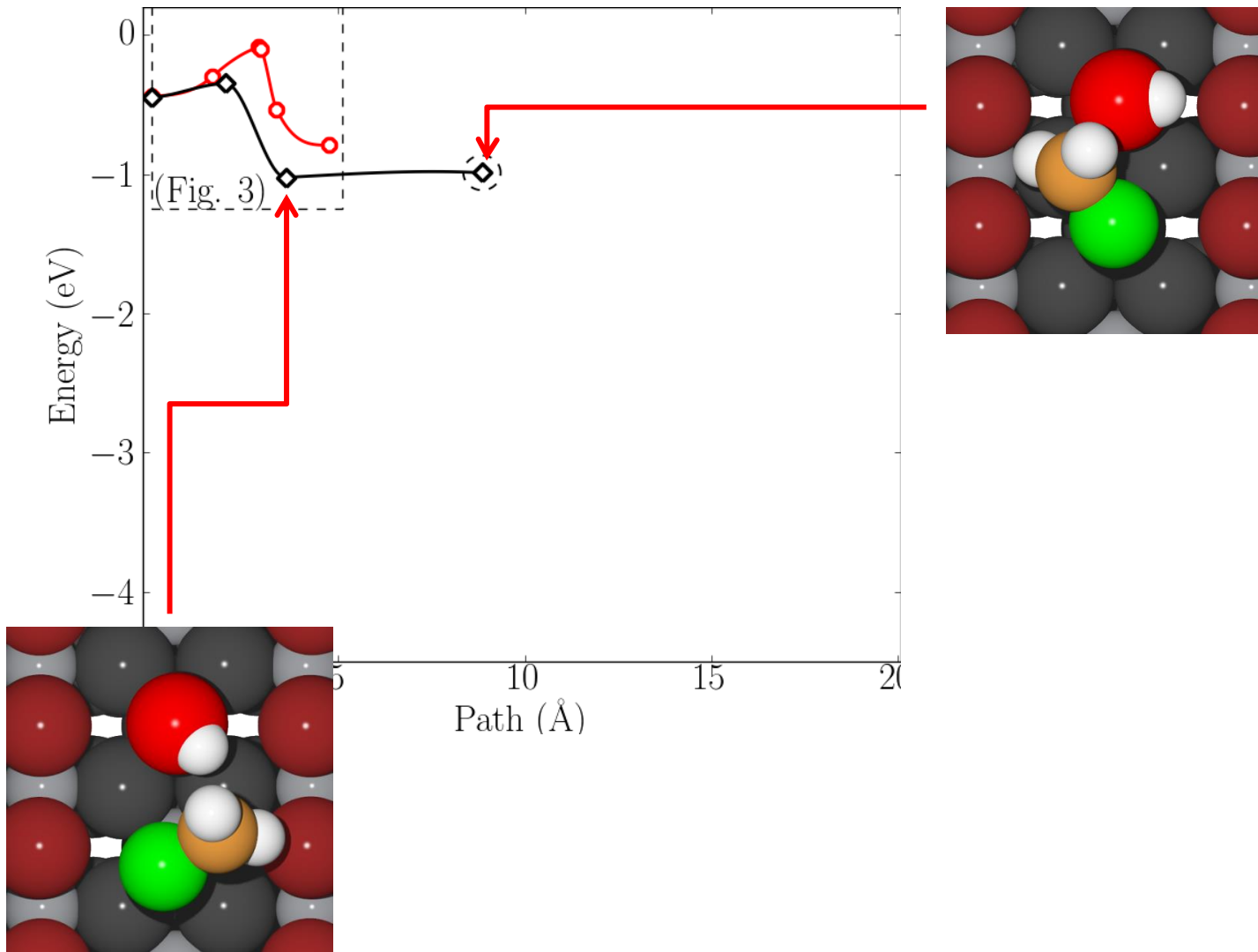
# Photo-Oxidation with $O_t$ (Dark)



# Complete Mechanism

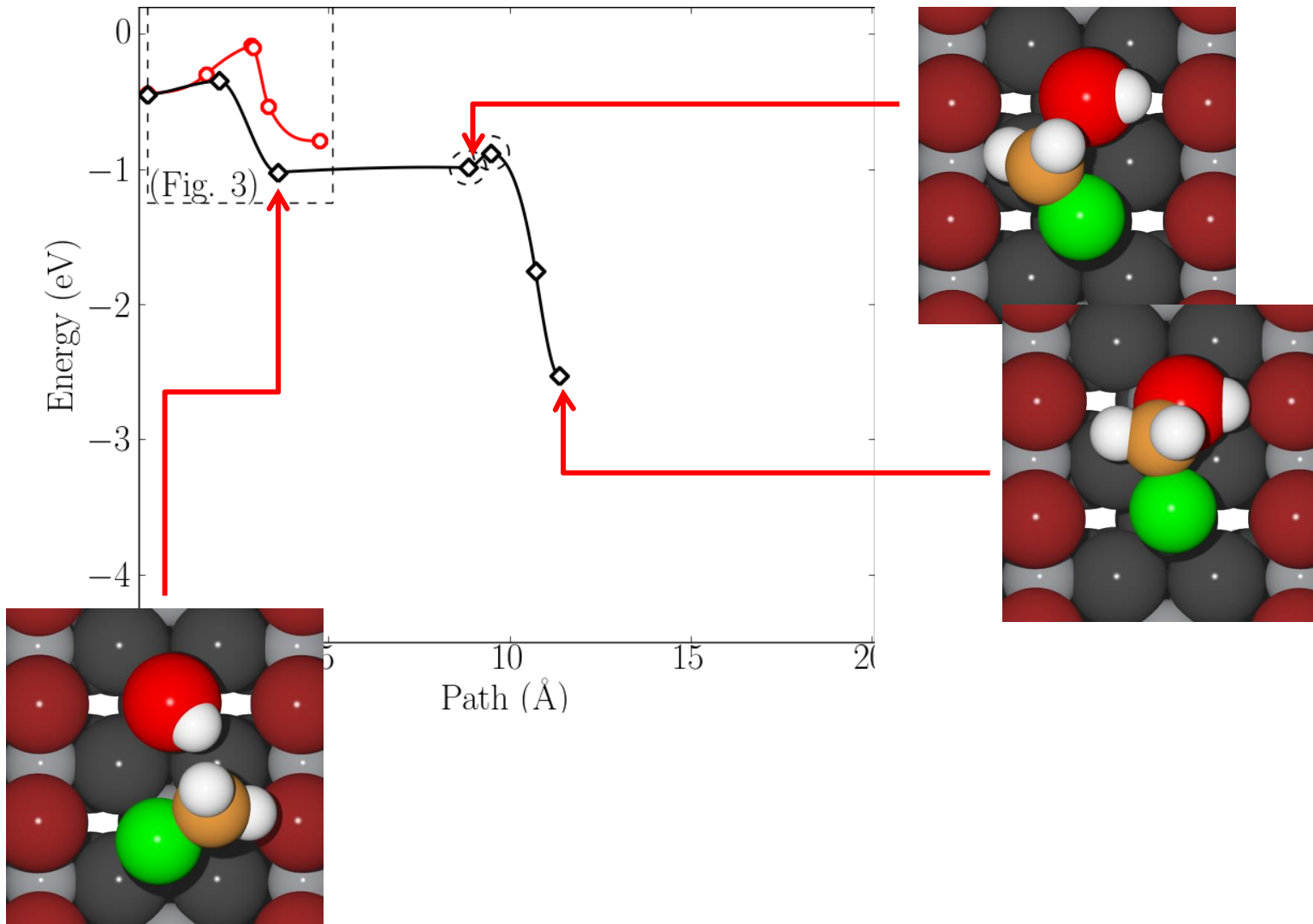


# Complete Mechanism

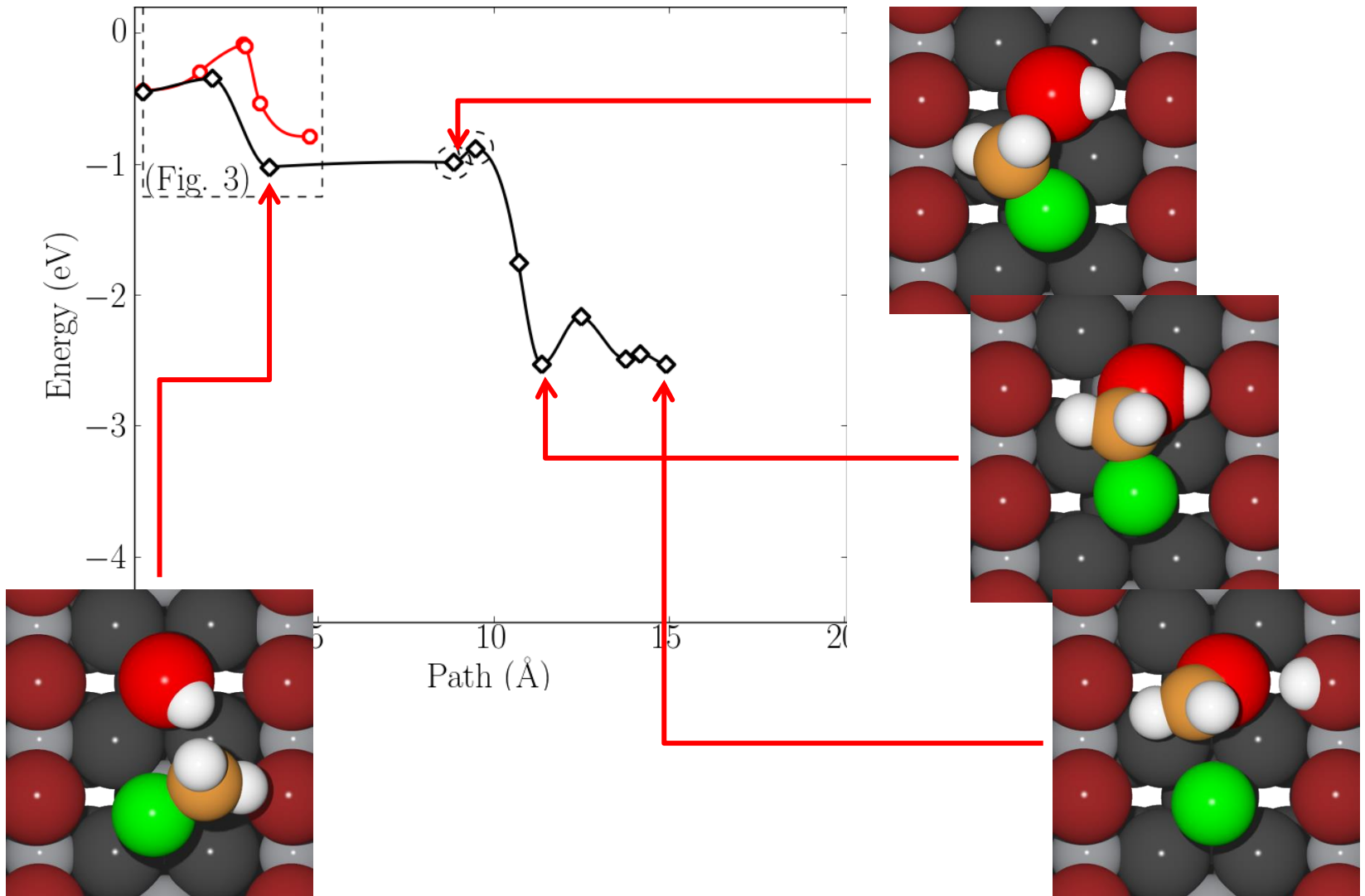




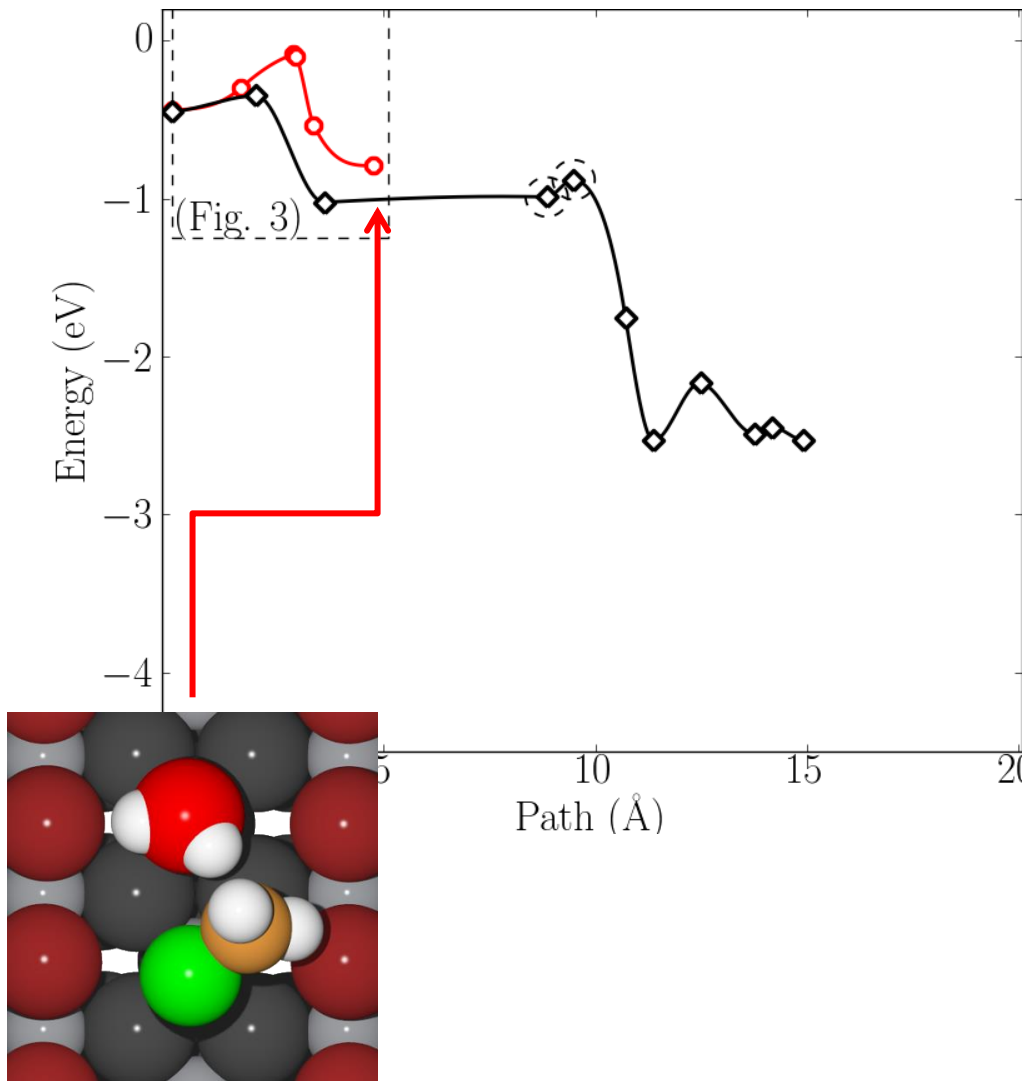
# Complete Mechanism



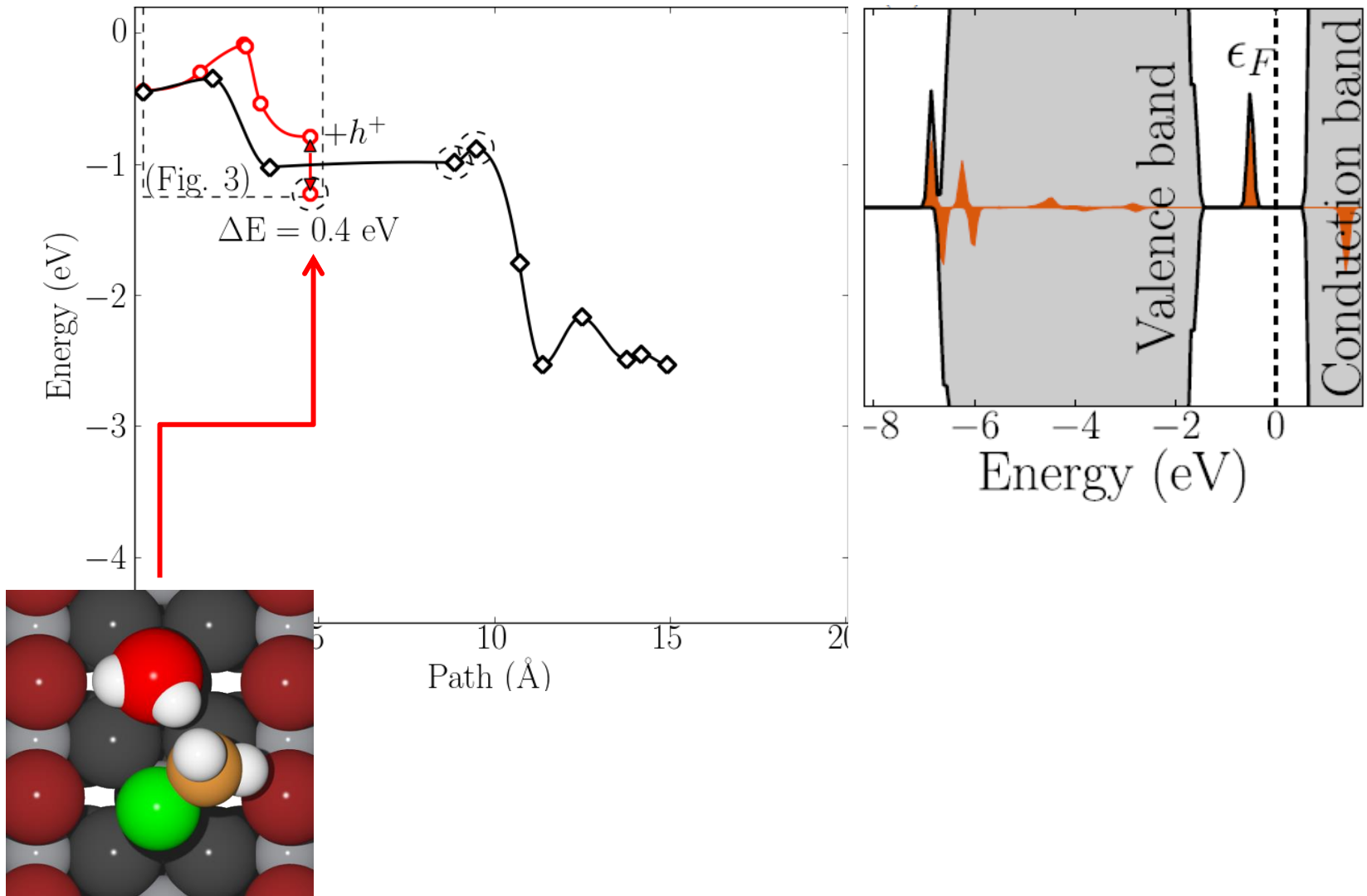
# Complete Mechanism



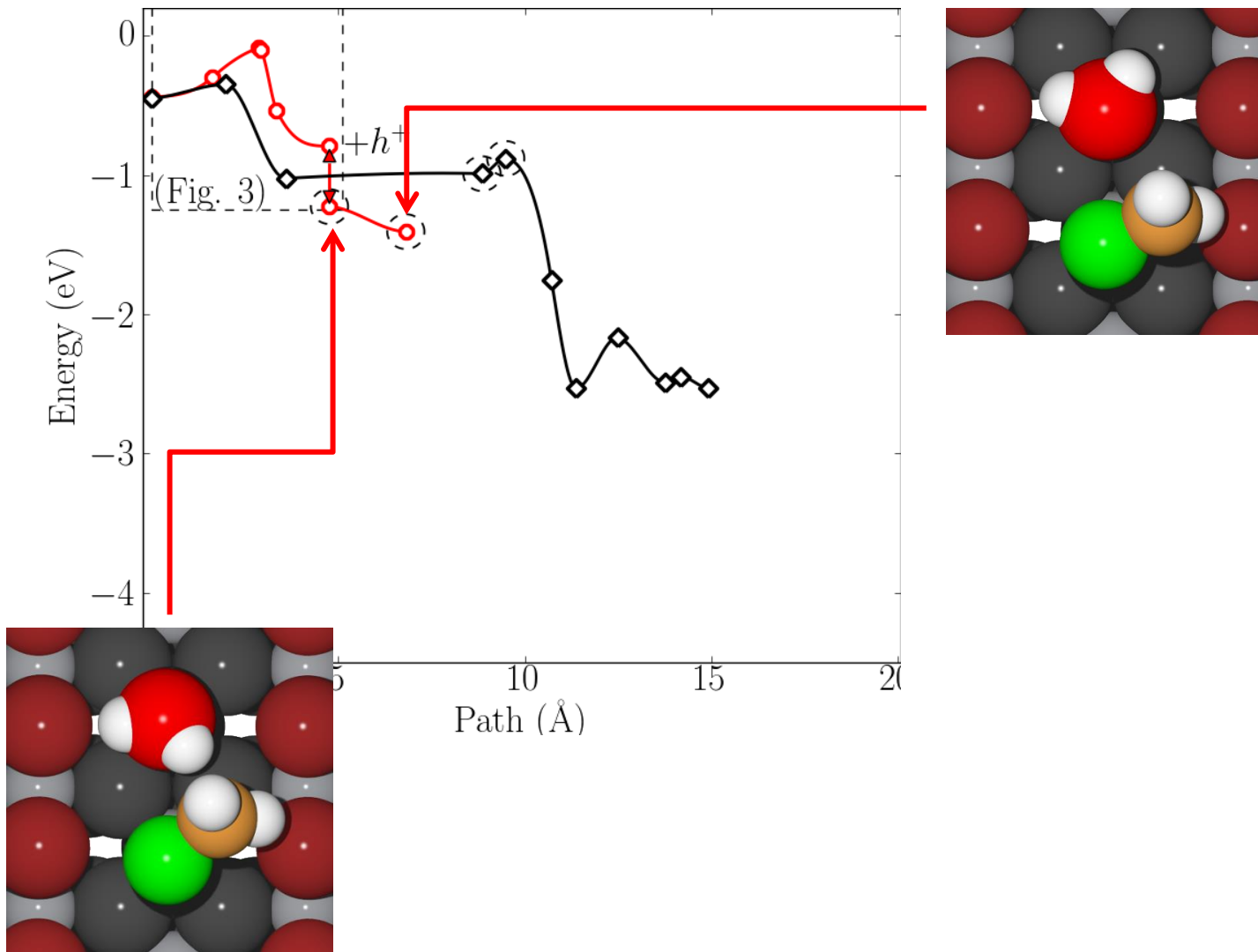
# Complete Mechanism



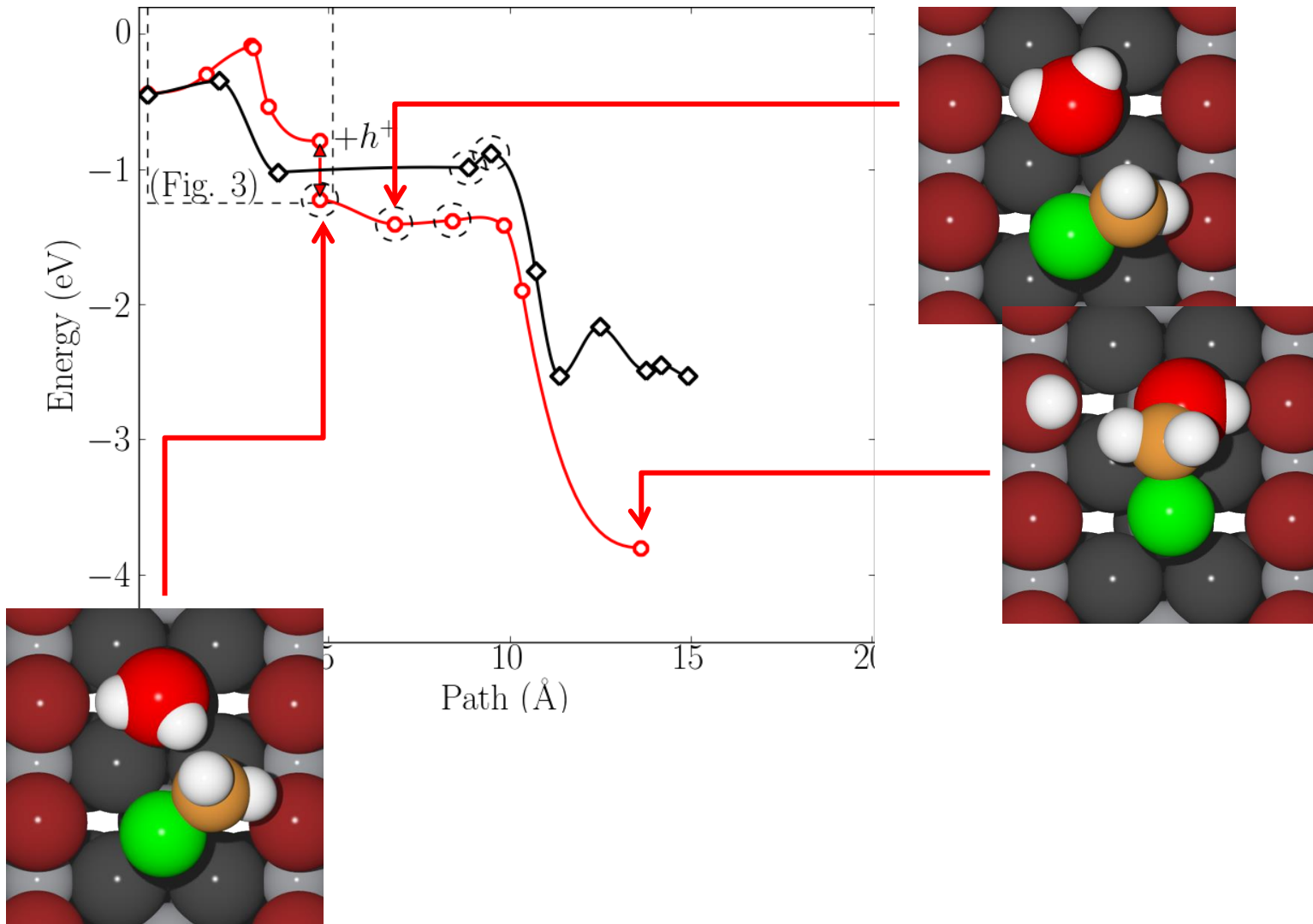
# Complete Mechanism



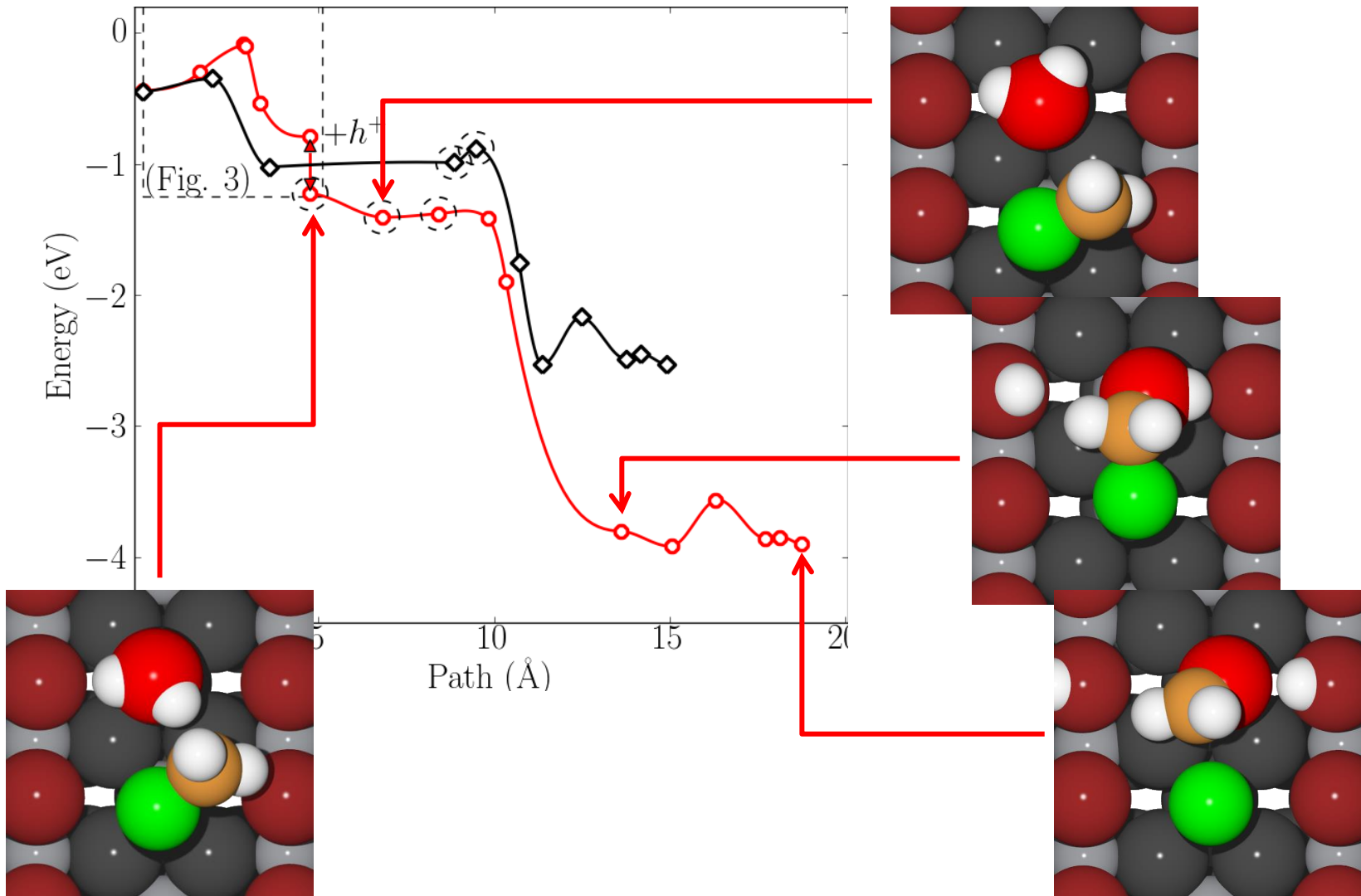
# Complete Mechanism



# Complete Mechanism

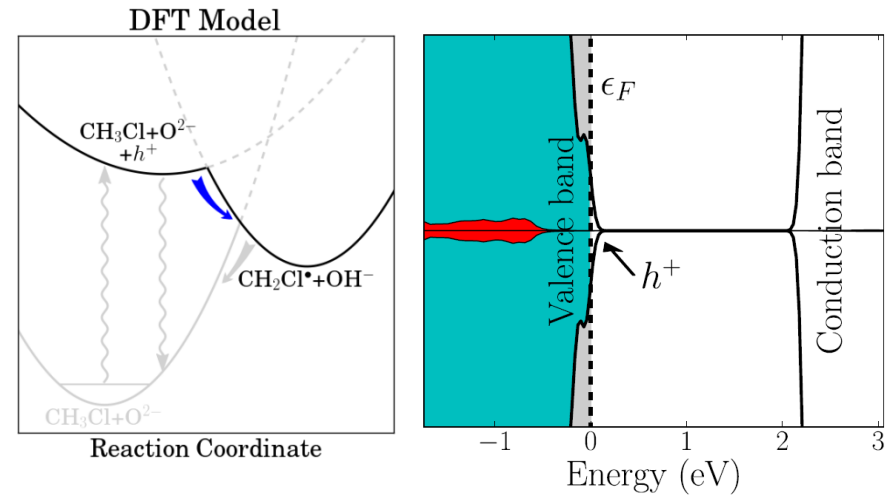


# Complete Mechanism



# Conclusion

- DFT approach

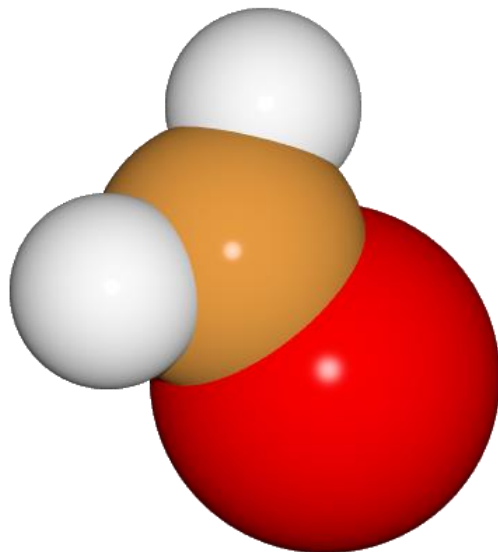


- Holes needed to oxidize  $\text{CH}_3\text{Cl}$
- $\text{O}_t$  ( $\text{OH}_t$ ) promotes photo-oxidation

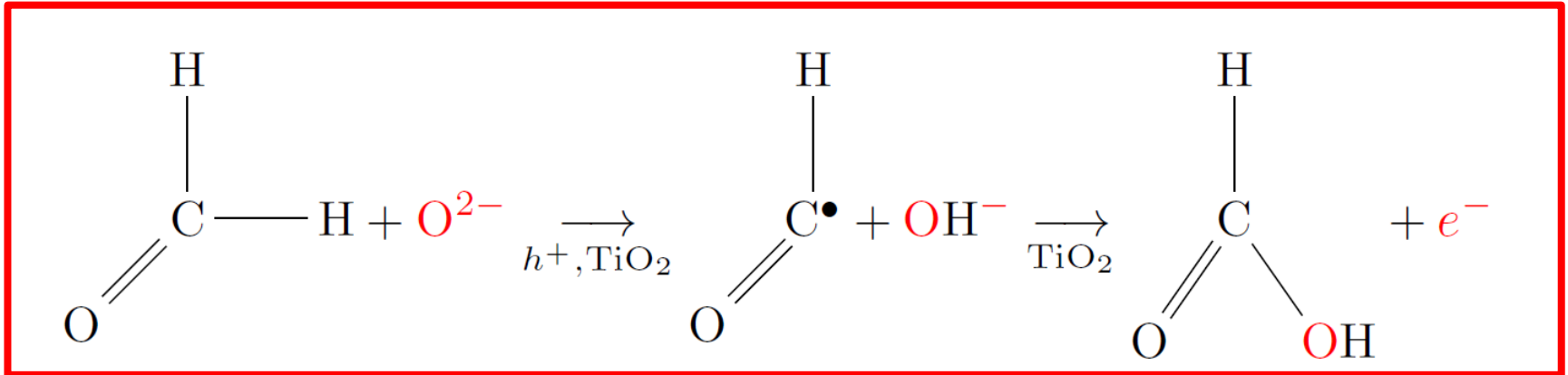




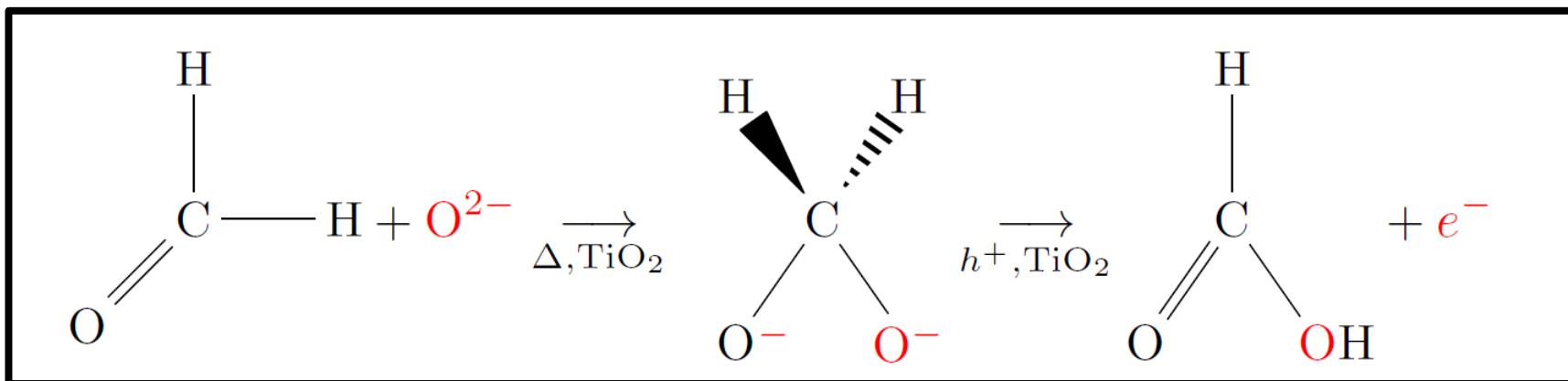
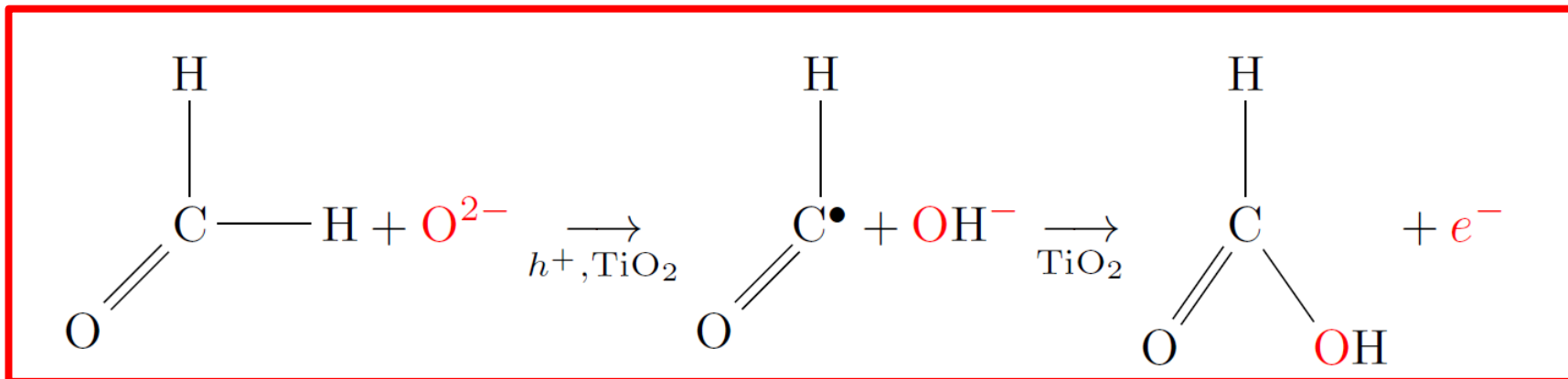
# Directing Photo-Oxidation of CH<sub>2</sub>O



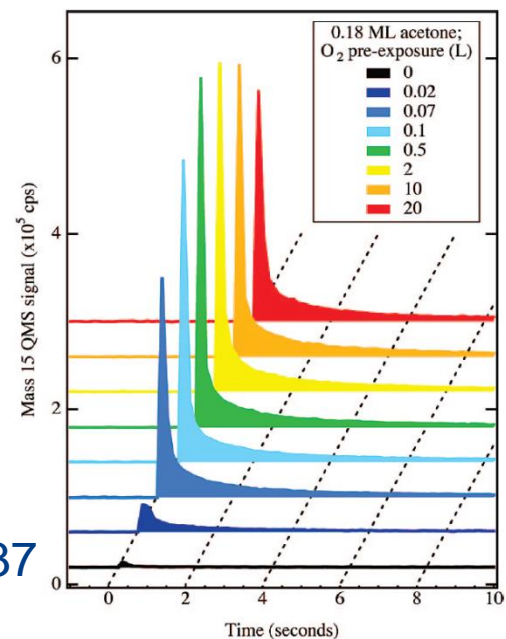
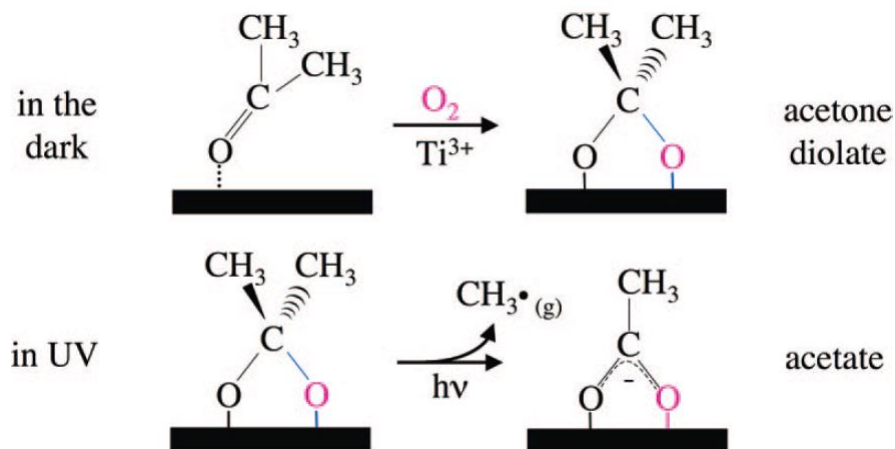
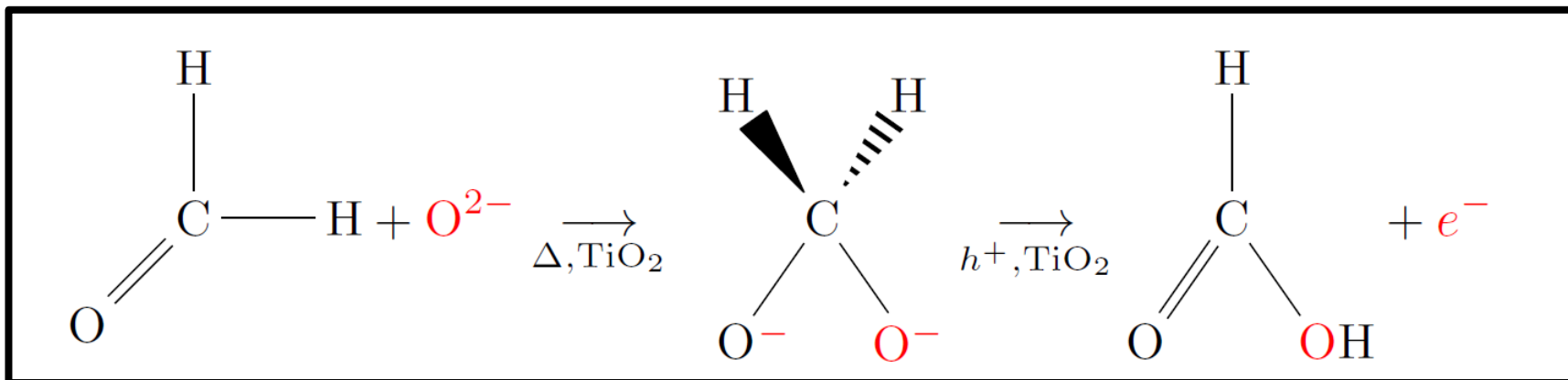
# Possible Mechanism



# Possible Mechanism

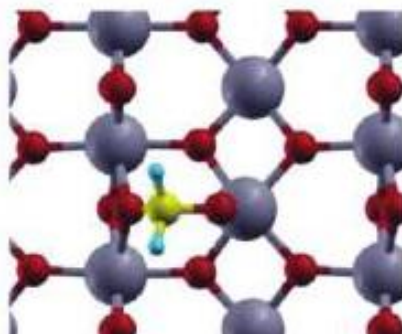
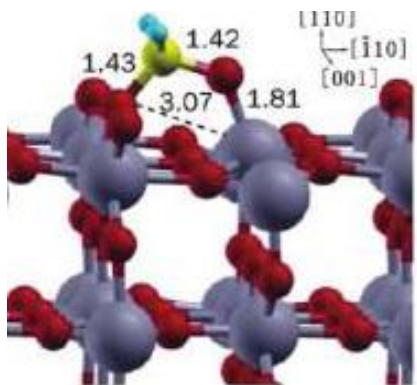
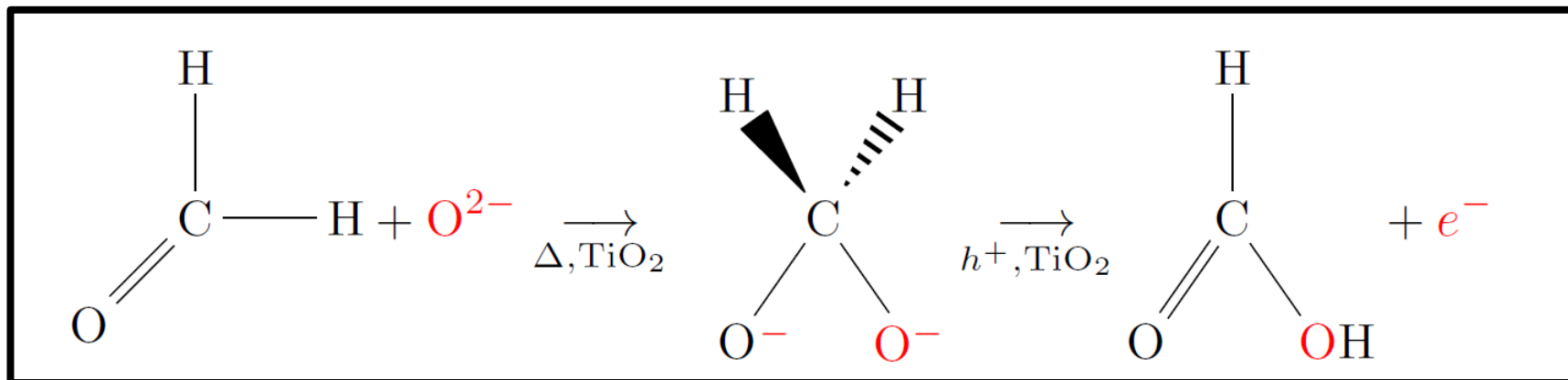


# Possible Mechanism



M. A. Henderson, J. Phys. Chem. C, 112, (2008) 11437

# Possible Mechanism



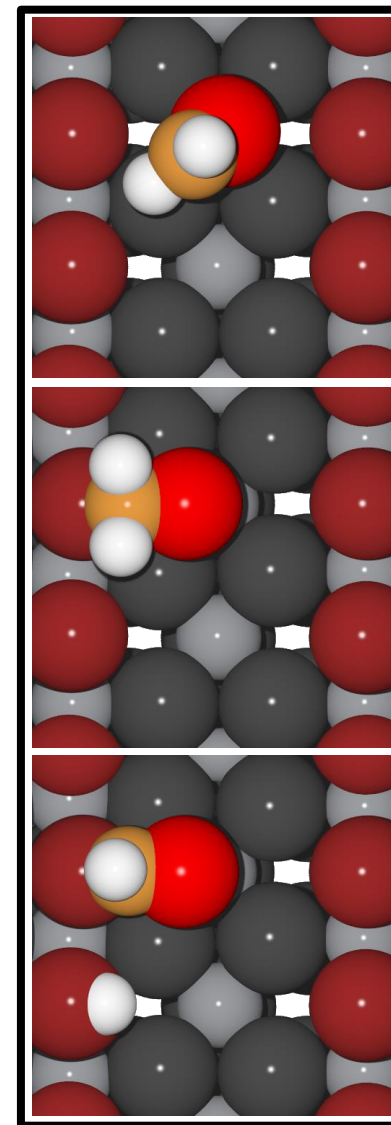
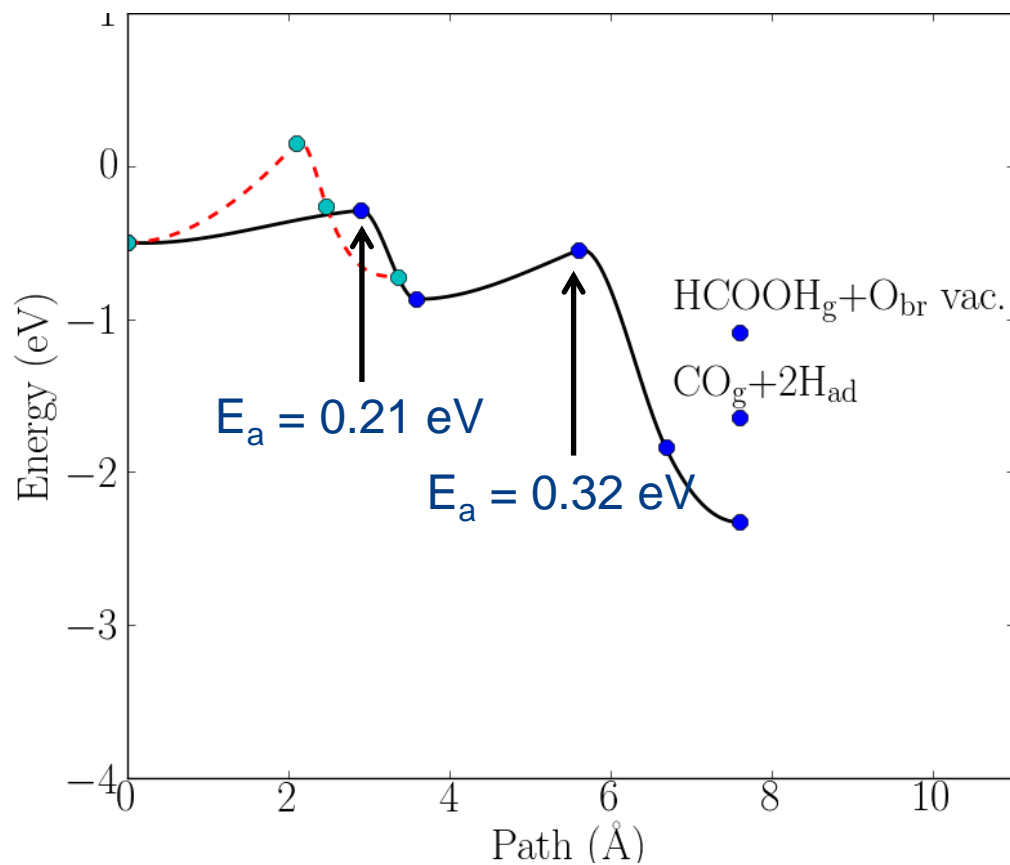
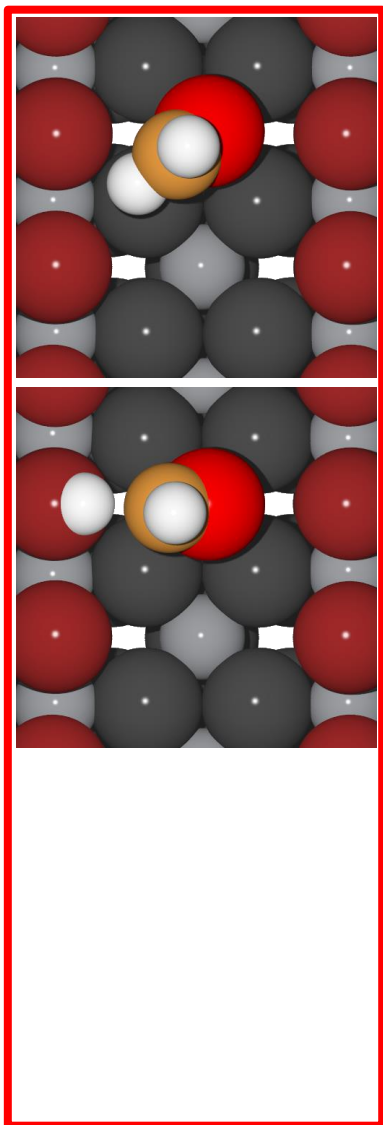
$E_{\text{ads}}$  (eV)

1.10

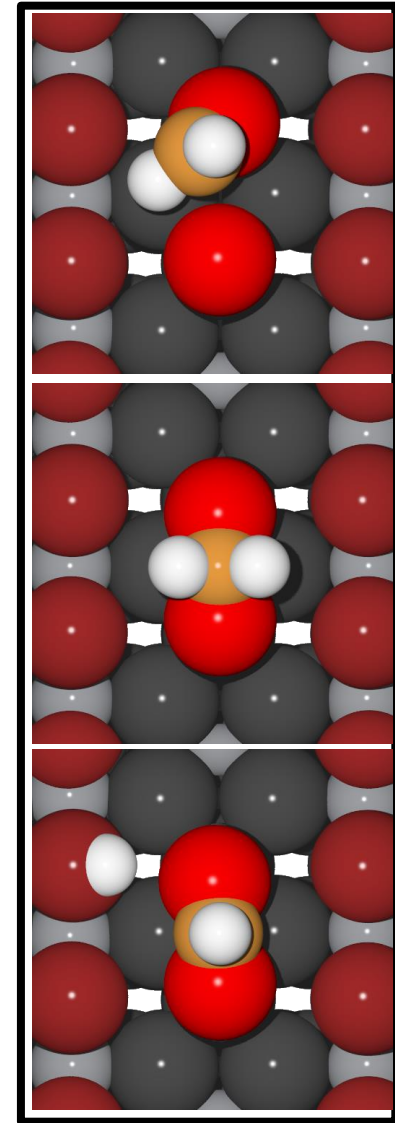
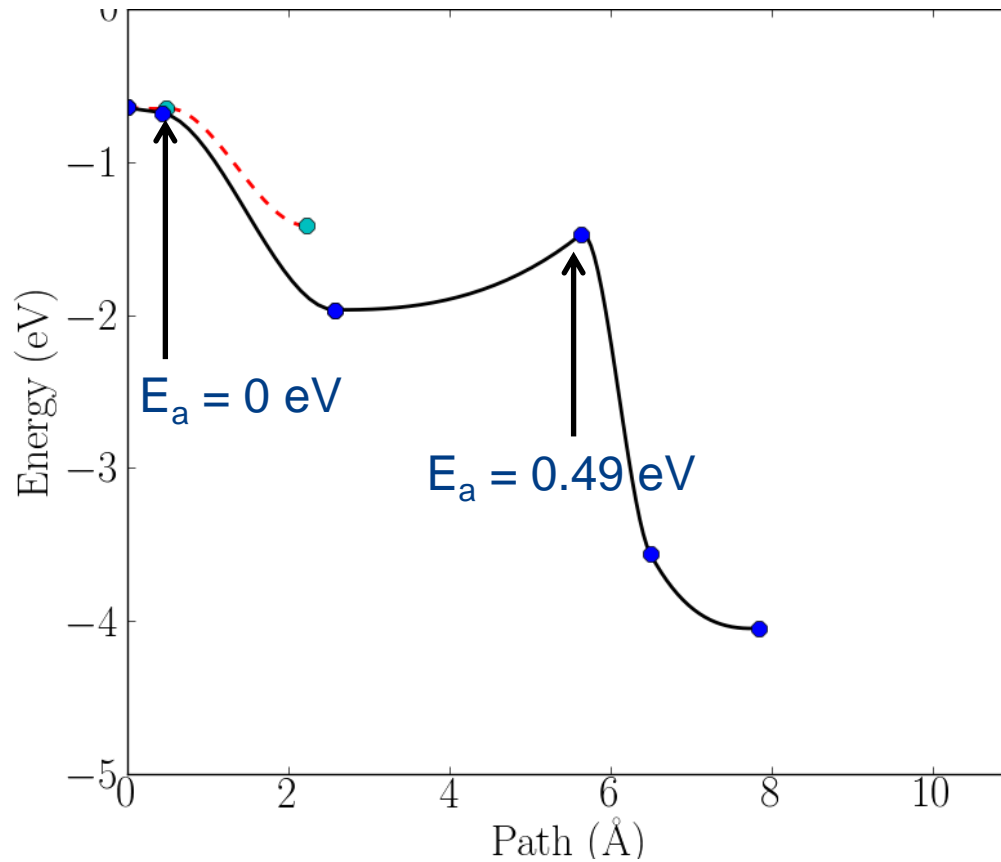
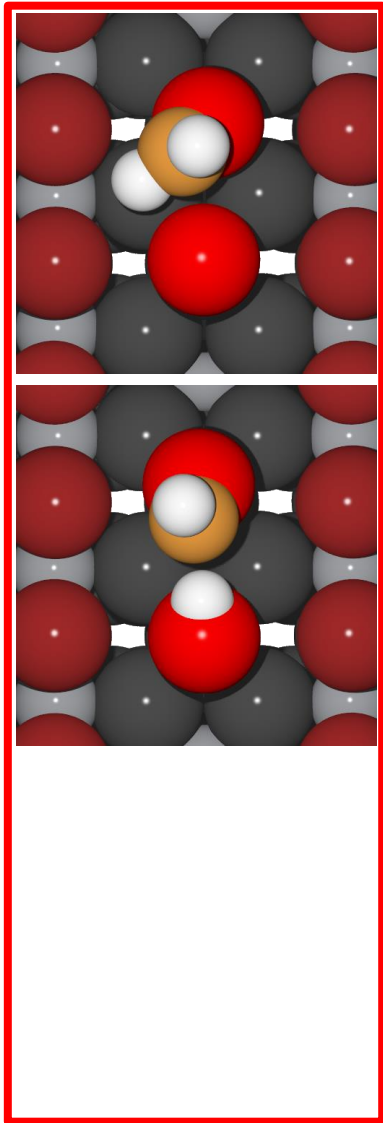
0.56

H. Liu, et al., J. Phys. Chem. C, 116, (2012) 8044

# Photo-Oxidation with $O_{br}$

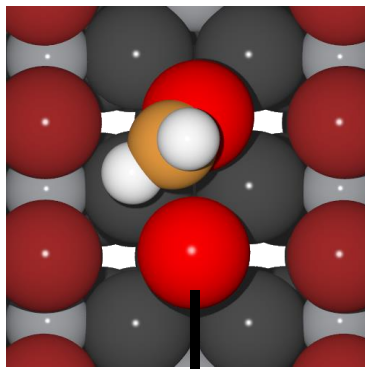


# Photo-Oxidation with $O_t$

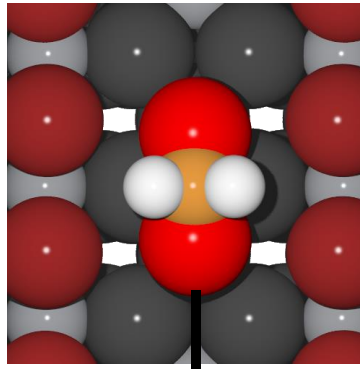




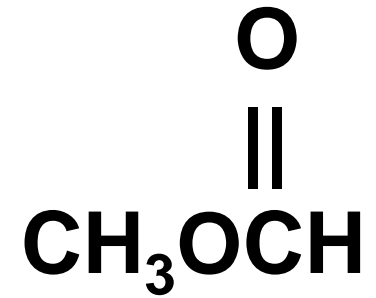
# Photo-Oxidation with CH<sub>3</sub>O?



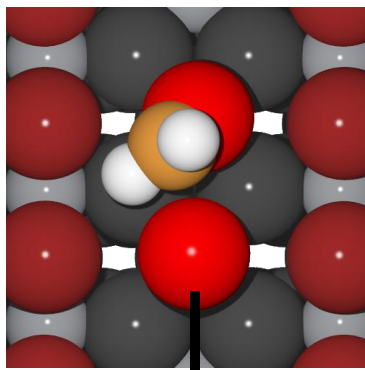
CH<sub>3</sub>



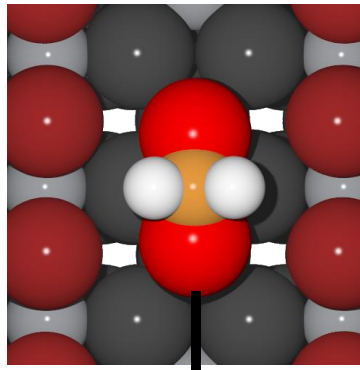
CH<sub>3</sub>



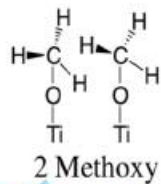
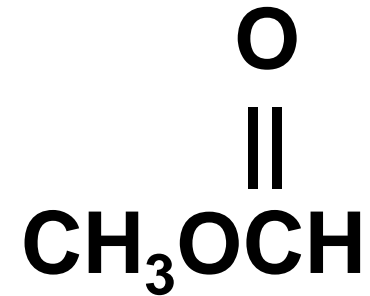
# Photo-Oxidation with CH<sub>3</sub>O?



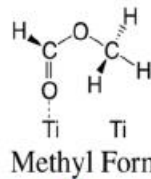
CH<sub>3</sub>



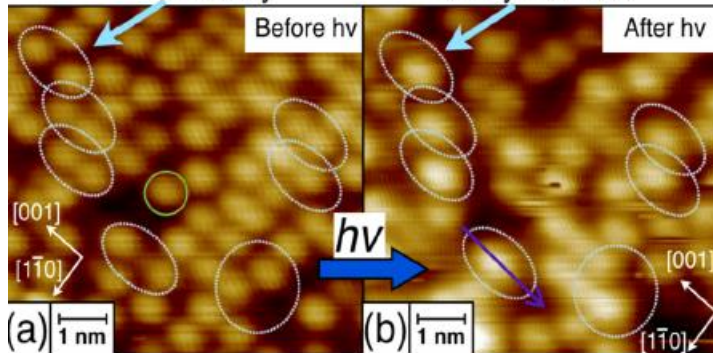
CH<sub>3</sub>



2 Methoxy



Methyl Formate



K. R. Phillips, et al., JACS, 135, (2013) 574

Done at 200 K