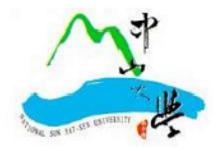# Investigation of Adsorption and Dissociation of the O_2 Molecule on W(111) Surface: A Density Functional Theory Study
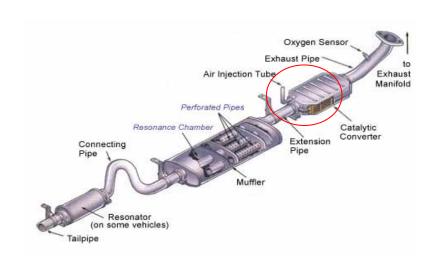
Reporter : Meng- Hsiung Weng

Advisor   Shin-Pon Ju

Department of Mechanical and Electro-Mechanical Engineering, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan
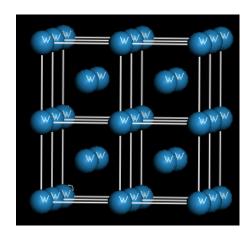
Catalysis

Three-Way Converter (TWC): Pt, Rh, Pd

Catalyst

$$Pt, Pd : CO \longrightarrow CO_2$$

$$HC \longrightarrow CO_2 + H2O$$

$$Rh \quad : NOx \longrightarrow N_2 + O_2$$

Catalysis of O_2 molecule on W metal surface.

Catalyst: **Tungsten (W)**

Potential Application of Tungsten Carbides as Electrocatalysts. 2. Coadsorption of CO and H₂O on Carbide-Modified W(111)

Henry H. Hwu, Brian D. Polizzotti, and Jingguang G. Chen*

Center for Catalytic Science and Technology, Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716

The decomposition of water and CO over clean and carbide-modified W(111) is studied by using temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), and auger electron spectroscopy (AES). On both clean and modified W(111) surfaces, the activity toward the decomposition of water is found to be significantly higher than Pt group metals. For the CO experiments, both molecular and dissociative adsorption are observed on W(111) and C/W(111). Approximately 52% and 10% of the adsorbed CO dissociates to produce atomic oxygen and carbon on W(111) and C/W(111), respectively. In contrast, CO molecules undergo reversible desorption on oxygen-modified C/W(111) at temperatures as low as 242 K. Finally, coadsorption experiments of water and CO on C/W(111) show that the presence of surface hydroxyls hinders the adsorption of CO, and that only trace amount of gas-phase CO₂ is detected.
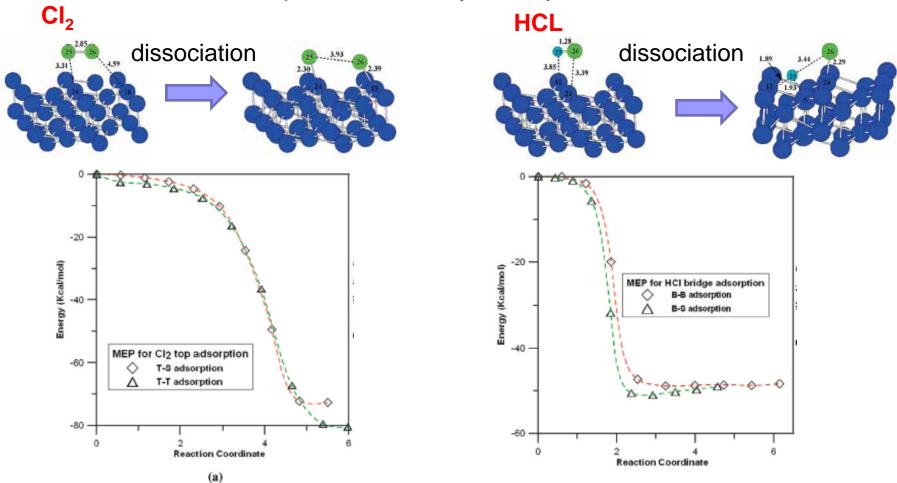
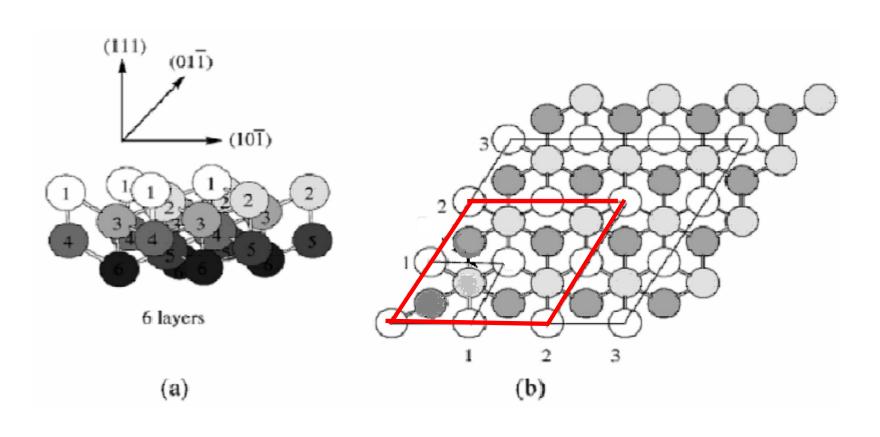# Adsorption and Dissociation of the HCl and Cl$_2$ Molecules on W(111) Surface: A Computational Study

Hui-Lung Chen,[†] Shin-Pon Ju,*,[‡] Hsin-Tsung Chen,[§] Djamaladdin G. Musaev,*,[†] and M. C. Lin*,[†,§]

Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, Department of Mechanical and Electro-Mechanical Engineering, Center for Nanoscience and Nanotechnology, National Sun-Yat-Sen University Kaohsiung, Taiwan 804, and Center for Interdisciplinary Molecular Science, Institute of Molecular Science, National Chiao Tung University, Hsinchu, Taiwan 300
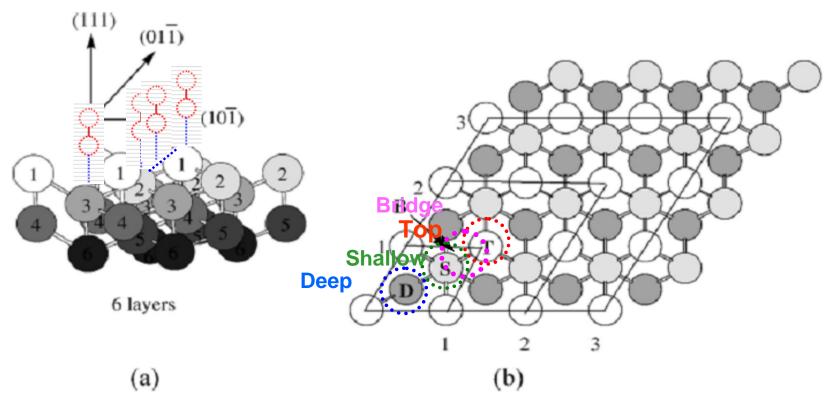
(a)

Simulation model for W(111)

Side view   **Top view**

Adsorbed sites

(a)

(b)

On top (T): On the top of the first layer W1 atom.

Bridge (B): On between the first layer W1 and second layer W2 atoms.

3-fold-Deep (D) : On the top of the third layer W3 atom.

3-fold-Shallow (S): On the top of the second layer W2 atom.

DFT calculation:

Package : VASP

Functional: rPBE

Cutoff energy : 400 eV

Spin polarization

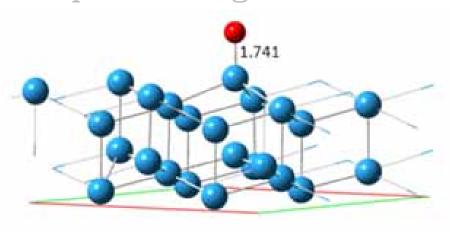Energy convergence : $1 * 10^{-4} eV$

Bulk W:

Bulk W	*Lattice constants($\mathring{A}$)*	*W-W distance($\mathring{A}$)*
This work	*3.170*	*2.745-2.754*
Experiment value	*3.165[a]*	*2.741[a]*

a. Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phase*, 2nd ed.; ASM International: Materials Park, OH, 1991.

O_2 molecule:

O_2	*Bond length($\mathring{A}$)*
This work	*1.23*
Experiment value	*1.21*

Optimized geometries of adsorbed O atom on W(111)
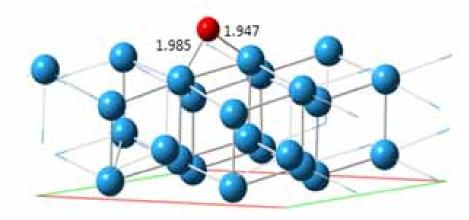
Top (**T**)

Bridge (**B**)
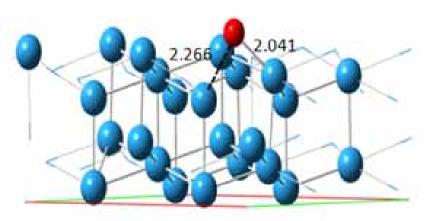
3-fold-shallow (**S**)

3-fold-deep (**D**)

Optimized Structural Parameters and Adsorption Energies[a] of O atoms adsorbed on W (111) surface.

	Bond length O-W (Å)	Adsorption energy
top (**T**)	1.741	- 155.54
bridge (**B**)	1.985, 1.947	- 154.17
3-fold-deep(**S**)	2.283	- 146.80
3-fold-shallow (**D**)	1.819	- 137.21

[a] The unit of energy is kcal/mol.

Vibrational Frequencys[a] of O adsorbed on the W(111) surface:

Site	V(W-O)
On-top (**T**)	884
Bridge (**B**)	586
3-fold-deep(**D**)	524
3-fold-deep(**D**)	643

Experiment value: 400 – 800cm^{-1}
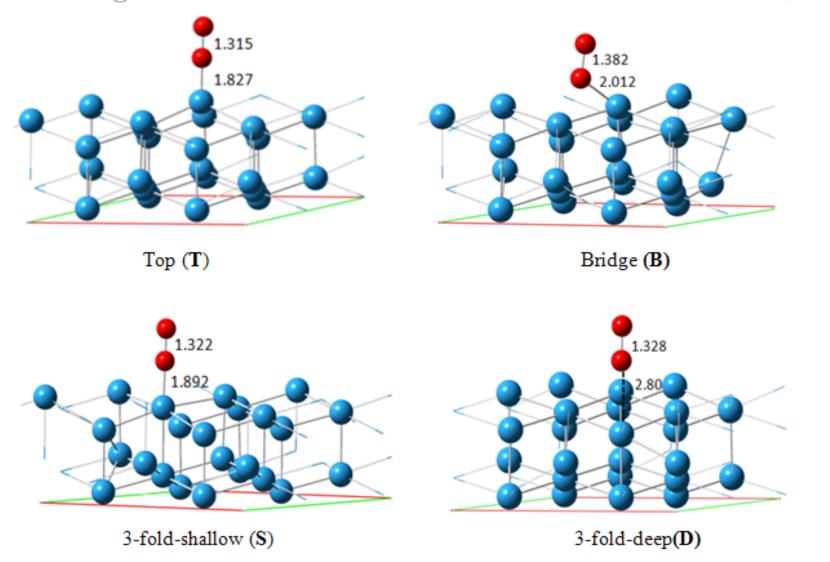
[a]The unit of Vibrational Frequencys is wavenumber(cm-1)

O2 on W(111) surface

End –On:

O
|
O
⋮
—— W —— W ——

Side –On:

O——O
⋮
—— W —— W ——

End- On:

Optimized geometries of adsorbed O2 molecule on W(111)

Top (**T**)

Bridge (**B**)

3-fold-shallow (**S**)

3-fold-deep(**D**)
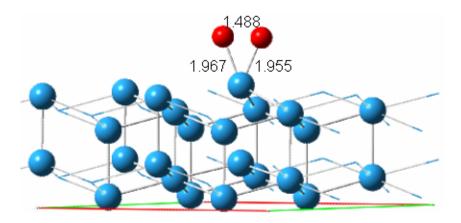
Optimized Structural Parameters and Adsorption Energies[a] of O2 atoms adsorbed on W (111) surface.

	Bond length O_a-W (Å)	Bond length O-O (Å)	Adsorption energy
top (**T**)	1.827	1.315	-44.30
bridge (**B**)	2.012	1.382	-23.4
3-fold-shallow (**S**)	1.892	1.322	-24.2
3-fold-deep (**D**)	2.805	1.328	14.30

[a] The unit of energy is kcal/mol.

Side- On

On-Top**(T)**

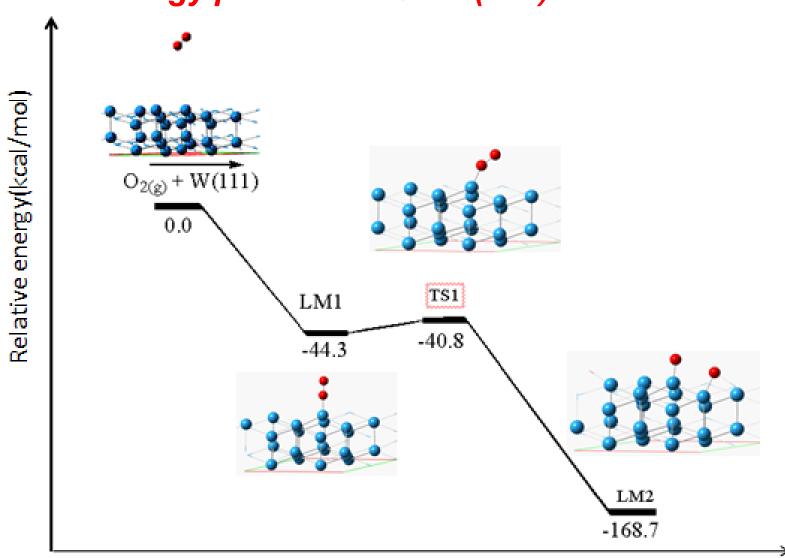| Side-on	Length(W-O) (Å)	Length (O-O) (Å)	E_{ad} (Kcal/mol)
On-Top (T)	1,955 ; 1.967	1.488	-65.55
Bridge (B)	N/A	N/A	N/A
Deep (D)	N/A	N/A	N/A
Shallow (S)	N/A	N/A	N/A

Dissociation of O_2 on W(111) surface.

Reaction:

$$O2 + W(111) \rightarrow O/W(111)/O$$

Nudged elastic band (NEB) Method:

1. 16 Images

2. Energy convergence : $1*10^{-4}$ eV

3. Force convergence: 0.04 eV/A

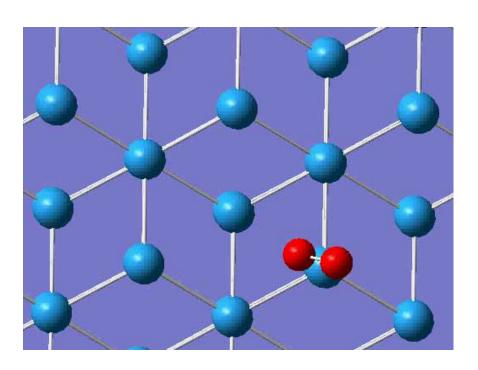# Potential energy profiles for O2-W(111)
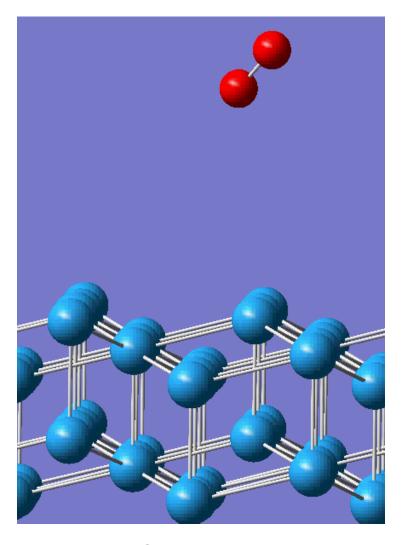
DFT –MD simulation

Temperature: 10 K

canonical ensemble (NVT)

Time step: 2fs

First O2 deposition: case1

Side view

Top view

First O2 deposition: case1
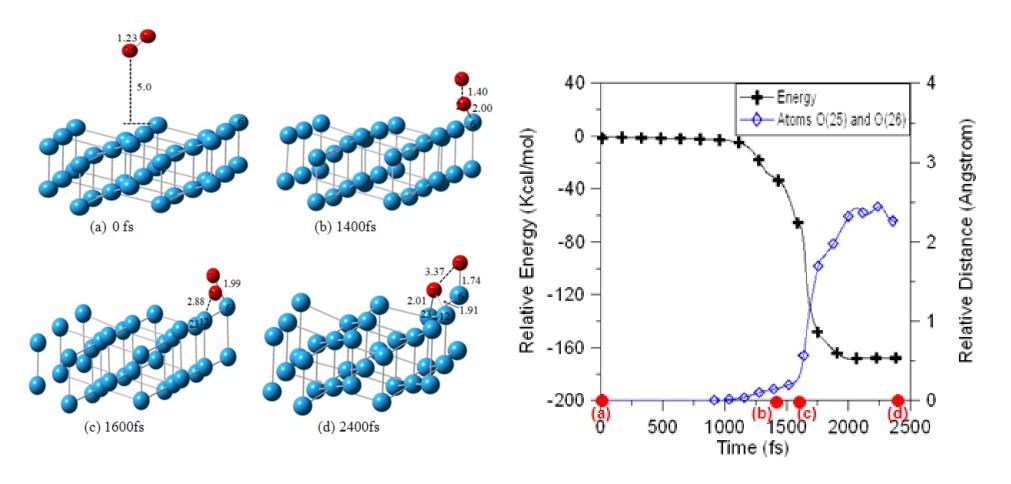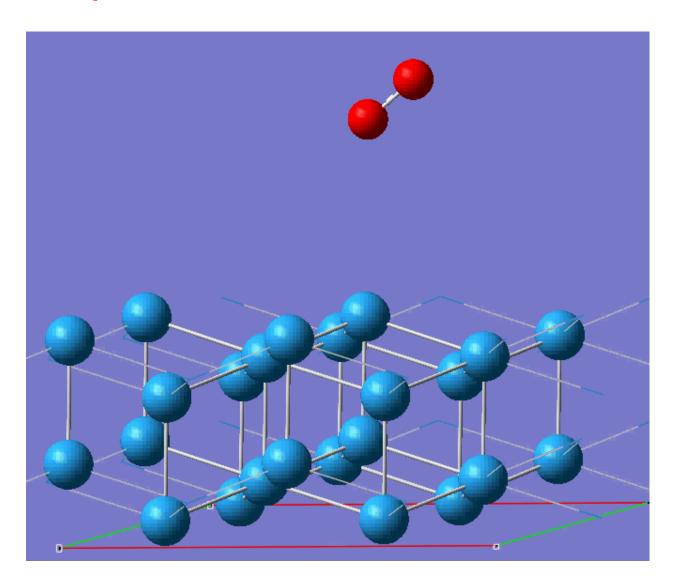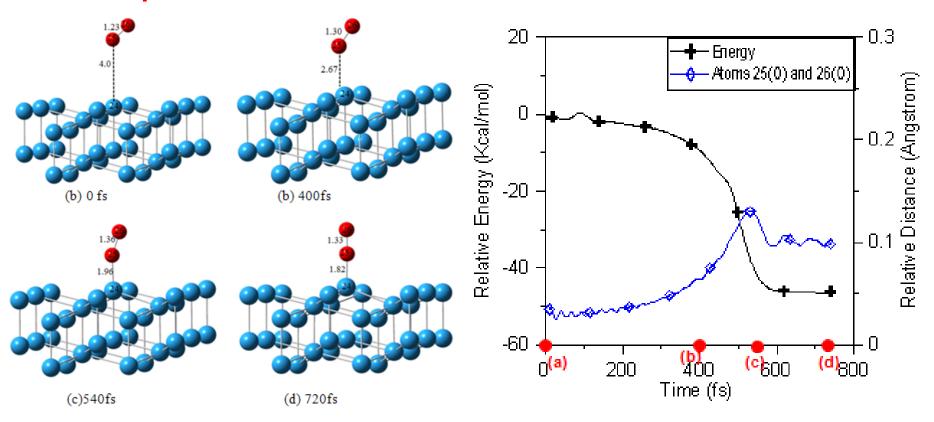

Fig. Snapshots of the O_2 dissociation on the W(111) surface at (a) 0, (b) 1400, (c) 1600, and (d) 2400 fs. The blue and red spheres represent W, and O, respectively. The bond lengths are given in Å.
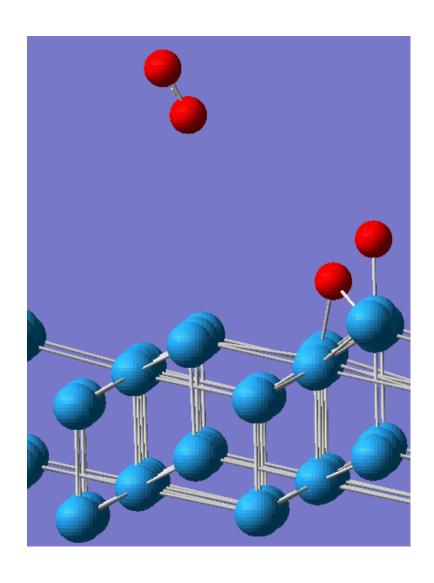
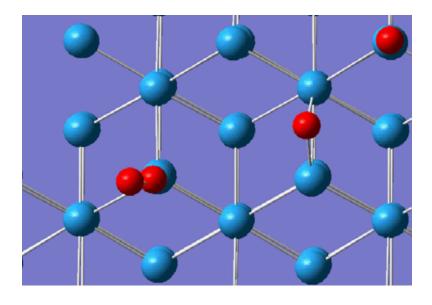# First O2 deposition: case2

First O2 deposition: case2

Figure 4. Snapshots of the O_2 adsorption on the W(111) surface at (a) 0, (b) 400, (c) 540, and (d) 720 fs. The blue and red spheres represent W, and O, respectively. The bond lengths are given in Å.

Second O2 deposition: Without dissociation
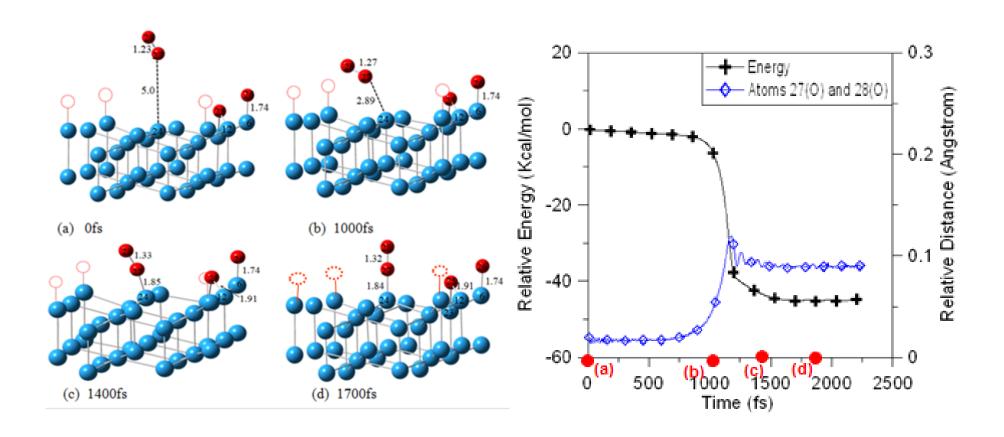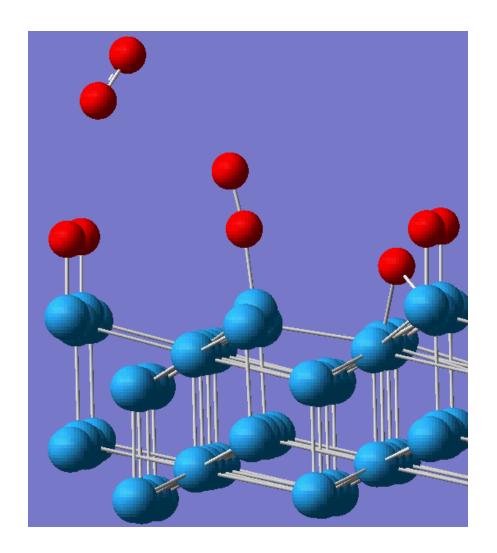
Second O2 deposition

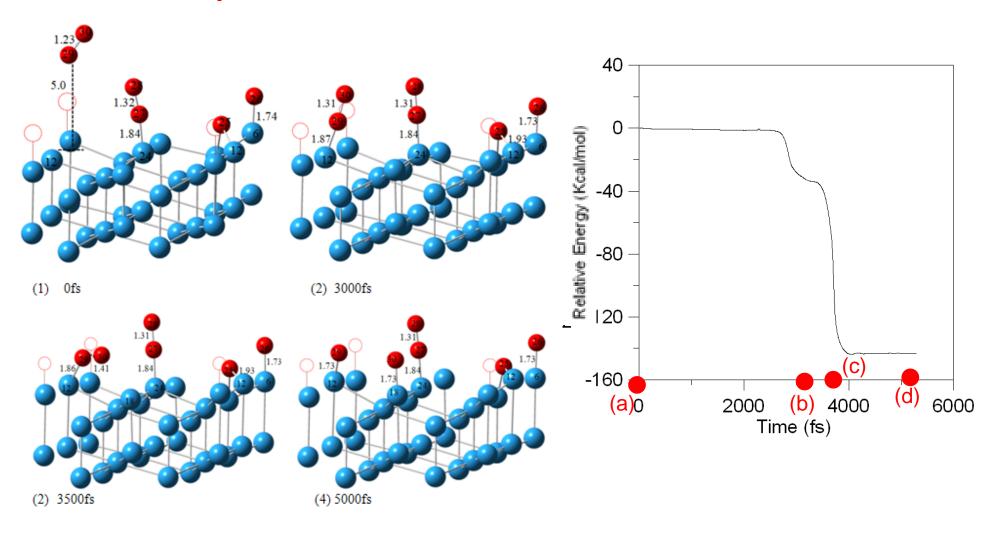**Fig.** Snapshots of the second O2 molecules on the W(111) surface after the dissociation of first O2 molecules at
(a) 0, (b) 1000, (c) 1400, and (d) 1700 fs. The blue and Red spheres represent W, and O, respectively.
(b) The bond lengths are given in Å. (red dash circles respect the oxygen atoms by repeat of periodic boundary)

(1) 0fs

(2) 3000fs

(2) 3500fs

(4) 5000fs

Conclusions:

1. The preferable sites of O atom and O_2 molecules on W(111) surface is top site. the calculated adsorption energy are -158.8 , -46.3 kcal/mol for O and O_2 respectively.

2. The MEP profile from NEB calculations indicate that there is small barrier for the dissociation of O2 molecule.

3. O_2 molecule will always be dissociated by inclined deposition at temperature of 10K, but case of O_2 molecule without dissociation can still be found to adsorb at top site without rotation and angular momentum

4. O2 molecule prefers initially to adsorb at top site and the neighbor environment of O_2 molecule after adsorption determine whether dissociation occurs.

Thank You!!