Water reactivity with Tungsten Oxides: H_2 Production and Kinetic Traps

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Intro & Methods

- Goals
  - Understand chemistry of water—cluster interactions

- Experimental Collaboration
  - Mass Spec/PES experiments conducted in Prof. Caroline C. Jarrold's lab

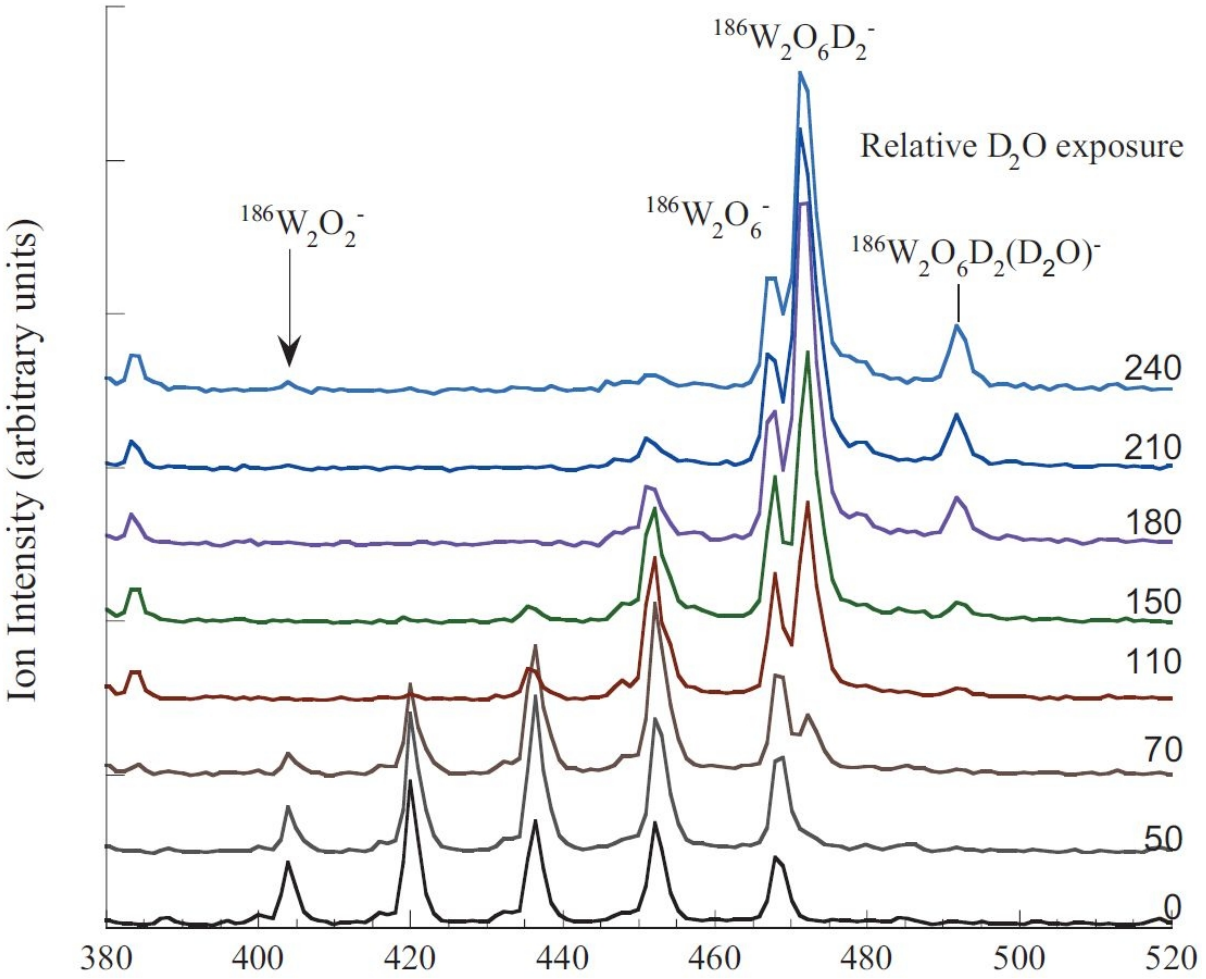
- Methods
  - DFT Calculations : typically B3LYP used with a triple zeta basis set and ECP

Experimental Observations

- Sequential Oxidation

$$W_2O_y^- + H_2O \rightarrow W_2O_{y+1}^- + H_2$$

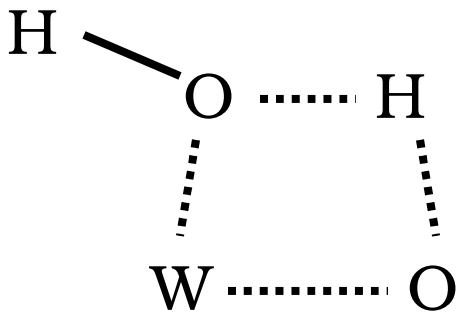
- Proceeds no further than y = 4 → 5



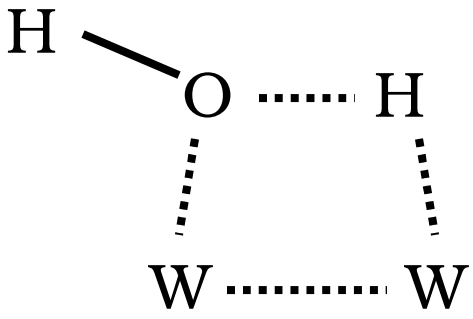
Rothgeb, JCP, 130, 124314, 2009

Initial Water Addition

- **Mode 1**
  - 2 hydroxyl groups



- **Mode 2**
  - 1 hydroxyl group
  - 1 hydride

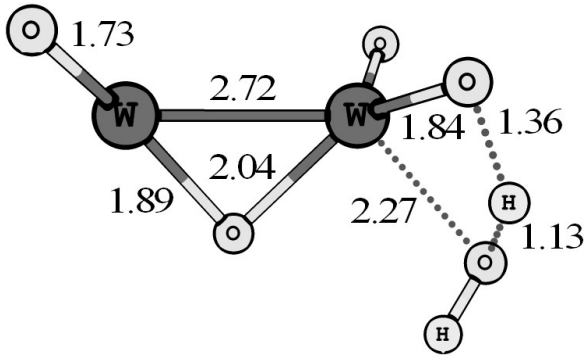


Initial Water Addition – Mode 1

$W_2O_4^-$

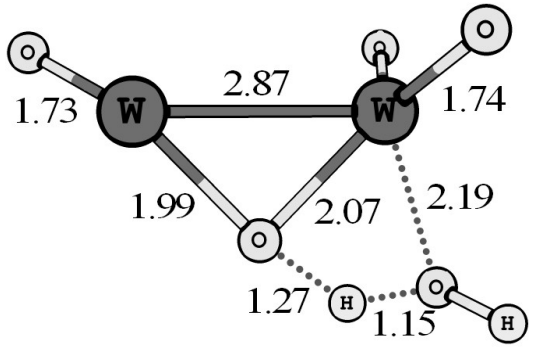
A

E(Complex) = --
E(Tran. State) = +22.5
E(Product) = −6.5



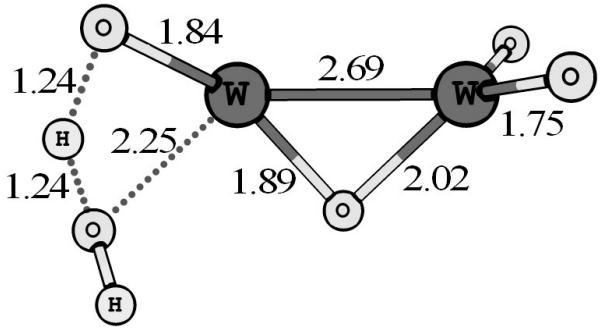
B

E(Complex) = --
E(Tran. State) = +9.9
E(Product) = −4.3



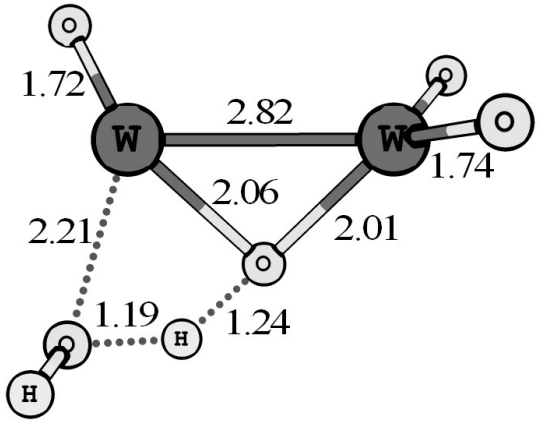
C

E(Complex) = +6.4
E(Tran. State) = +23.0
E(Product) = −18.8



D

E(Complex) = +5.7
E(Tran. State) = +7.2
E(Product) = −8.4



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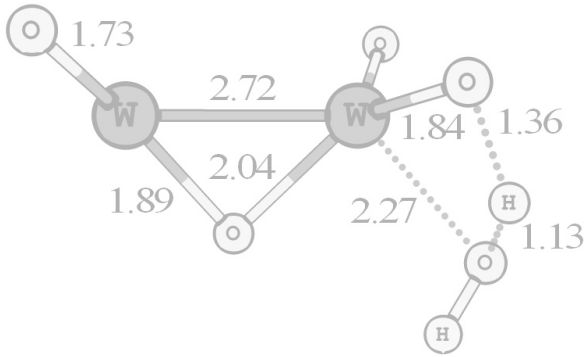

B

E(Complex) = --
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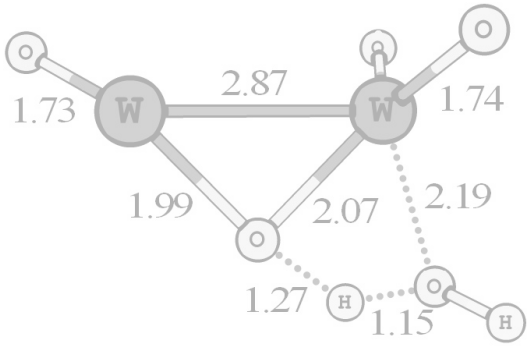
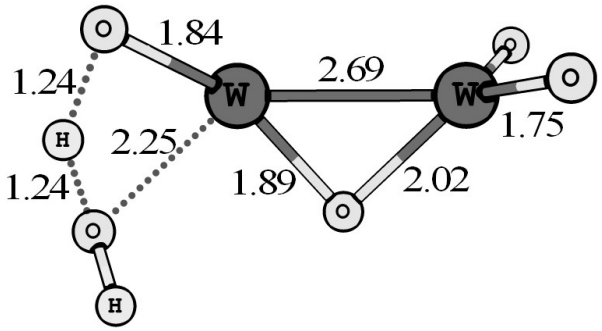
E(Product) = −4.3



C

E(Complex) = +6.4
E(Tran. State) = +23.0
E(Product) = −18.8



D

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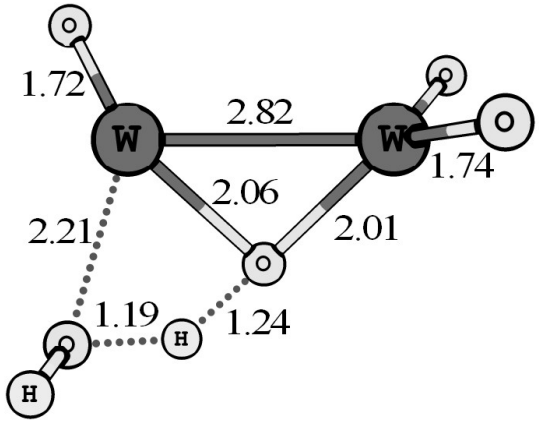
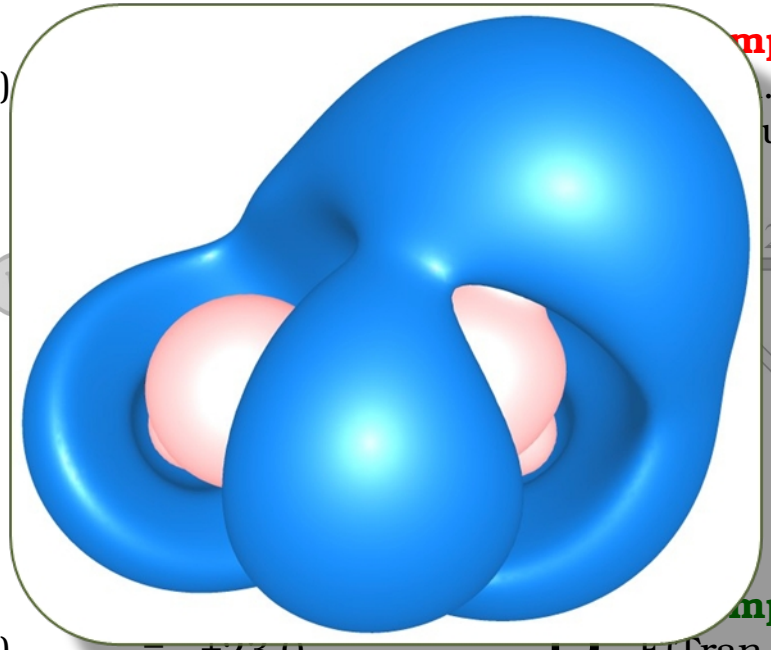
E(Product) = −8.4



Initial Water Addition – Mode 1

$W_2O_4^-$



A

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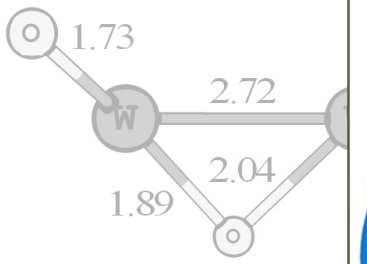
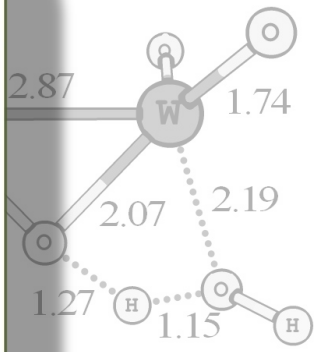
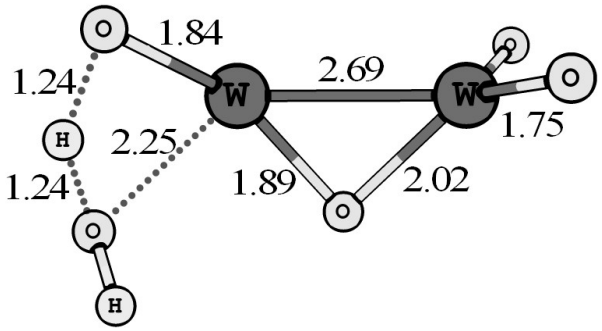




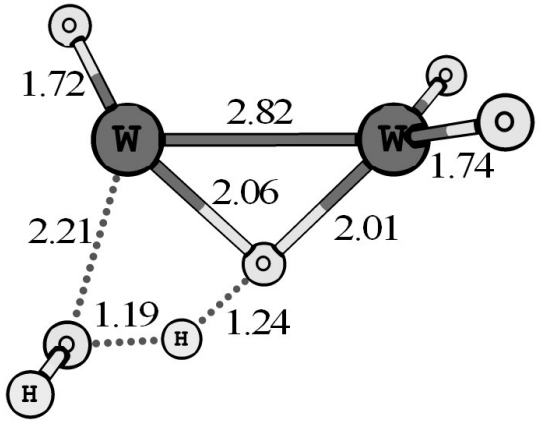
C

E(Complex) = +23.0
E(Tran. State) = −18.8
E(Product)



D

E(Complex) = +5.7
E(Tran. State) = +7.2
E(Product) = −8.4

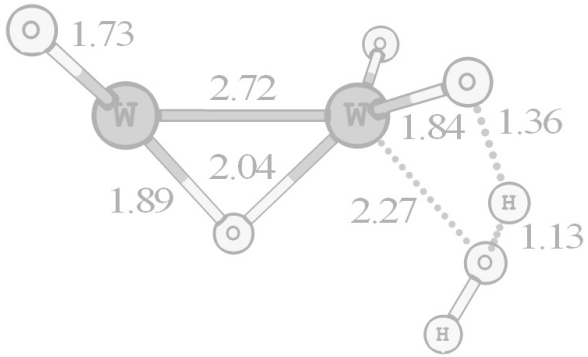


Initial Water Addition – Mode 1

$W_2O_4^-$

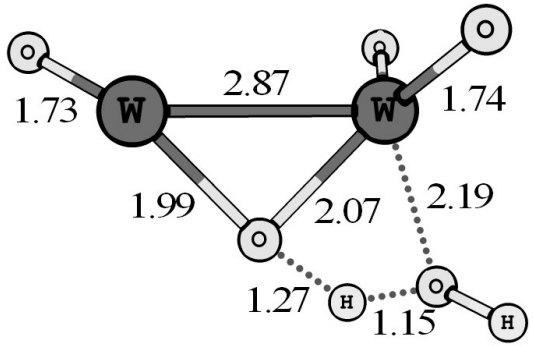
A

E(Complex) = --
E(Tran. State) = +22.5
E(Product) = −6.5



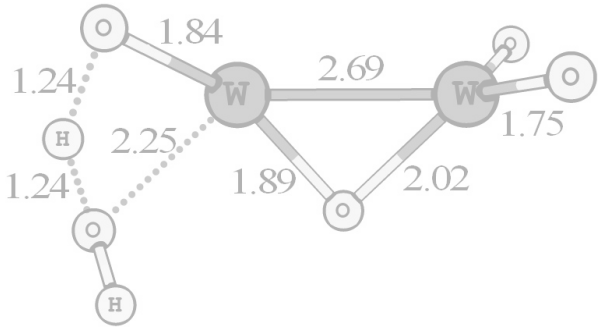
B

E(Complex) = --
E(Tran. State) = +9.9
E(Product) = −4.3



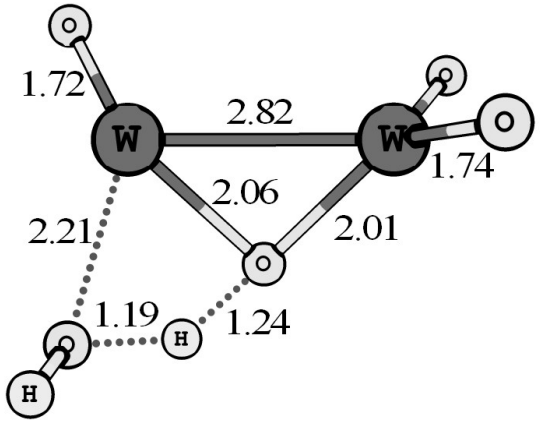
C

E(Complex) = +6.4
E(Tran. State) = +23.0
E(Product) = −18.8



D

E(Complex) = +5.7
E(Tran. State) = +7.2
E(Product) = −8.4

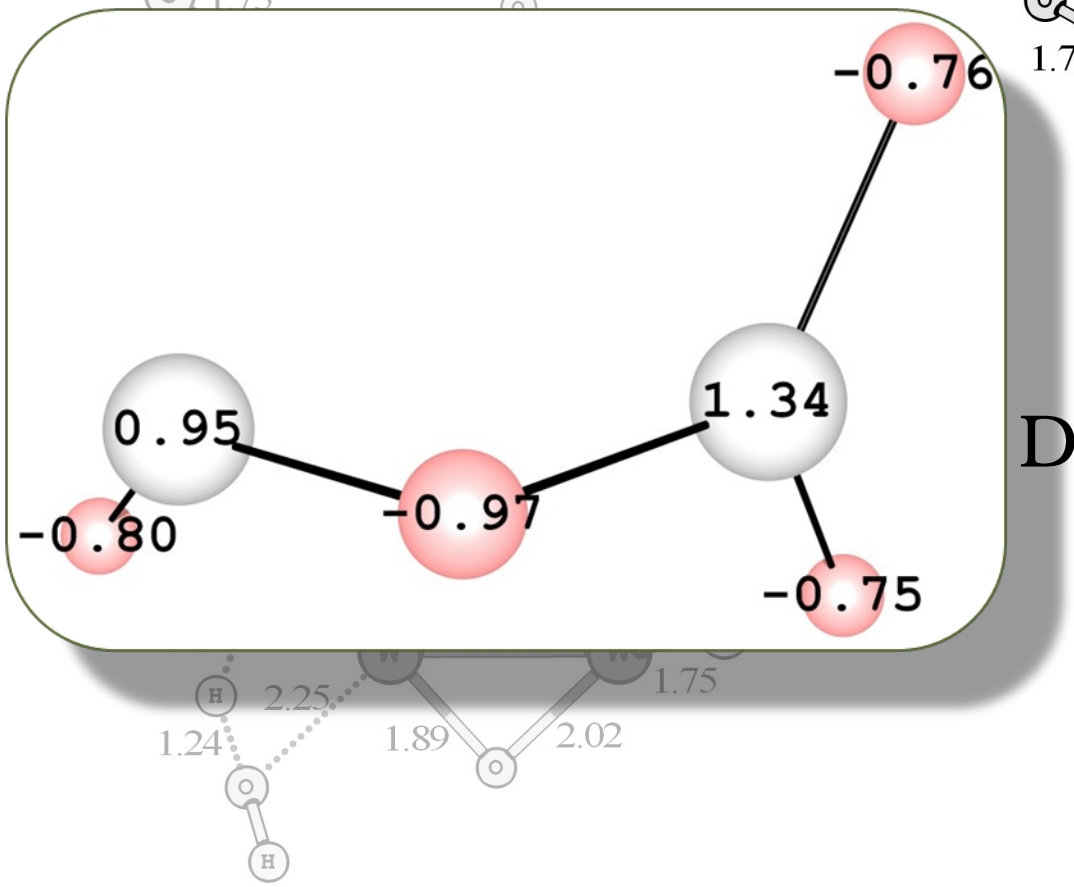


Initial Water Addition – Mode 1

$W_2O_4^-$

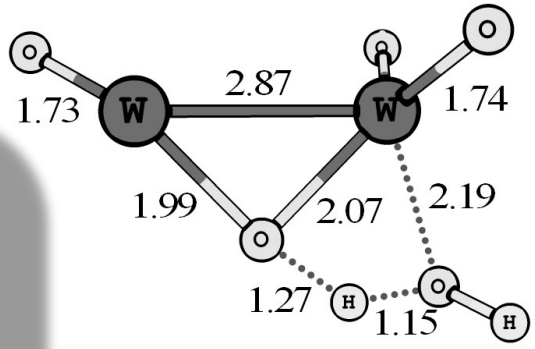
A

E(Complex) = --
E(Tran. State) = +22.5
E(Product) = −6.5



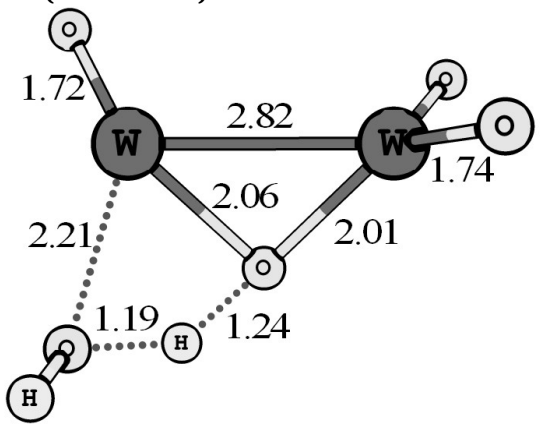
B

E(Complex) = --
E(Tran. State) = +9.9
E(Product) = −4.3



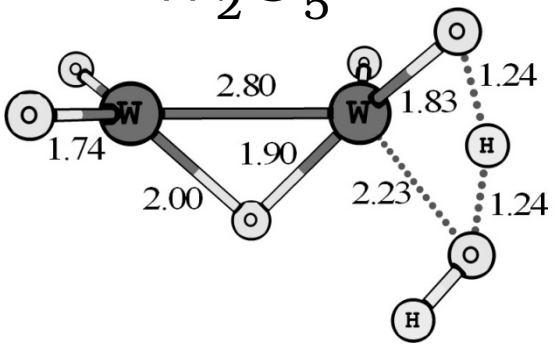
D

E(Complex) = +5.7
E(Tran. State) = +7.2
E(Product) = −8.4



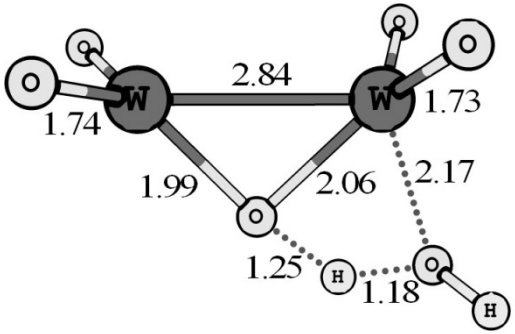
Initial Water Addition – Mode 1

$W_2O_5^-$



A

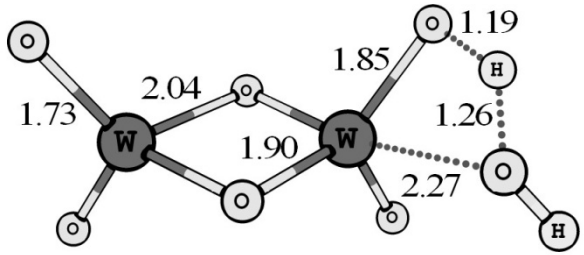
E(Complex)	=	+4.1
E(Tran. State)	=	+15.3
E(Product)	=	−13.0



B

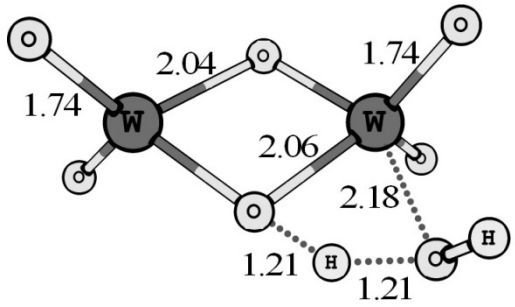
E(Complex)	=	+4.1
E(Tran. State)	=	+4.6
E(Product)	=	−9.6

$W_2O_6^-$



A

E(Complex)	=	+6.5
E(Tran. State)	=	+43.9
E(Product)	=	−7.7

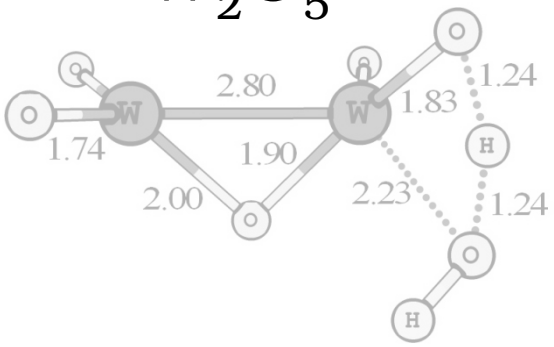


B

E(Complex)	=	+6.5
E(Tran. State)	=	+39.9
E(Product)	=	−1.5

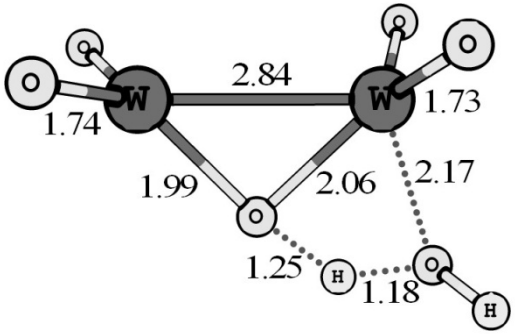
Initial Water Addition – Mode 1

$W_2O_5^-$



A

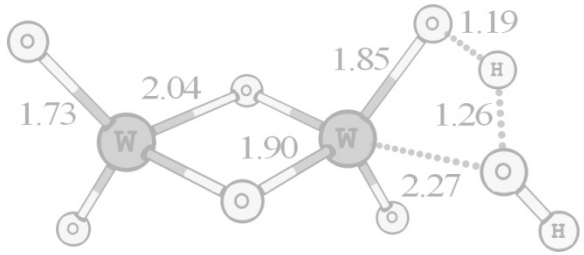
E(Complex) = +4.1
E(Tran. State) = +15.3
E(Product) = −13.0



B

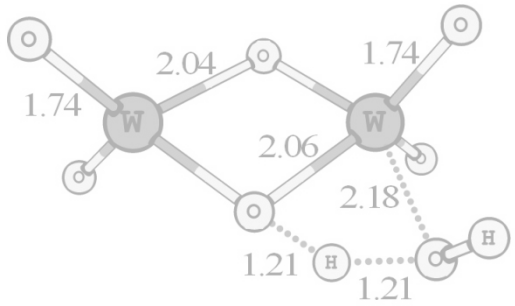
E(Complex) = +4.1
E(Tran. State) = +4.6
E(Product) = −9.6

$W_2O_6^-$



A

E(Complex) = +6.5
E(Tran. State) = +43.9
E(Product) = −7.7



B

E(Complex) = +6.5
E(Tran. State) = +39.9
E(Product) = −1.5

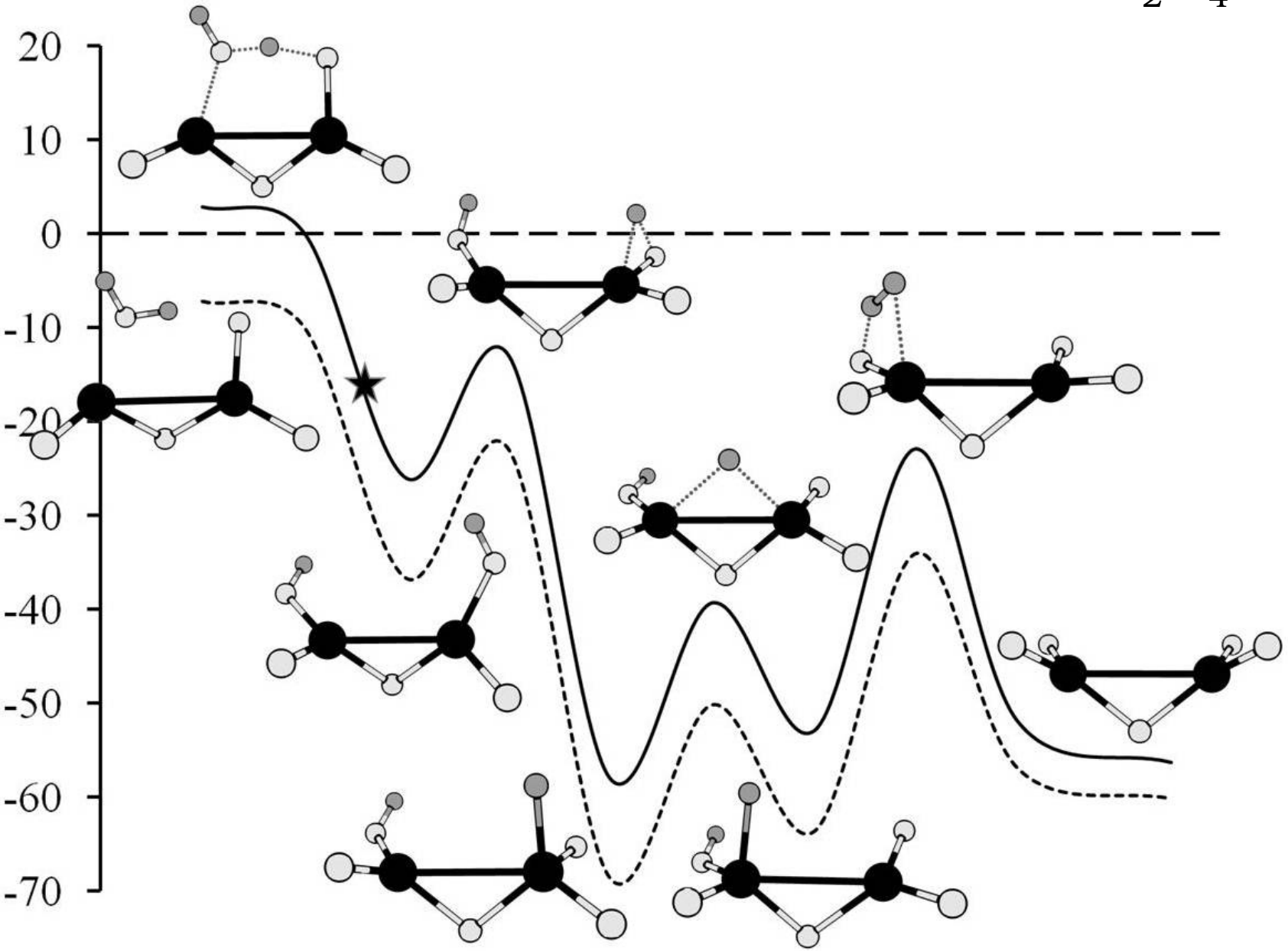
Initial Water Addition – Mode 1

- Both $W_2O_4^-$ and $W_2O_5^-$ clusters expected to react with water
- The $W_2O_6^-$ barriers high

Can we find H_2 elimination mechanisms?

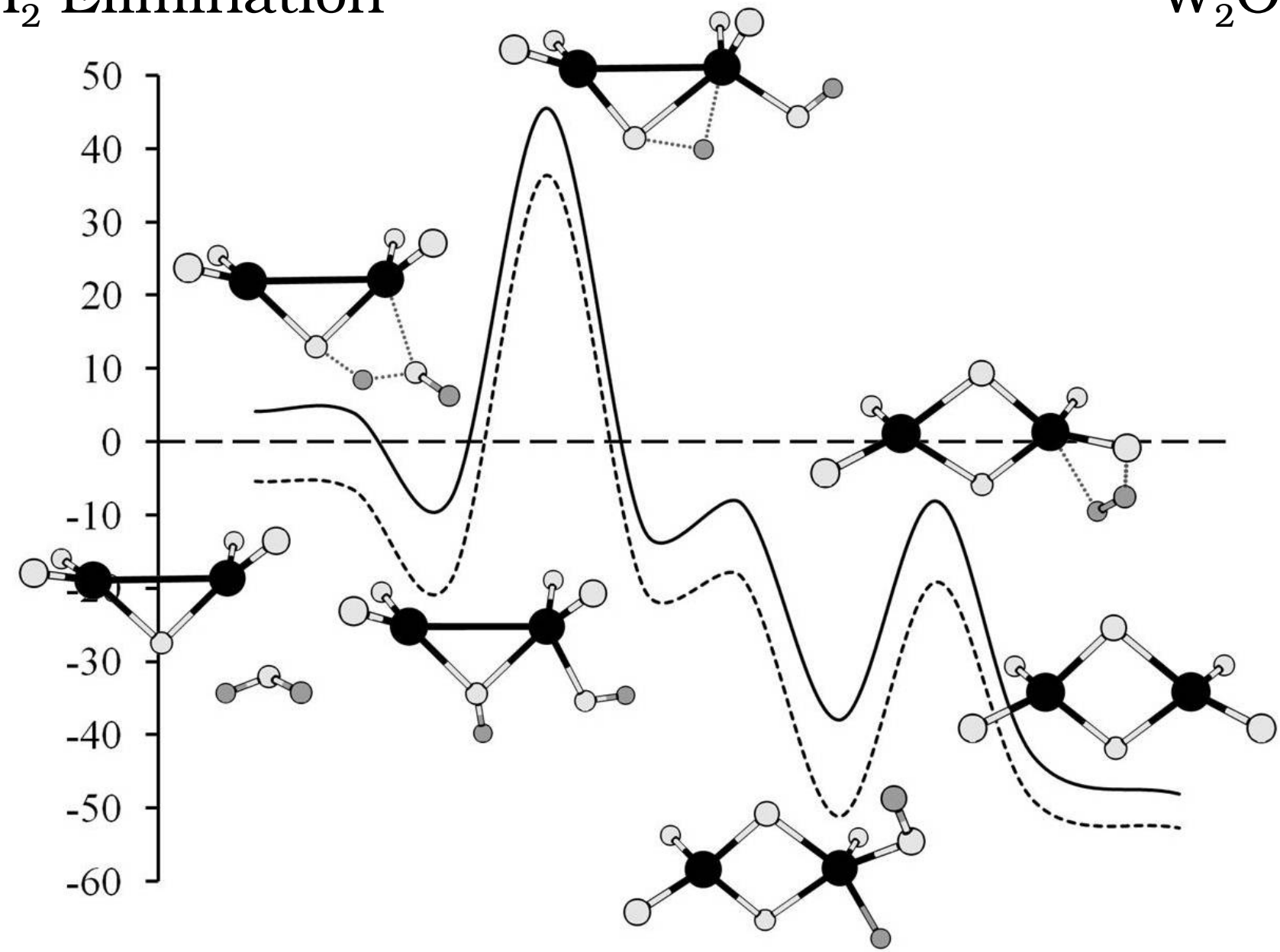
H_2 Elimination

$W_2O_4^-$



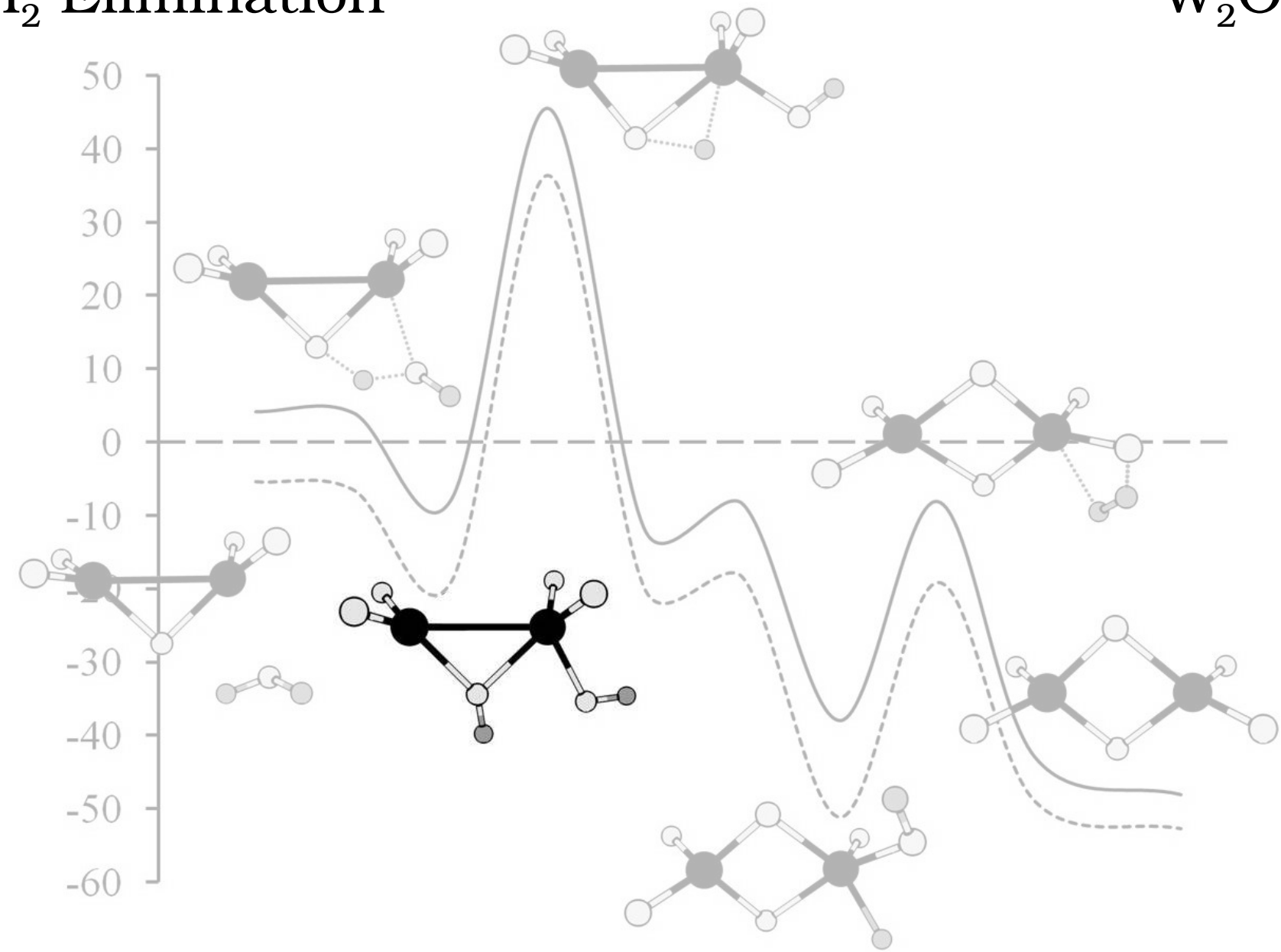
H_2 Elimination

$W_2O_5^-$



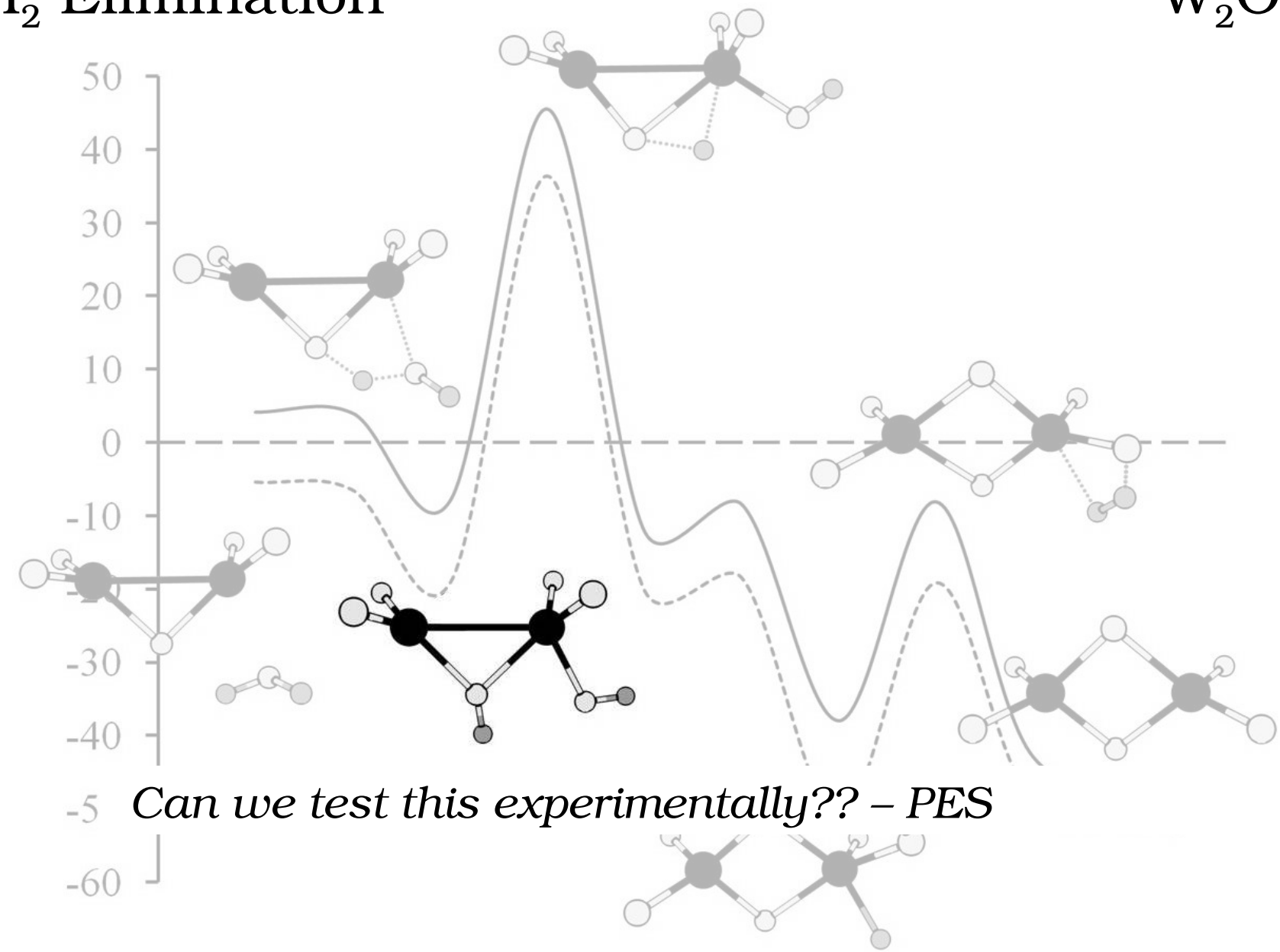
H_2 Elimination

$W_2O_5^-$



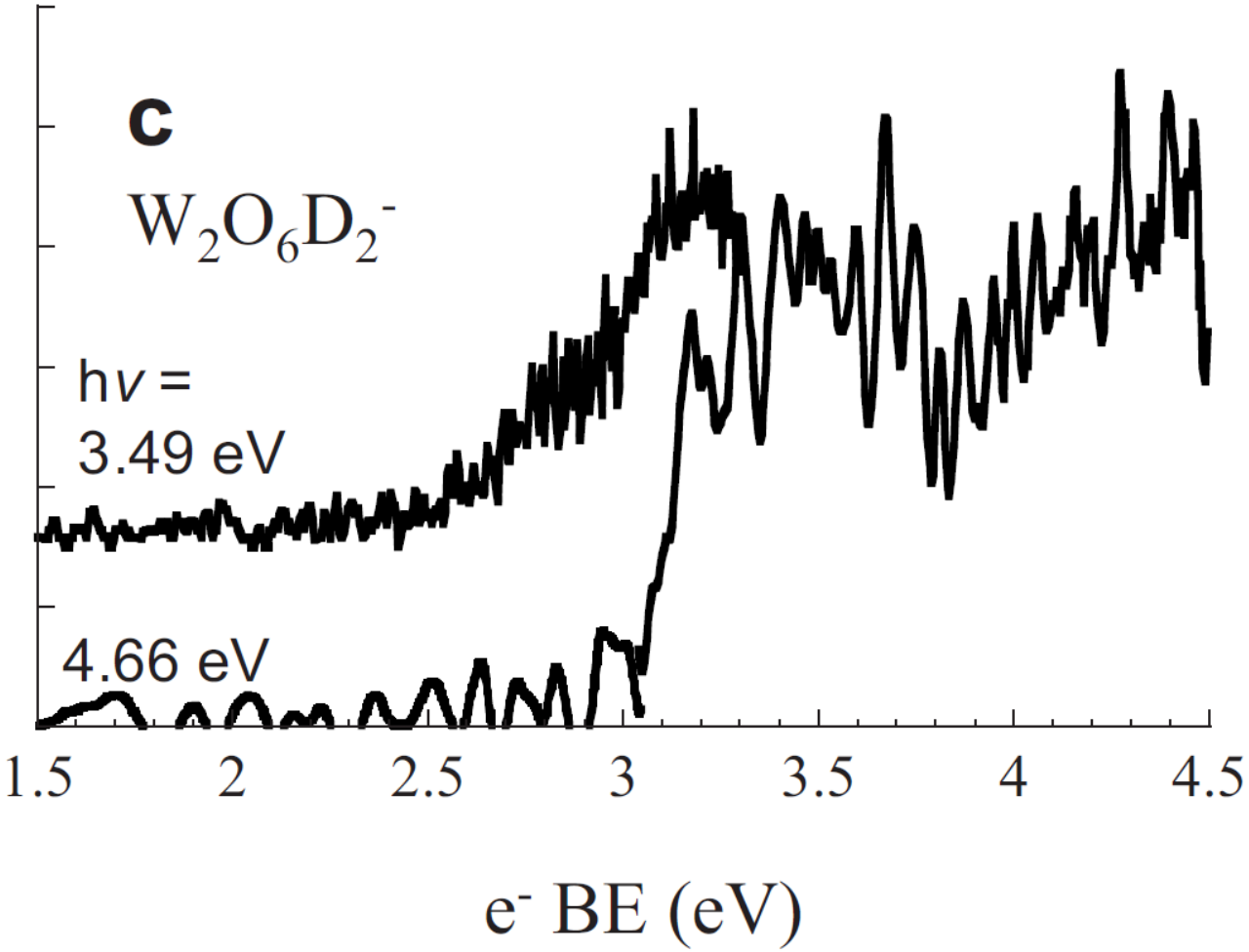
H_2 Elimination

$W_2O_5^-$

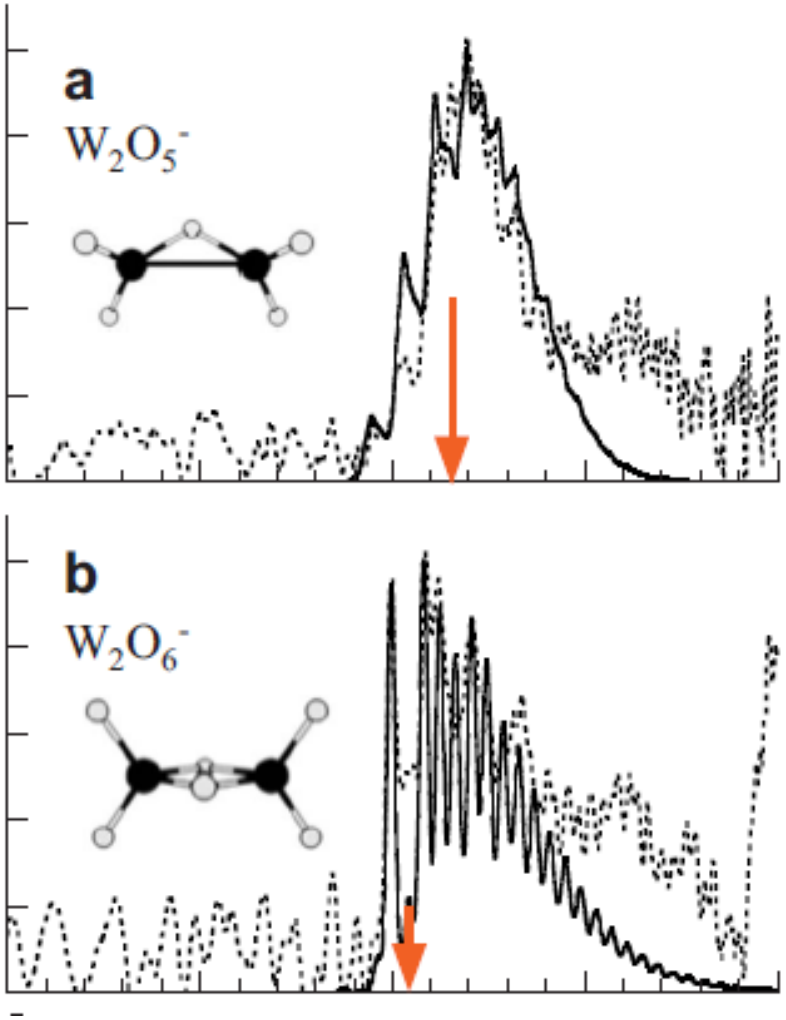


Can we test this experimentally?? – PES

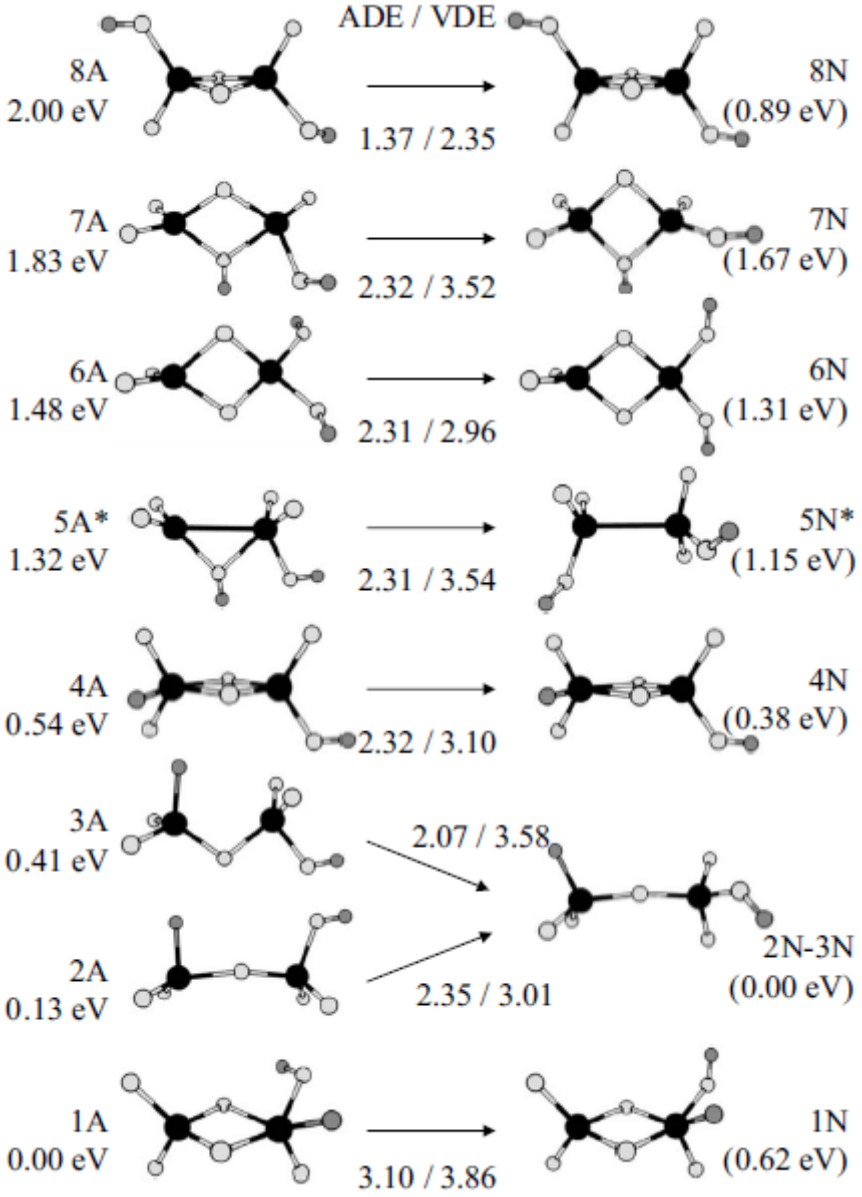
$W_2O_6H_2^-$: PES



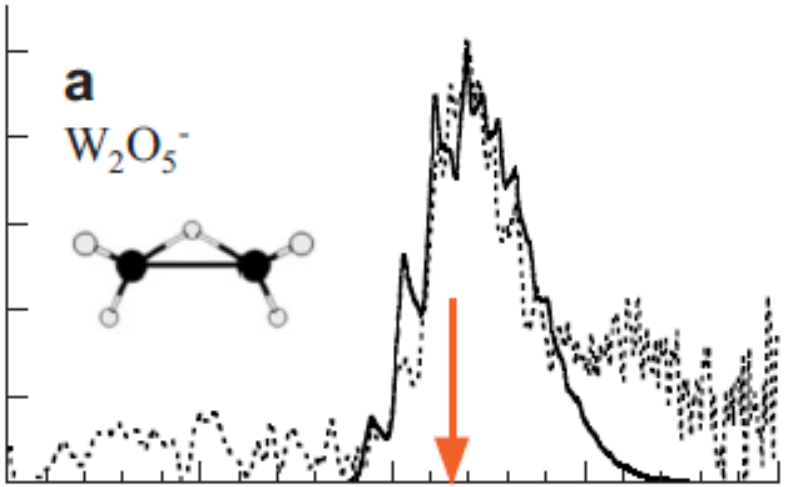
$W_2O_6H_2^-$: PES

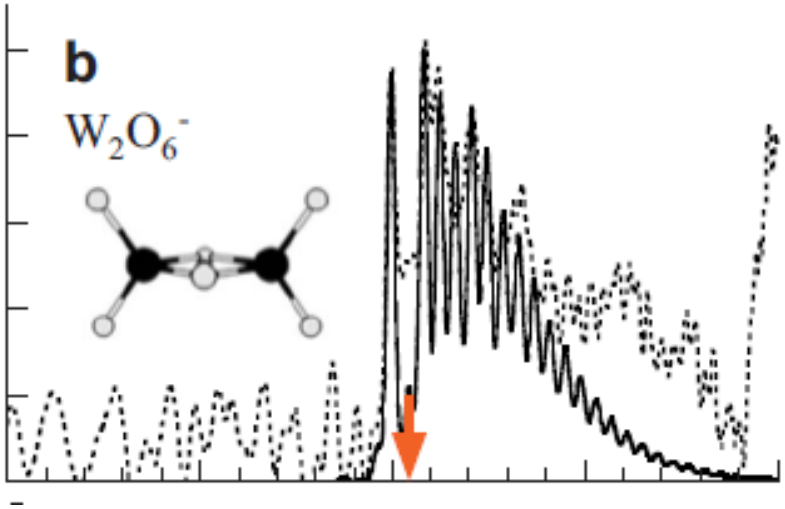


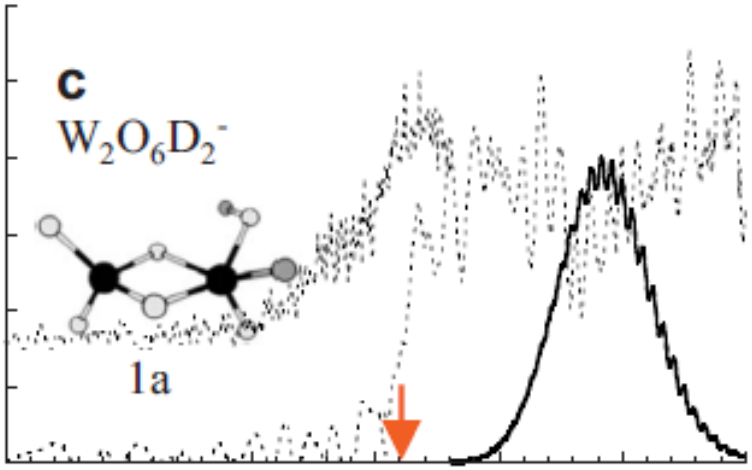
$W_2O_6H_2^-$: Geometries and Energetics



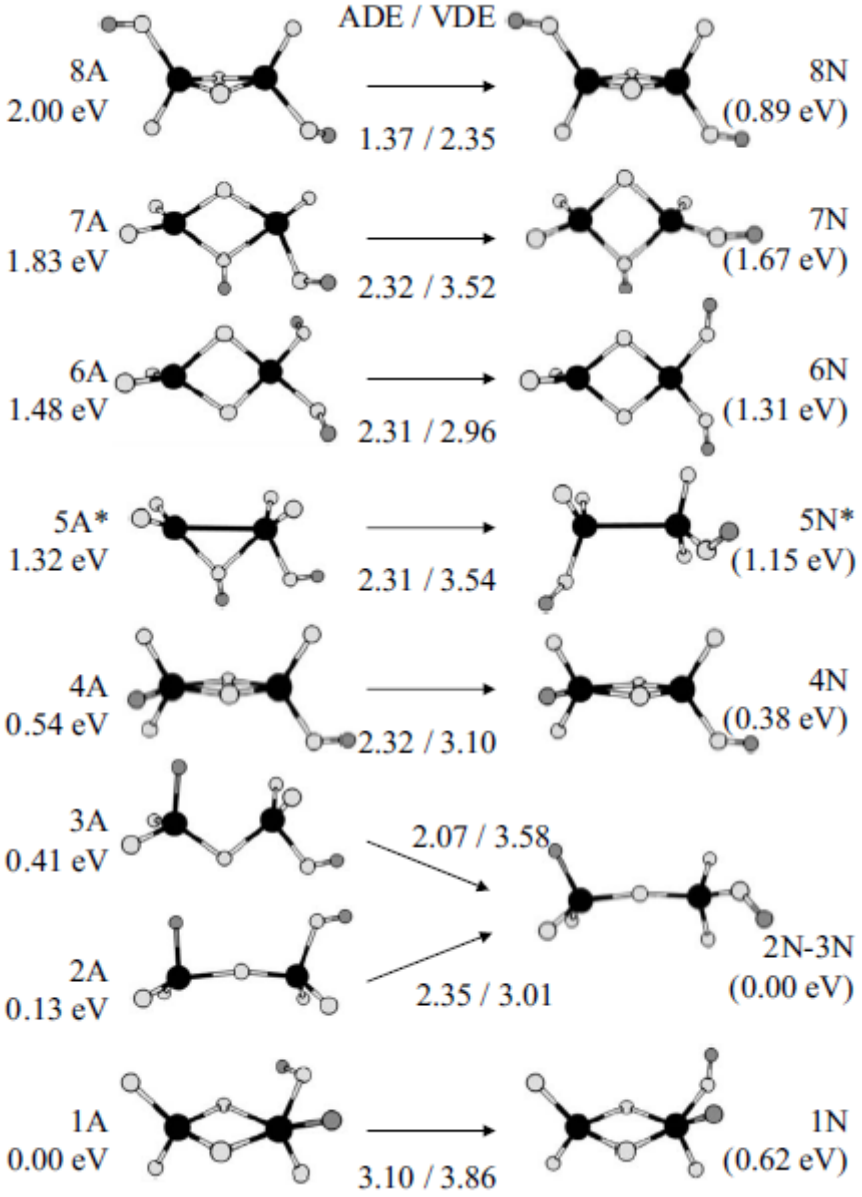
$W_2O_6H_2^-$: PES



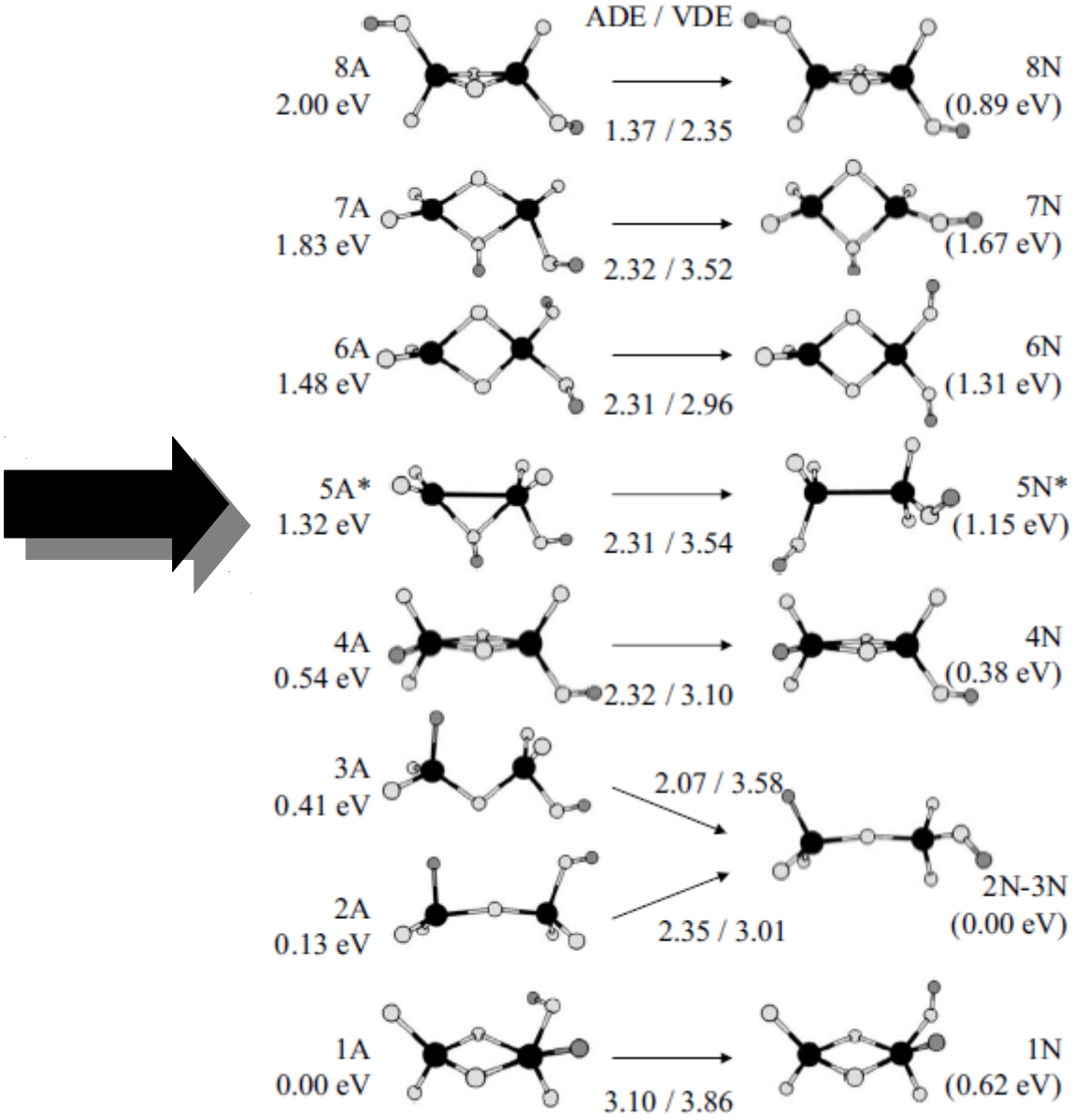




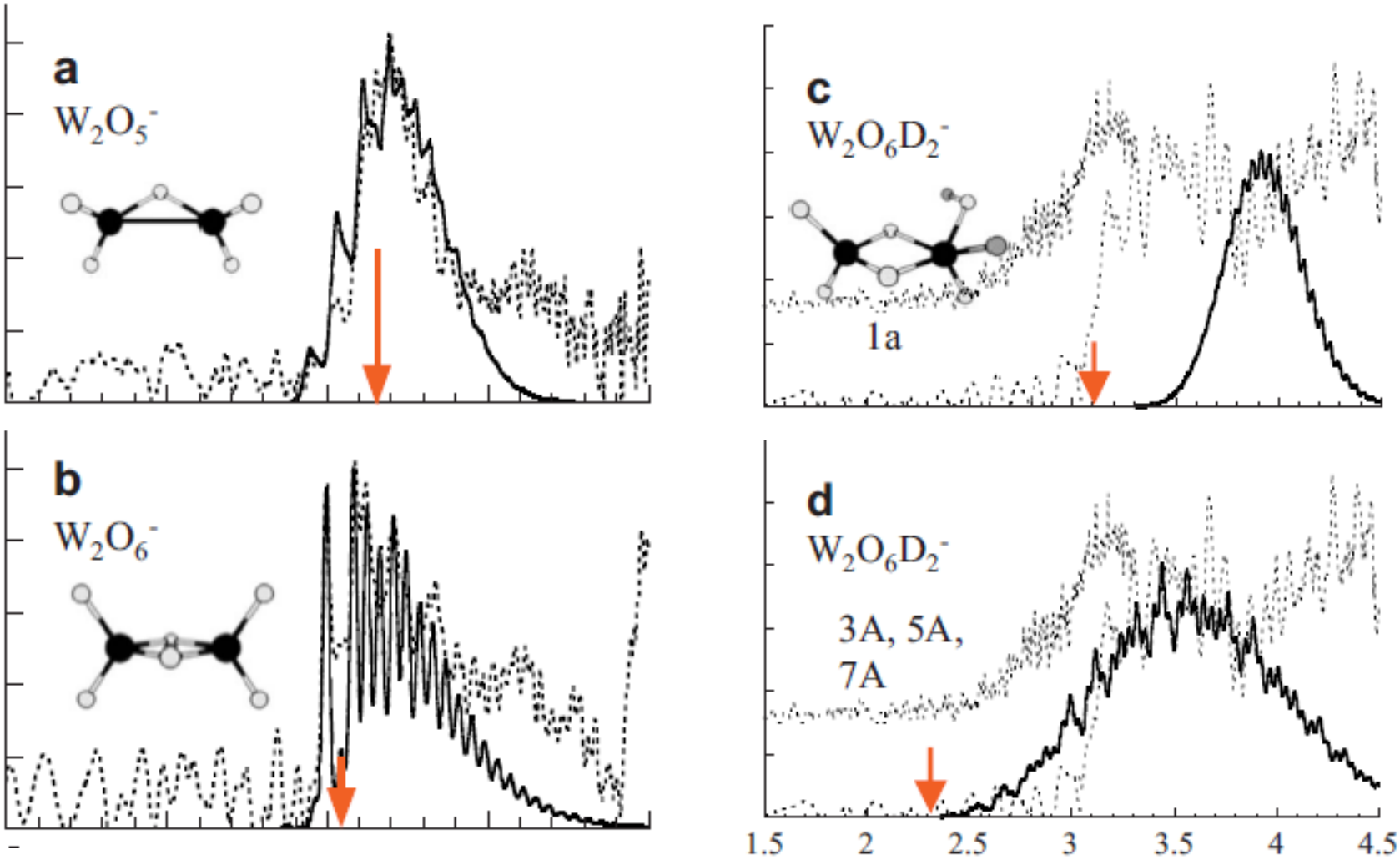
$W_2O_6H_2^-$: Geometries and Energetics



$W_2O_6H_2^-$: Geometries and Energetics



$W_2O_6H_2^-$: PES



Conclusions

- y<5,
  - $W_2O_y^-$ has been found to react with with a single water molecule to produce H_2.

- y=5
  - $W_2O_5^-$ dissociatively adds water, but large barriers prevent H_2 elimination.

- y=6
  - $W_2O_6^-$ does not react with water.

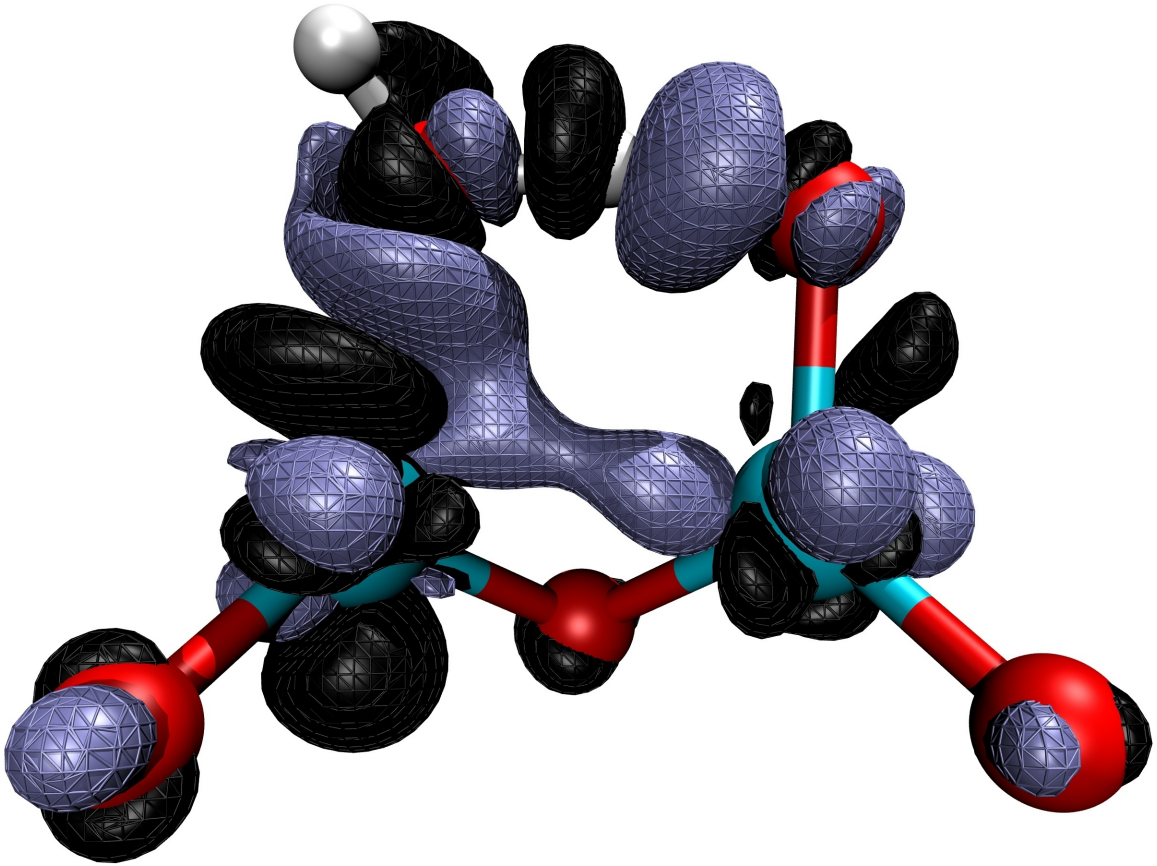
- Theoretical mechanisms explain experimental observations.

- Exp PES provides strong support of mechanisms

Acknowledgements

- Professor Krishnan Raghavachari
  - Raghunath Ramabhadr
- Professor Caroline C. Jarrold
  - Jennifer Mann
  - David Rothgeb
  - Ekram Hossain
  - Sarah Waller
- DOE for funding

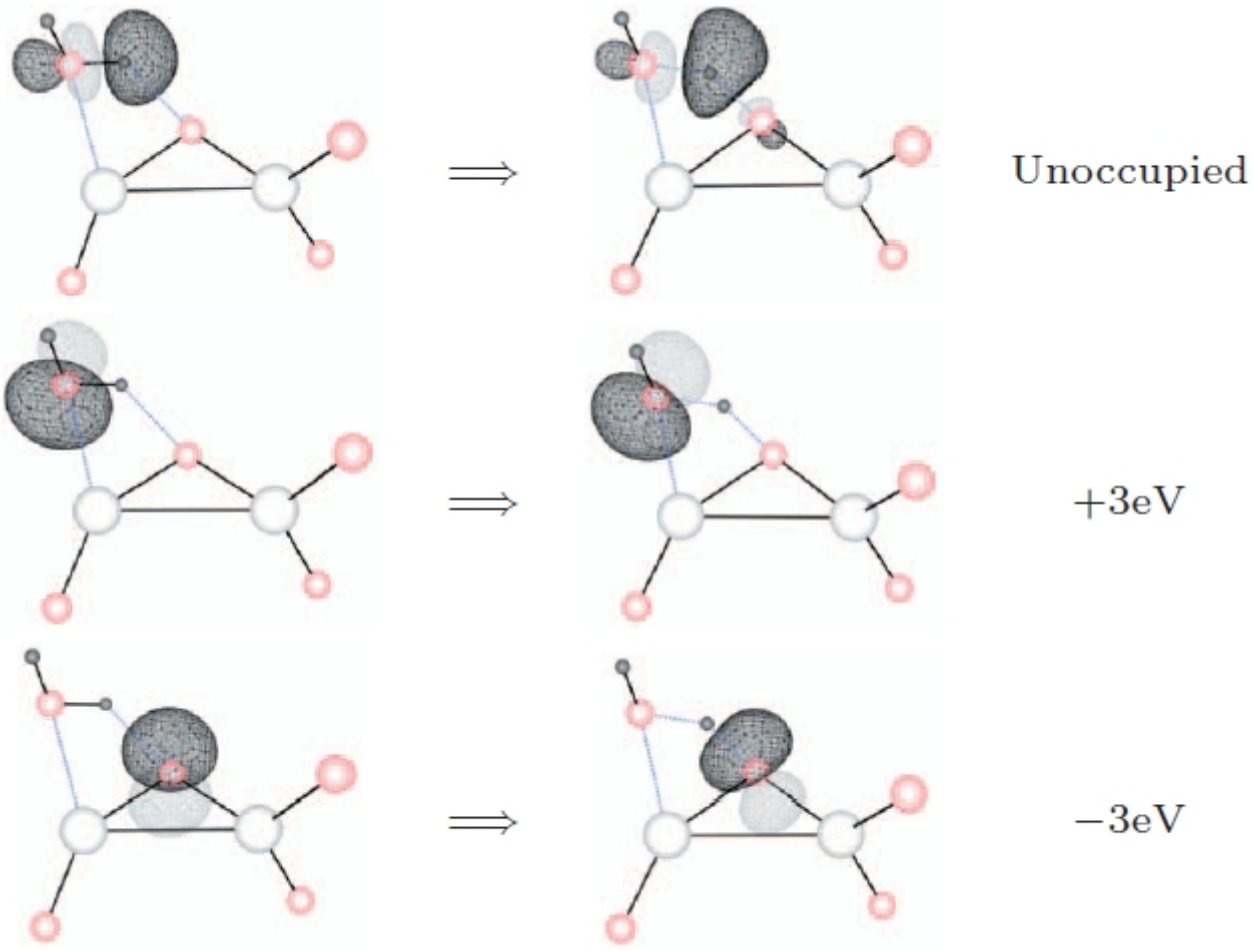
Density Change during Chemisorption

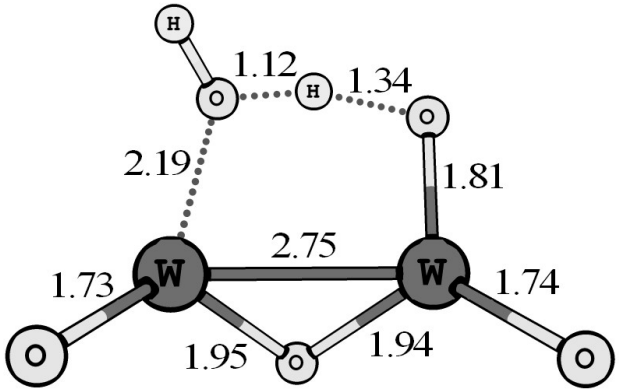


Thermodynamics of H_2 Elimination

Reaction	ΔG (kcal/mol)
$W_2O_4^- + H_2O \rightarrow W_2O_5^- + H_2$	−56.3
$W_2O_5^- + H_2O \rightarrow W_2O_6^- + H_2$	−48.1
$W_2O_6^- + H_2O \rightarrow W_2O_7^- + H_2$	+30.9

Orbitals

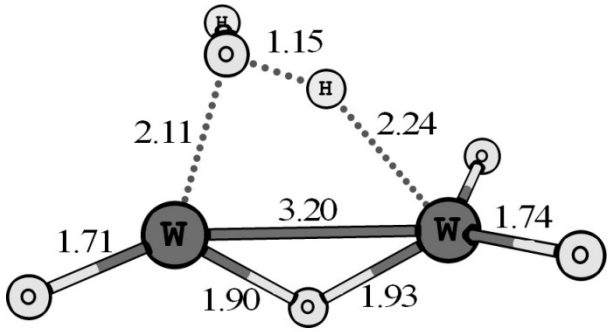



H
1.12
H
1.34
2.19
1.81
2.75
1.73
W
W
1.74
1.95
1.94

Initial Water Addition – Mode 2

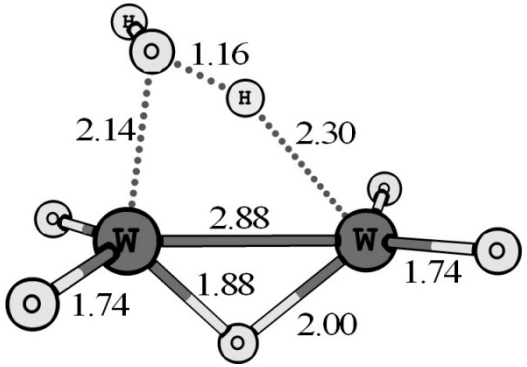
$W_2O_4^-$

E(Complex) = +4.5
E(Tran. State) = +3.5
E(Product) = −58.0

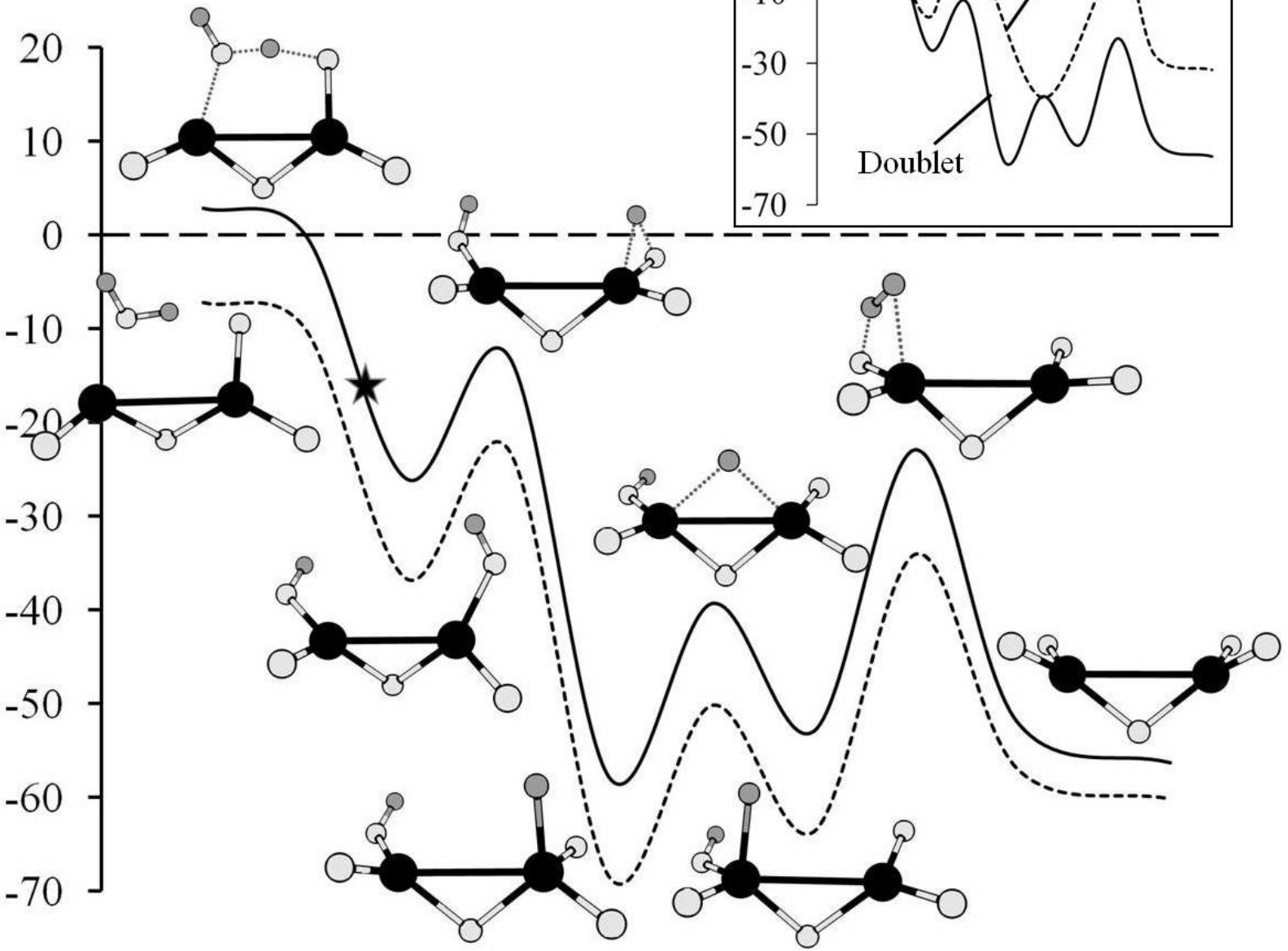


$W_2O_5^-$

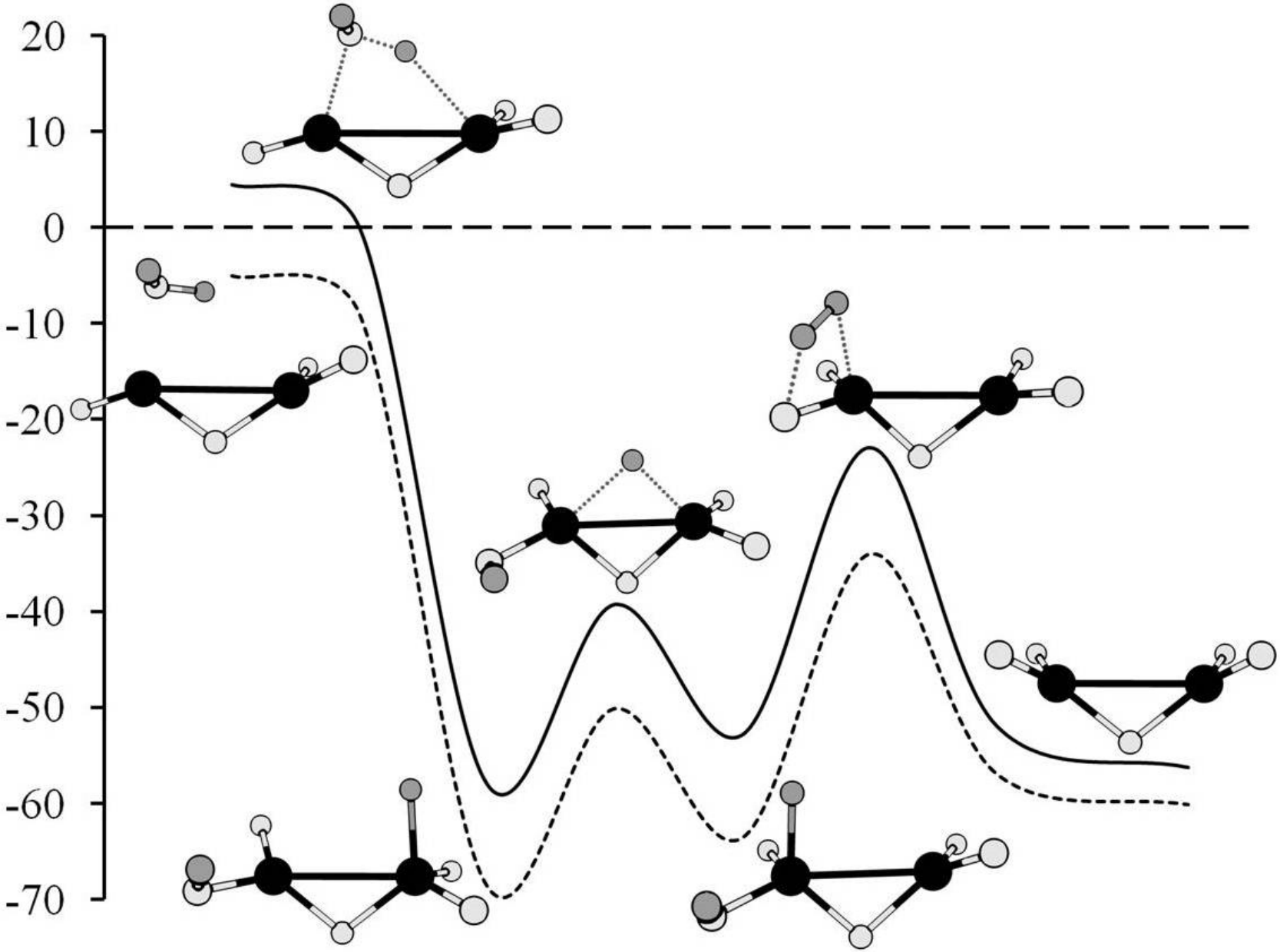
E(Complex) = +8.3
E(Tran. State) = +9.9
E(Product) = −33.0



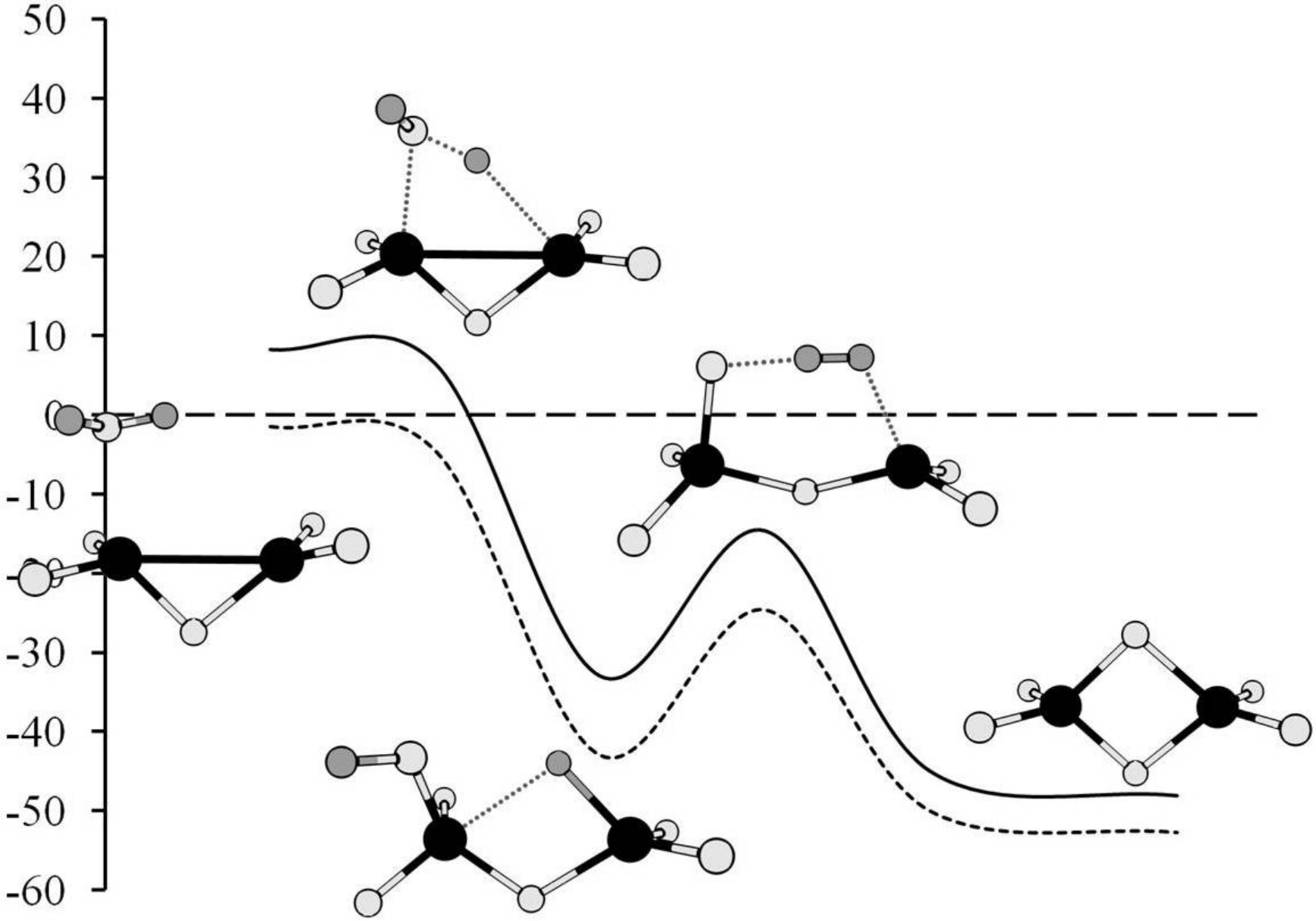
H_2 Elimination



H_2 Elimination



H_2 Elimination



H_2 Elimination Conclusions

- $W_2O_4^-$
  - H_2 evolution following water chemisorption occurs with no higher barriers
- $W_2O_5^-$
  - Most stable chemisorption pathway incurs large barrier before H_2 evolution
  - Explains $W_2O_6D_2^-$ peak
- $W_2O_6^-$
  - Barriers too high to be reactive

Can we test this experimentally?? – PES