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Analysis of Solvation Model, Adsorption Site, and Adsorbate Coverage Effects on Adsorption Energies at the Anode in Direct Methanol Fuel Cells

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Motivation

o Fuel cells are currently too cost prohibitive for widespread application
   o Large portion of cost is due to the expensive transition metals used as catalyst
o Modeling using Density Functional Theory (DFT) could be used to screen catalyst materials for a cheaper alternative to transition metals
o Modeling of these systems are hindered by several factors
   o Solvation effects between surface species and solvent molecules
   o Coverage effects between various adsorbed molecules
      o Coverage: the number of adsorbed molecules per unit surface area of catalyst

Objectives

o Use Density Functional Theory (DFT) to model adsorption of reactants for the rate-limiting mechanism step[1] at the anode in Direct Methanol Fuel Cells (DMFCs):

$$CO_{ads} + OH_{ads} \rightarrow COOH_{ads}$$

o Analyze effects of various solvation models, adsorption sites, and adsorbate coverages on adsorption energies. Establish trends for use in future work.
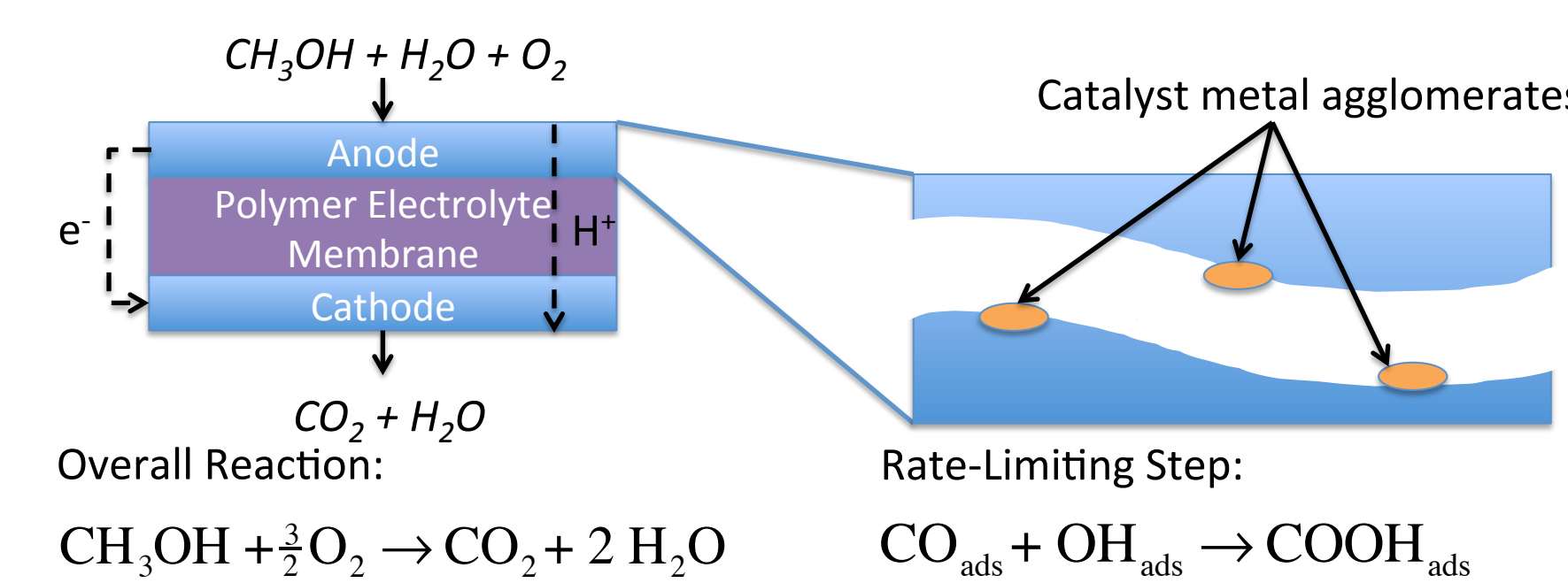

$CH_3OH + H_2O + O_2$

Anode
Polymer Electrolyte Membrane
Cathode

$CO_2 + H_2O$

Overall Reaction:
$$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2\,H_2O$$

Catalyst metal agglomerates

Rate-Limiting Step:
$$CO_{ads} + OH_{ads} \rightarrow COOH_{ads}$$

Figure 1: Representation of DMFC showing inlet and outlet flows and close-up of catalyst metal agglomerates on the porous anode surface.

Methods

o The plane-wave implementation of DFT in the Vienna Ab-Initio Software Package (VASP) was used for all calculations in this study.

Table 1: Parameters used in VASP calculations

VASP Computational Parameters	
Cutoff Energy	400 eV
Electronic Iteration Tolerance	1x10⁻⁵ eV
Geometric Iteration Tolerance	0.03 eV/A
Pseudopotential	Projector Augmented Wave (PAW)[2]
Exchange-Correlation Functional	Perdew-Burke-Ernzerhof (PBE)[3]
K-points	11x11x1
Dispersion Force Correction	DFT-D2 (Grimme)[4]

Table 2: Model system variables analyzed in this study

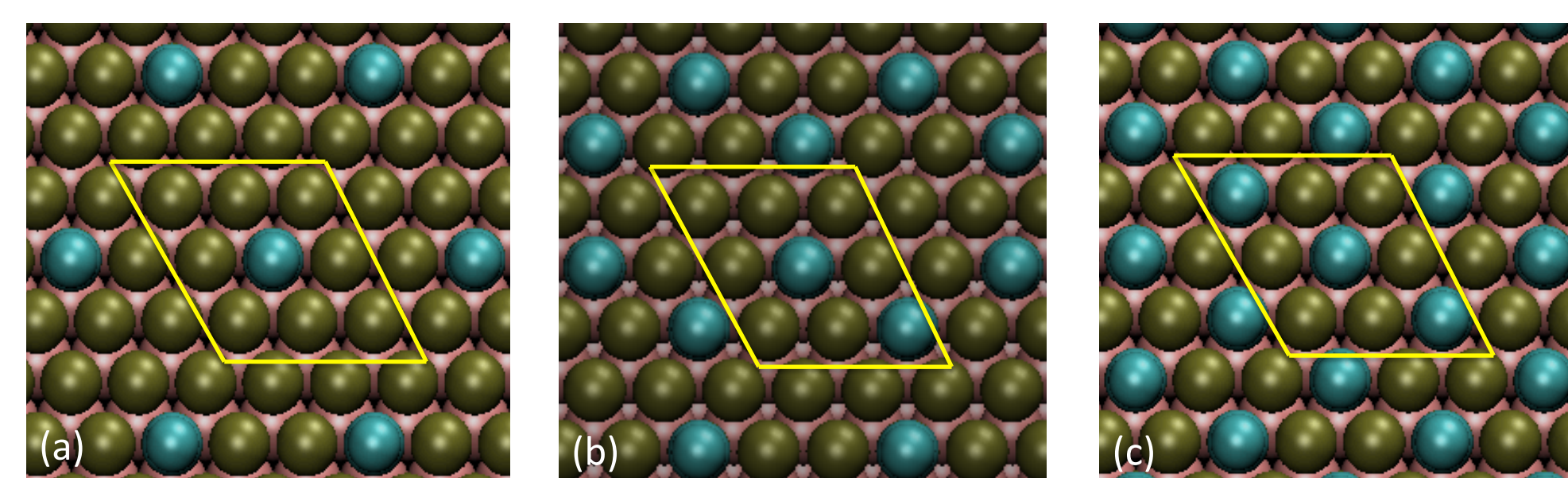| Variables	
Adsorbate	CO, OH
Solvation Model	2D model[5] (H-up or H-down), center adsorbate 3D model[6] (H-up or H-down), center adsorbate 2D model[5] (H-up or H-down), displaced water 3D model[6] (H-up or H-down), displaced water
Adsorption Site	Atop, HCP, FCC
Adsorbate Coverage	1/9th ML, 2/9th ML, 1/3rd ML

Figure 2: Surface coverages of (a) 1/9th, (b) 2/9th, and (c) 1/3rd monolayer (ML) shown from a top view of a (111) surface. The yellow diamond represents the 3 atom by 3 atom supercell used for VASP simulations. Bronze spheres are metal atoms and teal spheres are adsorbate atoms.
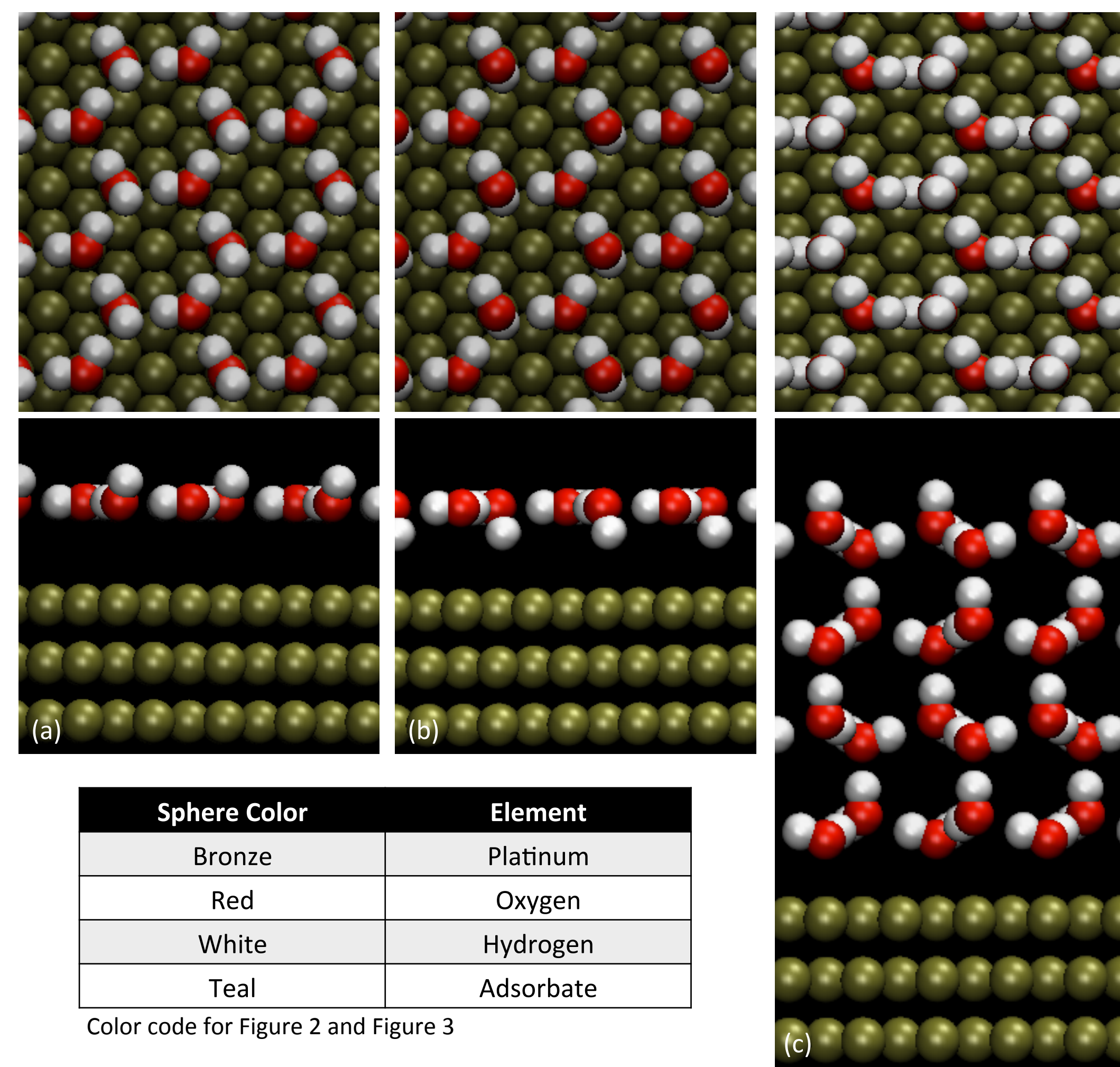

Sphere Color	Element
Bronze	Platinum
Red	Oxygen
White	Hydrogen
Teal	Adsorbate

Color code for Figure 2 and Figure 3

Figure 3: (a) 2D solvation model in the hydrogens up configuration. (b) 2D solvation model in the hydrogens down configuration. (c) 3D solvation model mimicking the Ih ice structure in the hydrogens up configuration.
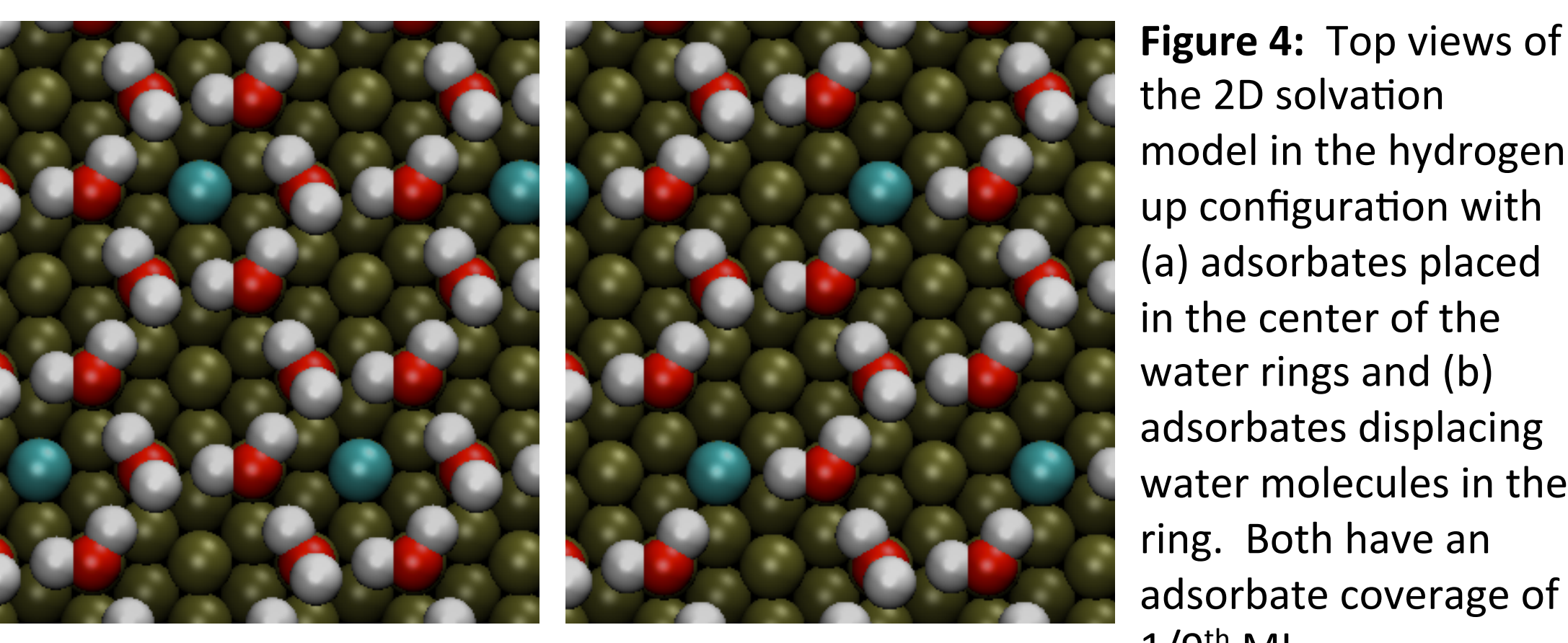

Figure 4: Top views of the 2D solvation model in the hydrogen up configuration with (a) adsorbates placed in the center of the water rings and (b) adsorbates displacing water molecules in the ring. Both have an adsorbate coverage of 1/9th ML.

Results and Conclusions

Adsorption energy equations for adsorption on a platinum (111) surface
   o Center adsorbate placement arrangement: $Pt\text{-}CO_{vac} + Pt_{ice} \rightarrow Pt\text{-}CO_{ice} + Pt_{vac}$
   o Adsorbate displacement of water arrangement: $Pt\text{-}CO_{vac} + Pt_{ice} \rightarrow Pt\text{-}CO_{ice} + Pt_{vac} + H_2O$
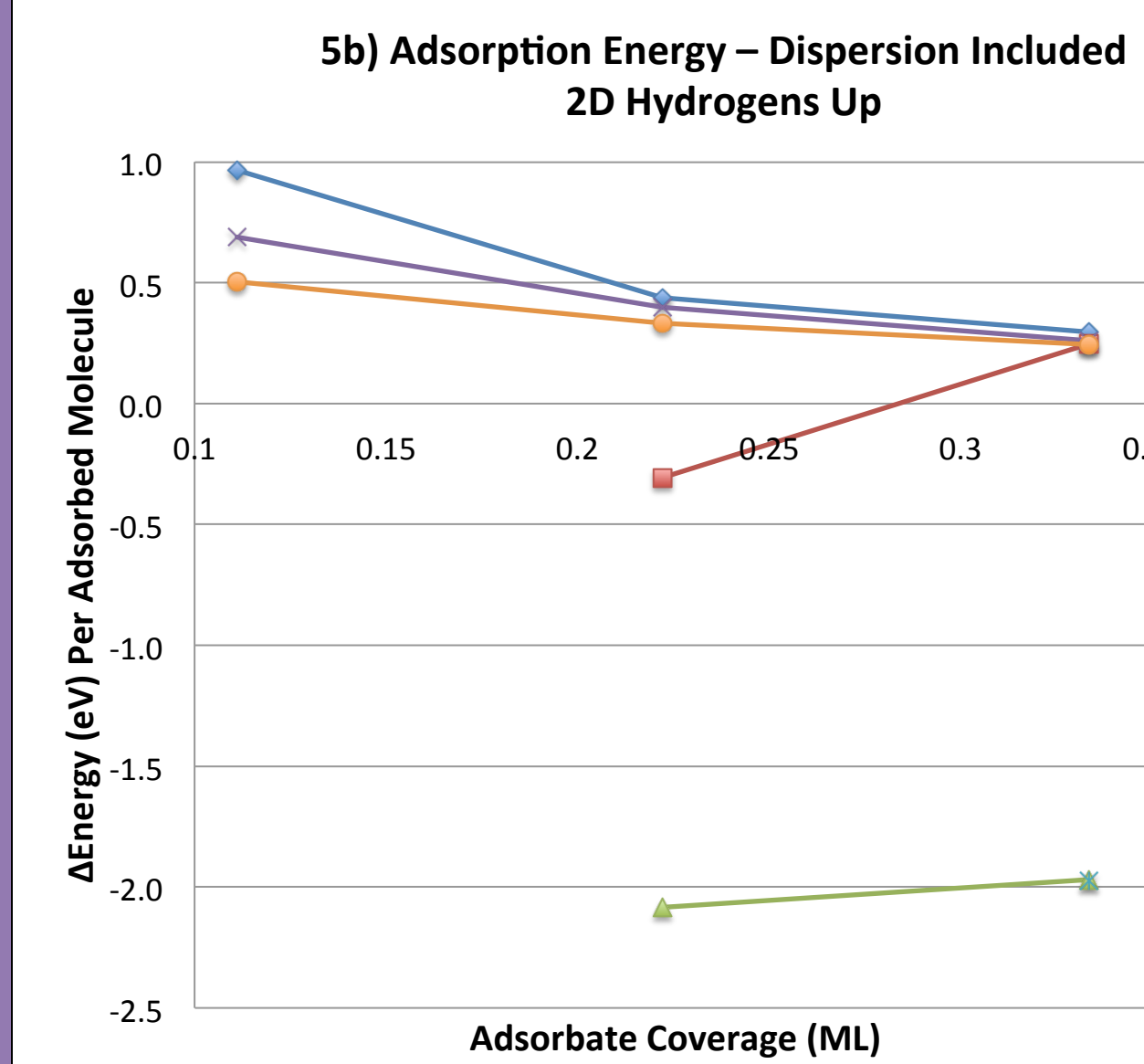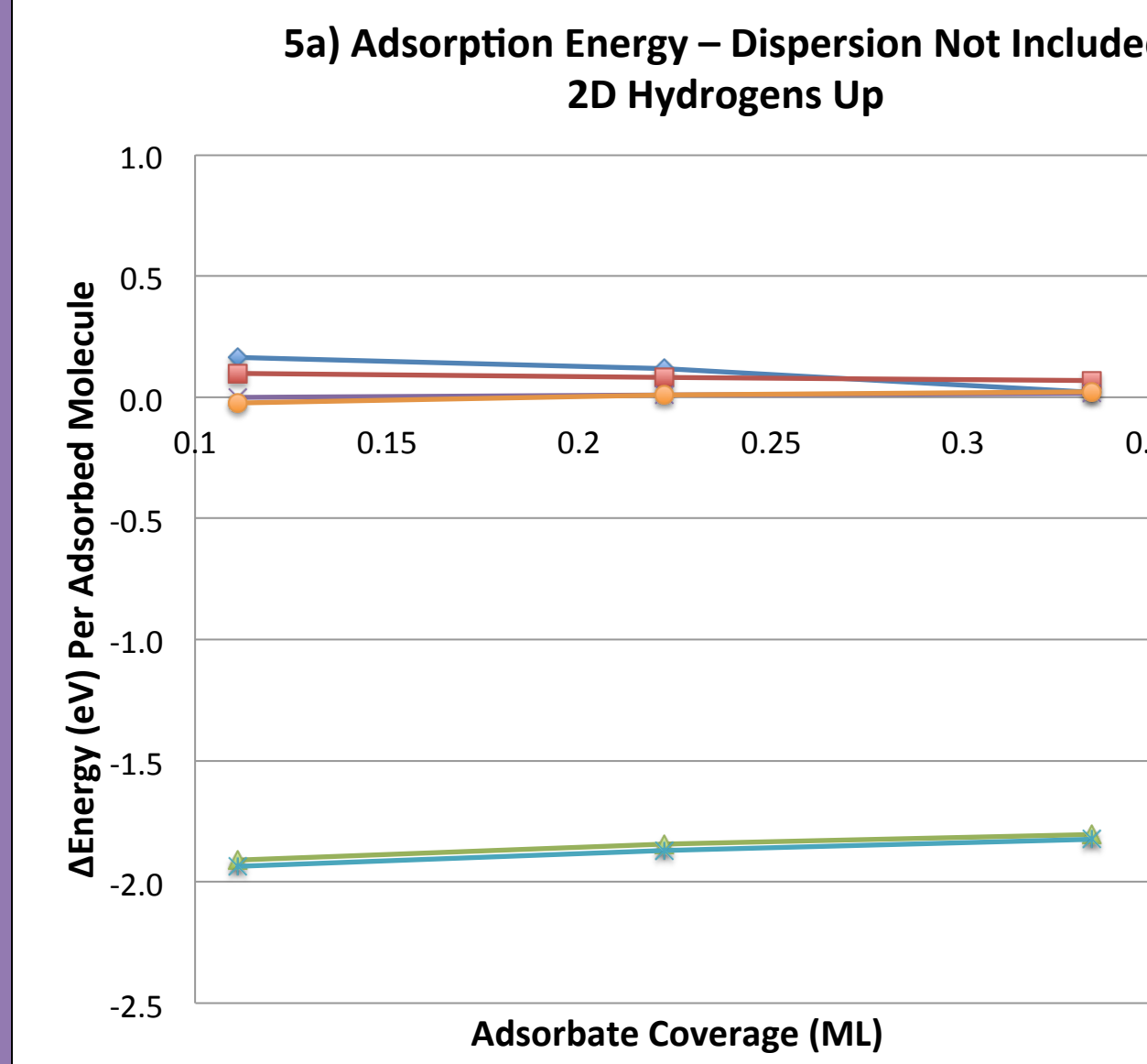

Figure 5: Effects of adsorption site and adsorbate coverage on the adsorption energy of CO and OH using the 2D solvation model in the hydrogens up configuration. Figure 5a shows effects without the inclusion of dispersion forces and Figure 5b shows effects with the inclusion of dispersion forces.
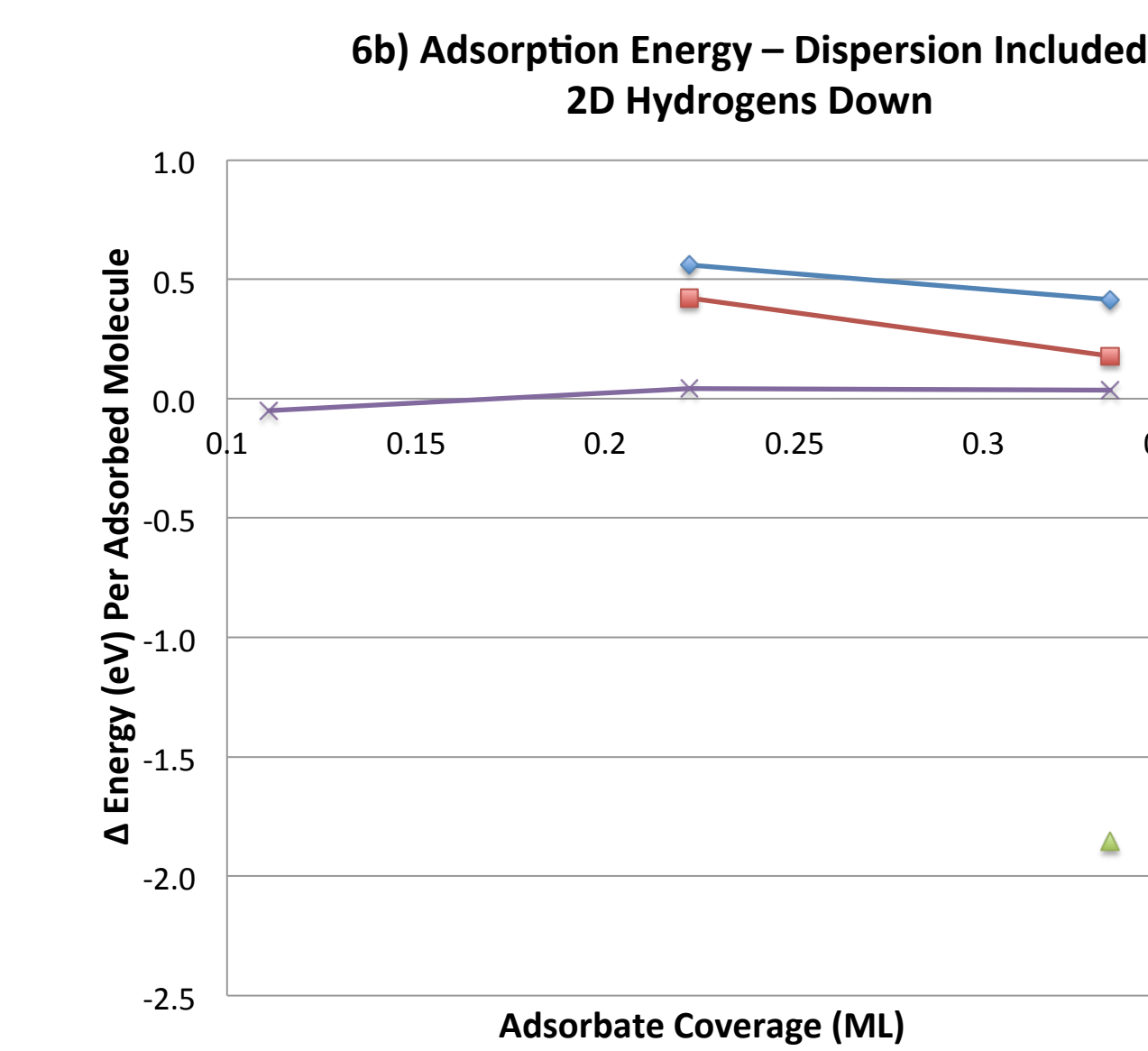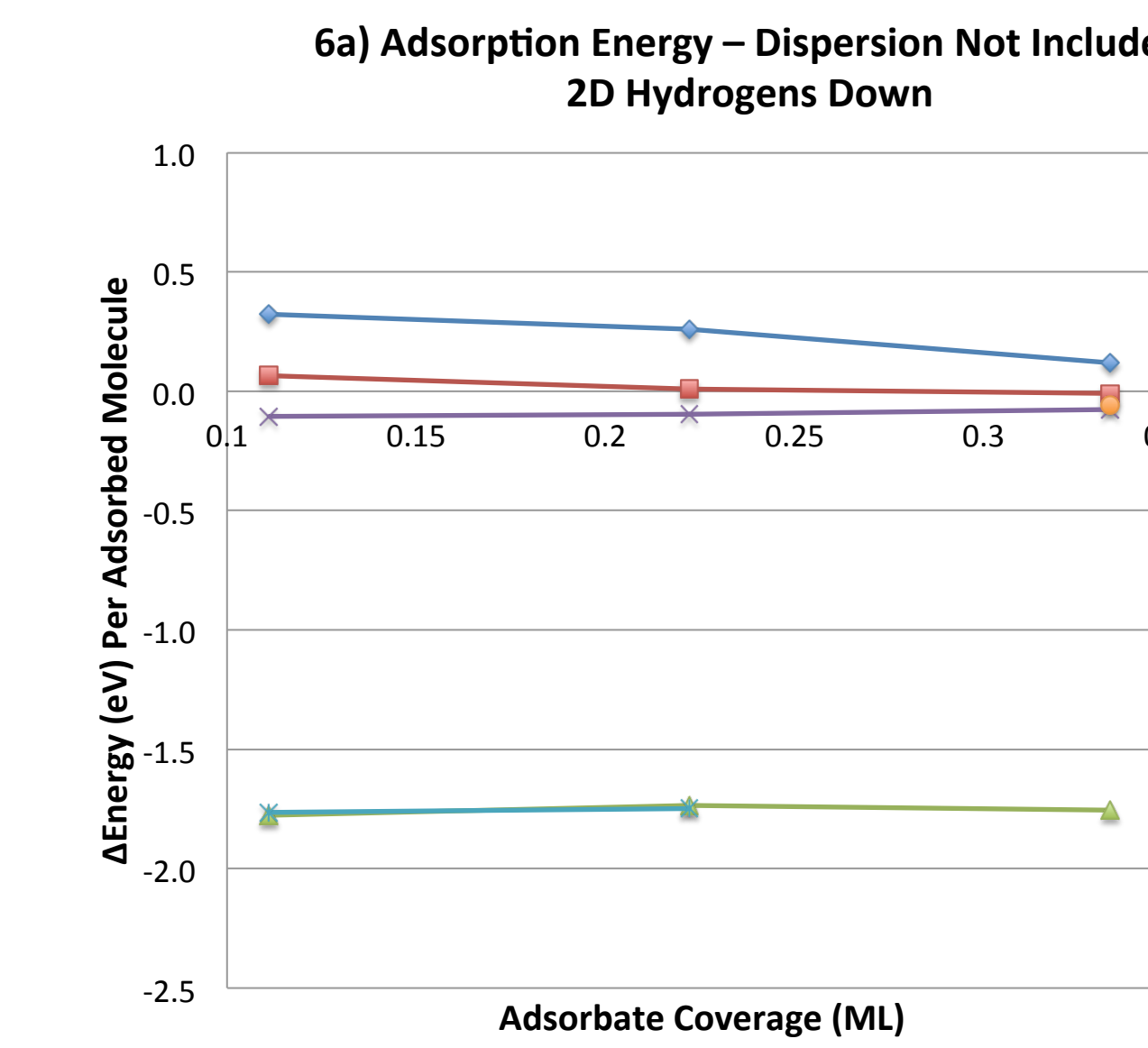

Figure 6: Effects of adsorption site and adsorbate coverage on the adsorption energy of CO and OH using the 2D solvation model in the hydrogens down configuration. Figure 6a shows effects without the inclusion of dispersion forces and Figure 6b shows effects with the inclusion of dispersion forces.
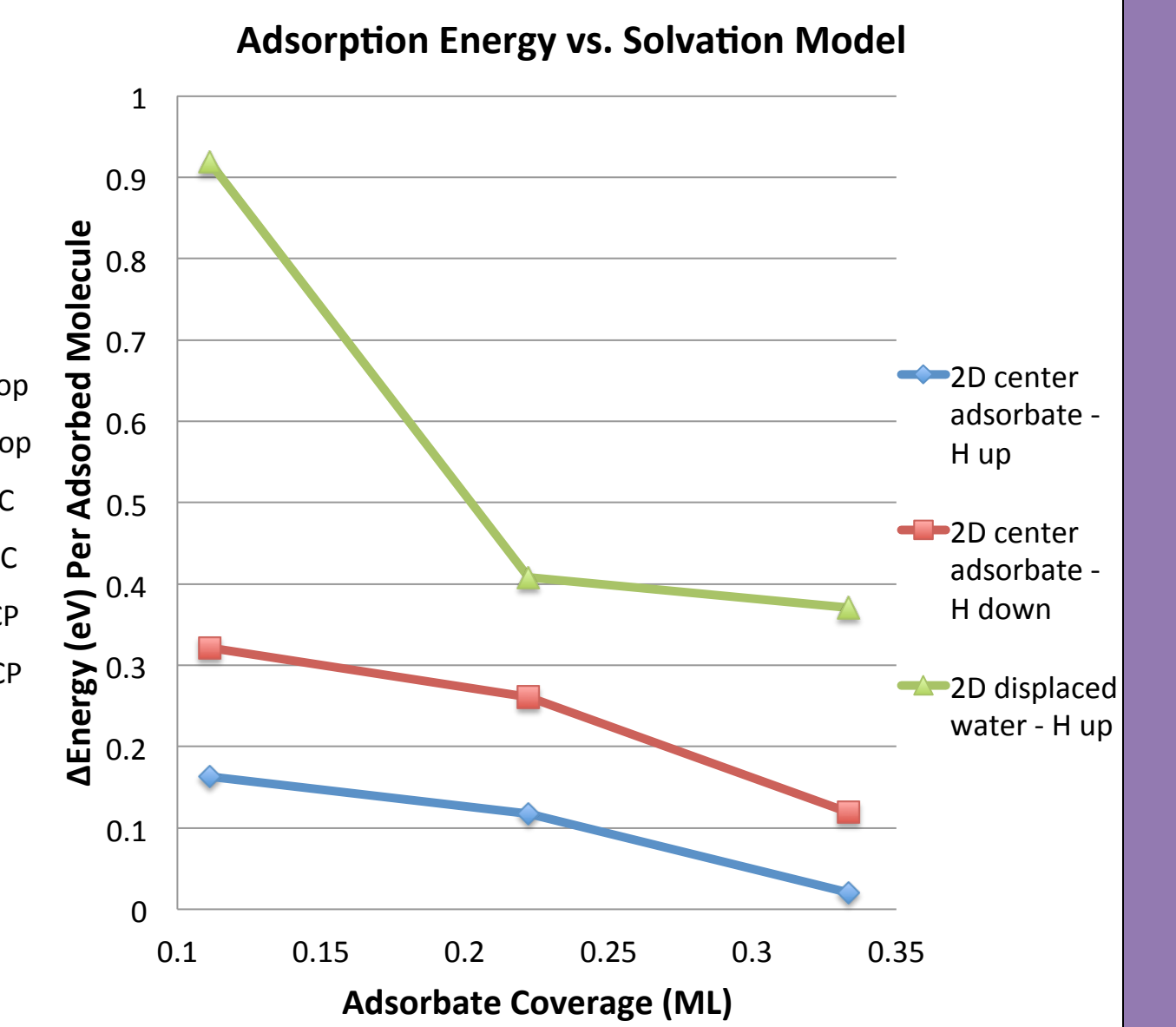

Figure 7: Effects of solvation model on adsorption energy for CO on the atop adsorption site at a coverage of 1/9th ML.

Conclusions

o Differences in adsorbate coverage significantly affect adsorption energies

o There are similar trends in adsorption energy as a function of adsorption site for different solvation models and adsorbate coverages

o Adsorption favorability changes significantly with different coverages and solvation models

o Inclusion of dispersion forces significantly affects adsorption energies

Future Work

o Develop a Grand-Canonical Monte Carlo (GCMC) code to sample adsorbate placements and coverages
   o Use trends established to minimize computational expense for electronic energy calculations
o Determine equilibrium adsorbate concentrations for single-adsorbate cases
   o Extrapolate for multiple-adsorbate cases
o Use GCMC code to sample adsorbate diffusion into metal catalyst as absorbates
   o Calculate equilibrium concentrations of absorbates
o Calculate kinetics parameters of DMFC rate-limiting step on newly determined catalyst compositions
o Screen potential catalyst materials to find a cheaper alternative for transition metal catalysts for use in DMFCs using developed method

References

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