A Density Functional Theory Study of the Surface Species on a Platinum-Ruthenium Catalyst used in a Methanol Fuel Cell

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Abstract

The platinum-ruthenium alloy has been of interest as a methanol fuel cell catalyst. Due to the presence of carbon monoxide a platinum catalyst becomes poisoned and loses effectiveness. A mixture of platinum and ruthenium lowers the possibility for creating carbon monoxide, and increases the potential for hydroxyl groups to adsorb and react with the carbon monoxide to release hydrogen and carbon dioxide groups. In this project, we investigated the surface bonding energies of methanol, carbon dioxide, carbon monoxide, carboxyl ions, water, hydrogen ions and hydroxyl ions on multiple catalyst surfaces (Platinum and Ruthenium). To do this we used density functional theory, a molecular modeling technique, with the computer program CP2K. The resulting model predicts the bond strength between these catalyst surfaces and each of the molecules involved in the methanol oxidation reaction. Compared against other calculations, this model has proved sufficiently accurate. We propose that these surface bond strengths can be further used in catalytic reaction studies towards the development of an optimal catalyst surface structure for the direct methanol fuel cell.

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List of Acronyms

Å	Angstrom
CP2K	Car-Parrinello 2000 (CP2K) project and computer code
DMFC	Direct Methanol Fuel Cell
DFT	Density Functional Theory
FCC	Face Centered Cubic
CCP	Closed Cubic Pack (same as FCC)
HCP	Hexagonal Closed Packing

CHAPTER 1: INTRODUCTION

The impending energy crises, global warming, rising costs of petroleum, the ongoing political disturbances of imported oil, and waning natural resources on a global scale are all factors which have brought the need for cleaner, efficient, and easily obtainable alternative energy sources to the forefront of scientific research. One such technology and alternative energy source that has been offered is the use of highly efficient fuel cells, which use a chemical reaction to produce electricity.

Fuel cells have proven useful in many applications due to their flexibility in design and fuel source. The flexibility of fuel cell technology can accommodate applications ranging from providing energy for a whole building to that of a light-duty vehicle. Currently the United States Department of Energy has implemented the Fuel Cell Technologies Program with President Obama's outline for improvements in energy efficiency. This program is aimed at creating opportunities for the continued growth and research of fuel cell technology both in the near and long term future. Through holding educational activities and sponsoring research to reduce costs, improve efficiencies and improve the fuel cell durability the Fuel Cell Technologies Program aims to have the US on the leading edge of clean, sustainable energy (U.S. Department of Energy, 2011)

Fuel cells were initially designed in 1839 for use with hydrogen gas. However, because isolated hydrogen gas does not naturally occur in large quantities, it must be generated by other processes, such as steam reforming. As a result of this complication other sources of fuel for the fuel cell have been investigated including methanol; chosen for its stability, high energy yield, and availability. Over the past 170 years many improvements have been made and a large variety of fuel cells are readily available for a myriad of applications.

Current problems in methanol fuel cell production involve low efficiencies and carbon monoxide poisoning of the catalyst, typically platinum metal. As a means of addressing these problems a platinum-ruthenium mixed catalyst alloy has been proposed that appears to show promise.

The primary focus of this paper is analysis of the different chemical interactions involved within the methanol oxidation over platinum and ruthenium catalysts. The work will analyze individual reactions involved, and predict the overall energies of adsorption. It is hoped that this research will identify important reaction steps on these catalysts and enable improvement of the fuel cell catalysts.

CHAPTER 2: BACKGROUND INFORMATION

2.0 Introduction

Over the past two decades, the urgency for the development of cleaner and more efficient energy sources has increased exponentially, and with this an expanding interest in fuel cell technology. First demonstrated by Sir William Grove's gas voltaic battery in 1839, the advances of fuel cells in recent years have progressed significantly through continuous research and newer advanced technologies and methods.

2.1 Basic Concepts of Electricity

Electric power, or energy, is the flow of electrons (an electrical current) in a circuit, and the amount of electrons flowing is defined as the current. This energy can then be converted into mechanical work. To create an electrical current, electrical force must be applied on both sides of a metallic substance.

Metals are unique in the sense that the outer electrons in their atoms are loosely bound; therefore many of these loose electrons exist inside a metal wire. When an electrical force is applied these loose electrons move in the direction of the force thus creating a current. To chemically create an electrical force (i.e. the movement of electrons), two electrodes are needed: an anode and cathode. An electrode is defined as an electric conductor used to make contact with a nonmetallic part of the circuit. For fuel cells this part is generally the electrolyte: a substance which contains free ions (a chemical that contains a different number of protons than electrons making it electrically charged). In fuel cells a solid electrolyte is generally used which promotes the movement of electrons and protons.

While both anodes and cathodes are regarded as electrodes, the difference between and anode and a cathode is that the electric current flows into an electric device at the anode, while the current flows *out of* an electric device at the cathode. Thus for a fuel cell the electrons enter the anode and reunite with another species at the cathode creating an electric current. Important to note is that electrons flowing in one direction create a positive current in the opposite direction.

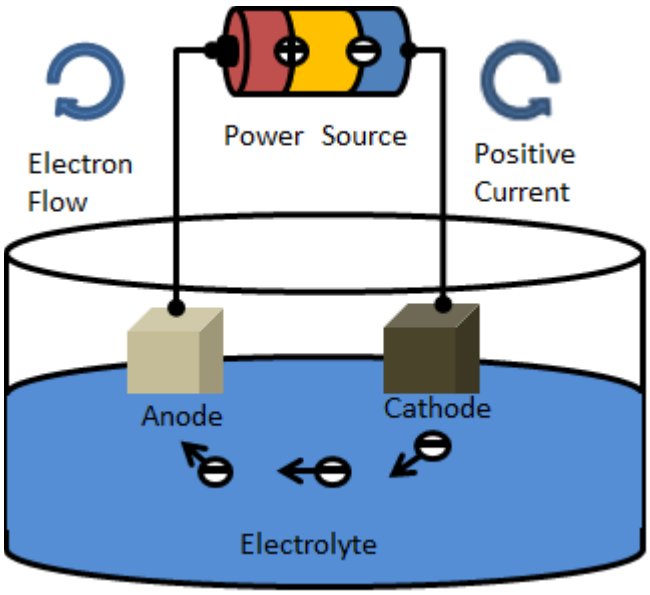


Figure 1: Electric current from Anode to Cathode

2.2 Catalysts

A catalyst is generally defined as a substance that promotes or speeds up a chemical reaction without being affected itself.

2.2.1 Catalyst Mechanism

The actual physical mechanism of a catalyst lies in the surface bonding between the catalyst and the adsorbed species. The molecule must first create a bond with the surface of the catalyst. From there the bonds within the molecule must weaken to either desorb from the surface, leaving a part of it behind or allow another molecule to attach to the original molecule. Once it has reached a stable configuration it should then desorb from the surface such that the final desired product is created and the catalyst left intact to be used again. Catalysts generally react with one or both of the initial reactants and then the reactants combine to form the product where it finally is released from the catalyst. This interaction has the possibility of making the overall reaction occur easier and quicker (Newns, 2007). For example, if the overall reaction being attempted is X and Y combining to form Z, would be denoted:

$$X + Y \rightarrow Z$$

And if a catalyst is denoted C then X and Y could interact with the catalyst in multiple reactions to form:

$$X + C \rightarrow XC \quad (1)$$

$$Y + XC \rightarrow XYC \quad (2)$$

$$XYC \rightarrow CZ \quad (3)$$

$$CZ \rightarrow C + Z \quad (4)$$

Giving the same overall reaction:

$$X + Y \rightarrow Z$$

X, Y, and Z could be in the gas (or liquid) phase, except when bound to C (the catalyst) where they would be in the solid phase. For each reaction an energy barrier prevents the reaction from proceeding spontaneously, called the activation energy. If the overall activation energy of the catalyst-induced reaction is lower than using no catalyst then the reaction is more likely to occur and will happen at a quicker rate. This can be easily seen in Figure 1.

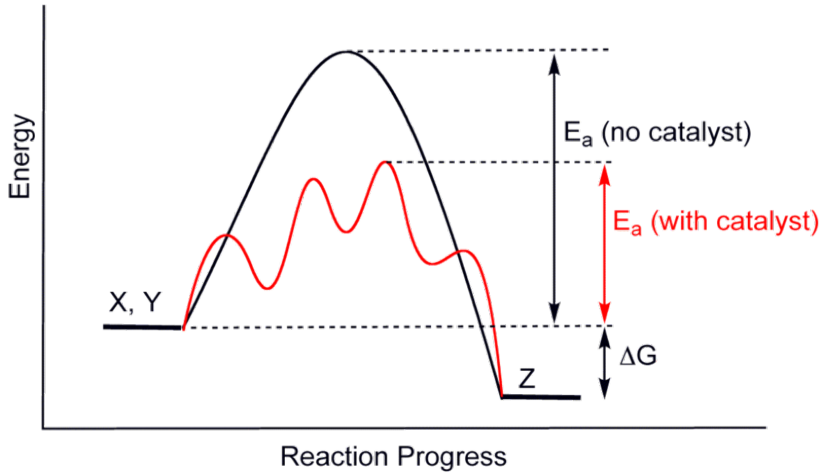


Figure 2: Activation Energies of reaction using catalyst vs. no catalyst (Smokefoot, 2008).

For a chemical reaction with initial species A and B and molar amounts n and m,

$$nA + mB \rightarrow C + D$$

The rate at which it reacts (r) is given by:

$$r = k(T)[A]^{n'}[B]^{m'}$$

where the variable k is a function of temperature (T), defined by the Arrhenius Equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

n' and m' do not necessarily equal n and m, but depend on how the species interact with the catalyst. A is defined as the frequency factor (the amount of collisions in a set time for a specific reaction), E_a is the activation energy, R is the gas constant, and T is the temperature. Therefore for higher activation energies (E_a) the rate is larger and the overall reaction will take longer. From this knowledge we can explain how catalysts can promote a reaction to completion. It is also important to note that within a fuel cell, the faster the reactions are taking place, the larger number of electrons will be completing the circuit making a higher current possible. In comparison, without a catalyst, reactions within a fuel cell would still take place, yet the output of energy would be too low to be useful. With better catalysts and lower activation energies we will receive a higher output current and more useful energy.

2.2.2 Catalyst crystal structure and active surface

The crystal structure of a compound refers to the arrangement of atoms or molecules in the compound. The crystal structure attempts to describe the pattern of the compound through use of a unit cell or smaller cell which can be expanded to simulate larger groupings. This is important when creating catalyst surfaces. Platinum and ruthenium each have such unique structures and thus the two main structures of interest are the platinum ccp (cubic closed packed, also known as the face-centered cubic, fcc, structure) unit cell, and the ruthenium hcp (hexagonal closed pack) unit cell. A variety of other notations may be used depending on the elements involved. Miller indices are notations used to define the active planes (or surfaces) in the crystal structure. A surface of platinum is thus notated as Pt(111) and ruthenium as Ru(0001). This paper focuses primarily on these two surfaces. For more advanced crystal structures other notations such as the Strukturbericht symbols are commonly used.

Due to the active planes for platinum and ruthenium the ccp (111) platinum surface and the hcp (0001) ruthenium surface are quite similar as seen in Figure 3 and Figure 4.

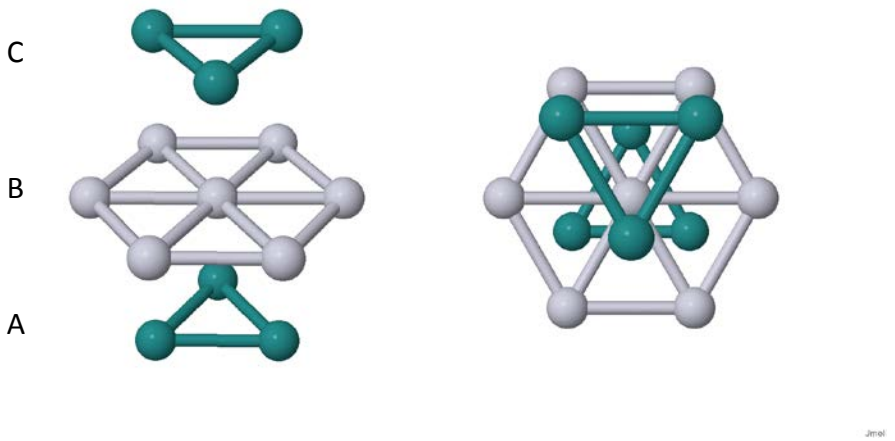


Figure 3: Platinum (111) cubic close packing (ccp) surface, side view (left) and top view (right)

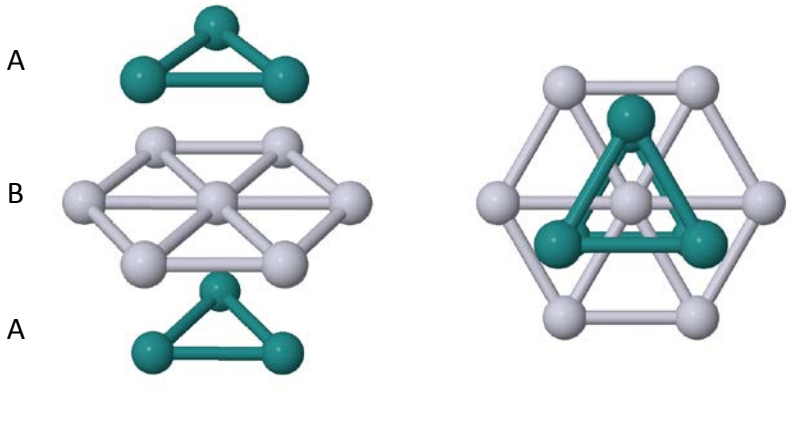


Figure 4: Ruthenium (0001) hexagonal close packing (hcp) surface, side view (left) and top view (right)

The main difference can be seen in the third layer where the third layer of the ccp is oriented opposite to that of the first layer while for hcp the 1st and third layers are oriented the same. For this reason it becomes difficult to mix multiple catalysts due to the way they would naturally align conflicting with each other.

2.3 Reaction Sites

Along the catalyst surface there are multiple sites upon which the different species could adsorb each with their own associated adsorption energies. There are four major sites of adsorption over the (111) Pt and (0001) Ru surfaces. These sites include the top site, bridge site, fcc site and hcp site which are illustrated in Figure 6.

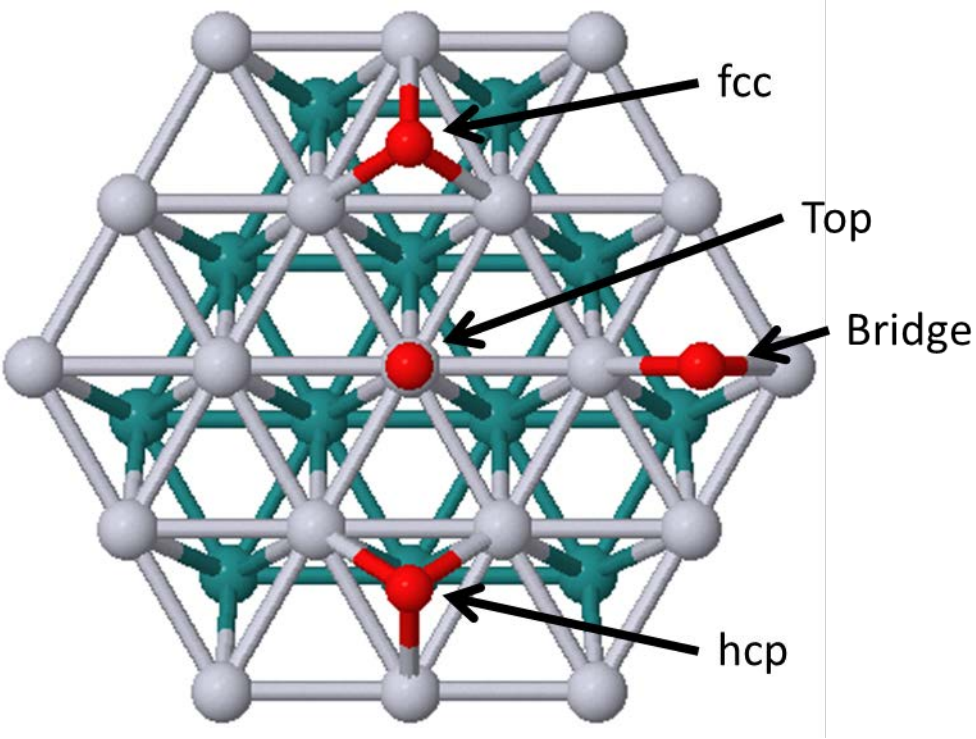


Figure 5: Available catalyst sites on a (111) Pt surface

These four sites will generally each have varying adsorption energies for an adsorbed species (i.e. carbon monoxide or a hydroxyl ion). Due to these differences the adsorbed species will preferentially adsorb to specific sites. Atoms or molecules adsorbed at different sites may react when in close proximity to each other.

2.3.1 Catalyst Poisoning and Mixed Surfaces

Catalyst poisoning refers the event which occurs when a species binds so strongly with the catalyst that it effectively renders the site useless and unable to interact with other species. In extreme cases the poisoning agent covers the whole catalyst, rendering the catalyst entirely useless. One example is that of carbon monoxide on a platinum catalyst, where the binding energy is very thermodynamically favorable and thus with enough CO the catalyst efficiency lowers. To counteract this problem many solutions have been formulated and tested. Primarily the one in question, a platinum-ruthenium mixed catalyst, may be useful as a fuel cell catalyst

2.4 Basics of a Fuel Cell

A fuel cell uses an electrochemical reaction in a thermodynamically open system, i.e. they are different from batteries in that they use reactants from an outside source which can be replenished while conventional batteries use stored energy that eventually runs out. The simplicity of fuel cell design and its reactants allow for higher efficiencies with fewer pollutants. Another promising feature is that instead of losing much of the energy in transport across wires, reactants can be moved to the fuel cell and then used to produce the energy on the spot without any significant loss of efficiency.

The first fuel cell demonstrated by Sir William Grove was the common hydrogen fuel cell. In this experiment it was first observed that running an electric current through water created oxygen and hydrogen on either side, and if the power source was later replaced by an ammeter it would show signs of a small current being created as the hydrogen and oxygen recombined. (Xiao-Zi Yuan, 2010)

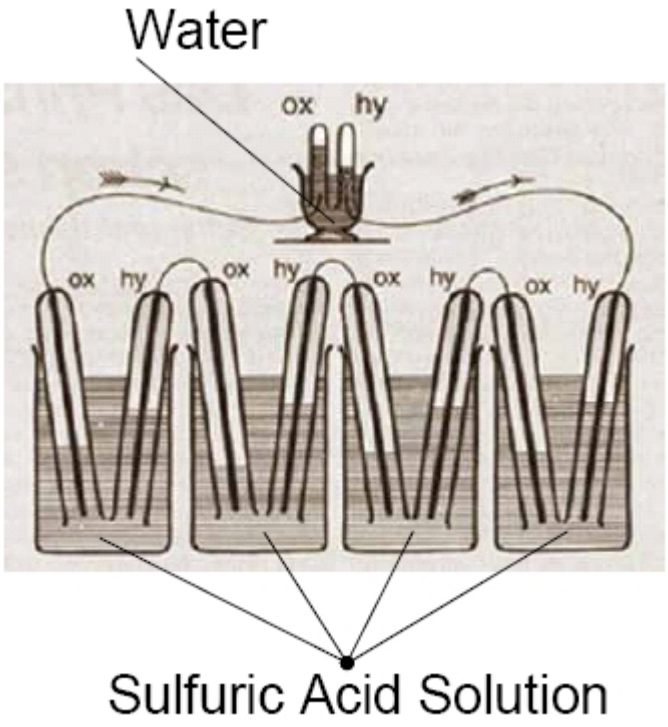


Figure 6: Reaction of the sulfuric acid produces water and electricity while the water in the upper beaker is electrolyzed breaking into oxygen and hydrogen at the anodes and cathodes (Fairbanks, 2004).

From these initial trials it was seen that electricity could be generated using a chemical reaction. Through the use of electrodes and an electrolyte, electrons and protons released in the chemical reaction can travel and recombine at another site. The electrons can then travel across an external circuit creating an electric current which can then be used to power other objects. With the improvement of catalysts and electrolytes this process was made easier and more effective, thereby generating larger amounts of energy over a specified time. Furthermore, due to the process of only using the chemical energies provided, a fuel cell is not bound to the same efficiencies of a conventional generator (i.e. the Carnot limit) and thus can be much more efficient. Electrical generators generally have an efficiency of 33% for coal and oil-fired plants, and up to 50% for combined-cycle gas-fired plants while a fuel cell can range from 10% up to 90% for a magnesium air fuel cell. (NPC Global Oil & Gas Study, 2007) (MagPower Systems Inc, 2006)

Even though the move to fuel cells may seem appealing, as it stands fuel cells are often more expensive, and risk a lower life expectancy. Current prices for platinum as of February 2012 give an average of $1658.38 per oz. In comparison ruthenium is much lower at $130 per oz. (Johnson Matthey Plc., 2012)

Modern fuel cells have incorporated new advances in catalysis to produce a more sophisticated set up:

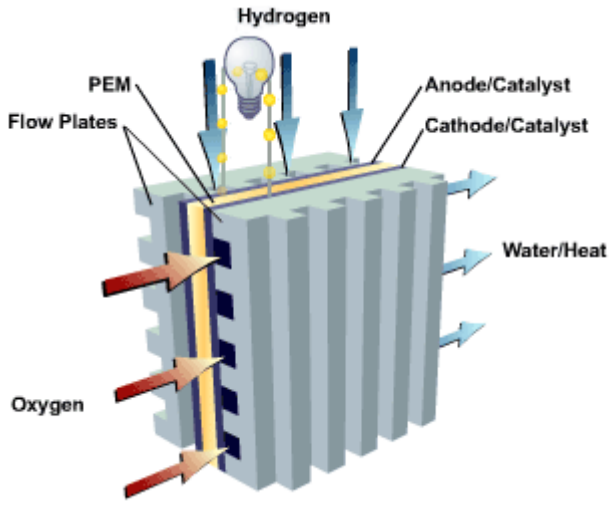


Figure 7: PEM Hydrogen Fuel Cell (EERE, 2007)

2.5 Direct Methanol Fuel Cells

Due to the low amount of naturally found hydrogen in nature other chemicals, such as methanol, have been proposed for use in fuel cells. The DMFC (Direct Methanol Fuel Cell) uses methanol, oxygen, and water as its primary sources of fuel. Methanol has been recently gained popularity due to its lower production price and ease of transport. A typical DMFC can run between 50 to 120°*C* with an efficiency of 40 to 50%. Currently, multiple companies have competed to show off the multiple uses of DMFCs.

In 2008 Toshiba created mini methanol fuel cells to fit inside a normal cell phone that can store twice the amount of power than a normal cell phone battery (Cadden, 2008). Another competitor, UltraCell has created a portable power source with twice the energy density as lithium batteries with refillable methanol fuel stacks. (Hanlon, 2005)

Current issues surrounding these fuel cells are the lower efficiencies due to methanol cross-over across the electrolyte (bypassing the catalysts) and the creation of carbon monoxide in the process which poses a problem for platinum catalyst poisoning.

The invention of the first methanol fuel cell was done in 1990 by work of Dr. Surya Prakash and Dr. George A. Olah. (Direct Methanol Fuel Cell (DMFC))

2.5.1 DMFC's Mechanism

The DMFC utilizes an oxidation and reduction reaction at the anode and cathode sides of the fuel cell respectively. As seen in Table 1 the combination of methanol (CH_3OH) and water (H_2O) creates free protons, electrons and carbon dioxide (CO_2). The protons continue to cross over to the cathode side while the electrons loop around and then both combine with the entering air on the cathode side to create water. The electrons going across the loop create electrical power. This process can be easily seen in Figure 10.

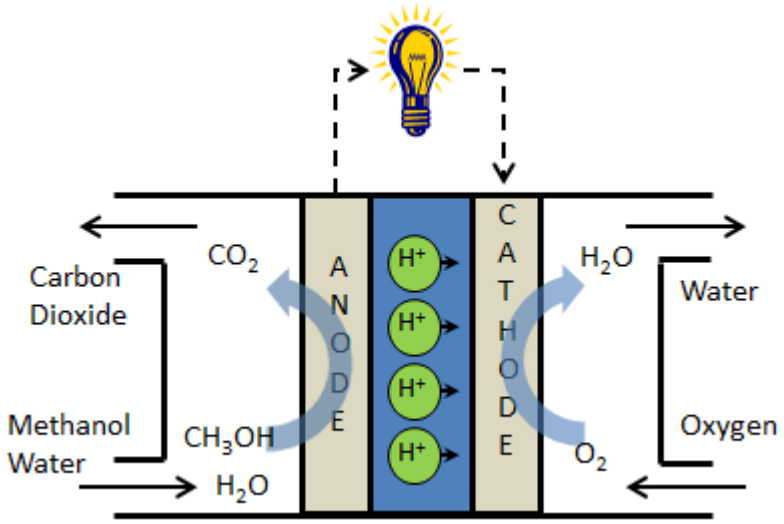


Figure 8: Methanol Fuel Cell Schematic

Table 1: Overall Fuel Cell Reactions

Anode Oxidation	$CH_3OH + H_2O \longrightarrow 6H^+ + 6e^- + CO_2$
Cathode Reduction	$\frac{3}{2}O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$
Overall Reaction	$CH_3OH + \frac{3}{2}O_2 \longrightarrow 2\,H_2O + CO_2$

In catalytic water-methanol reforming, i.e. water and methanol breaking down into Hydrogen ions and electrons, the methanol molecule forms a weak surface bond with the catalyst molecules. The electrons in the carbon P-orbitals form electron sharing bonds with the catalyst metal surface. This sharing reduces the necessary energy for the dissociation of methanol to carboxyl ions (COOH) and Hydrogen ions. The carboxyl ion, which is now more strongly bound to the surface, dissociates to in the presence of water to CO, CO_2, and H^+.

The surface bonding energies which these simulations calculate are a result of electron sharing with the catalysts metals. It is also these bonds, which reduce the energy required for the reactions to occur.

2.6 Methanol Oxidation

The full methanol oxidation reaction that occurs on the anode occurs as such:

$$CH_3OH + H_2O \rightleftarrows CO_2 + 6H^+ + 6e^-$$

To explain the methanol oxidation reaction, it is best to break it up into two components:

1. Methanol Dehydrogenation
2. Water Gas Shift Phase

2.6.1 Methanol Dehydrogenation

The primary fuel source in the methanol fuel cell comes from the dehydrogenation of methanol to produce hydrogen. This mechanism can be seen in Table 2, methanol adsorbs to the surface where it subsequently loses its hydrogen bonds to the surface. The bound hydrogen bonds react to produce free hydrogen molecules while carbon monoxide lies on the surface. Due to the poisoning effects of carbon monoxide the water gas shift phase is a crucial component of removing the carbon monoxide molecules from the surface.

Table 2: Methanol Dehydrogenation Mechanism (Callaghan, 2006)

$$CH_3OH + S \rightleftarrows CH_3OH \cdot S$$

$$CH_3OH \cdot S \rightleftarrows CH_2OH \cdot S + H \cdot S$$

$$CH_2OH \cdot S \rightleftarrows CHOH \cdot S + H \cdot S$$

$$CHOH \cdot S \rightleftarrows COH \cdot S + H \cdot S$$

$$COH \cdot S \rightleftarrows CO \cdot S + H \cdot S$$

$$4H \cdot S \rightleftarrows 2H_2$$

$$CH_3OH + S \rightleftarrows CO \cdot S + H_2 \quad \text{(Overall Reaction)}$$

S = Surface Site

2.6.2 Water Gas Shift Phase

Within the fuel cell perhaps one of the most important reactions that takes place on the anode is the combination of carbon monoxide and water to create carbon dioxide and hydrogen gas, i.e. the water-gas-shift (WGS) reaction:

$$H_2O + CO \rightleftarrows CO_2 + H_2$$

Along a surface there are many possible reaction routes this could take. The thesis of C. Callaghan (Callaghan, 2006) has an in depth review of some of the possible reaction mechanisms or routes of the reaction.

One of the more relevant reaction mechanisms, Callaghan showed, is the redox reaction mechanism shown in Table3. Here we see how both water and carbon monoxide adsorb to the surface (denoted as S). Water dissociates into an adsorbed hydroxyl and hydrogen atom, where the hydroxyl group continues to dissociate to adsorbed oxygen and a hydrogen atom. The adsorbed oxygen atom reacts with the adsorbed carbon monoxide group to form carbon dioxide. The third reaction in this mechanism messes with the overall reaction (OR) yet illustrates how the reaction is in equilibrium and could take multiple pathways.

Table 4 provides Temkin's Two-Step Redox Mechanism which is a much simpler version of the previous. Water dissociates with the surface leaving an adsorbed oxygen atom which is then reacted with carbon monoxide to produce carbon dioxide.

Table 5 provides a possible mechanism with formate as a possible intermediary from the reaction of adsorbed carbon monoxide and an adsorbed hydroxyl ion. The subsequent adsorbed formate is then broken into free CO_2 and an adsorbed hydrogen atom. This reaction warrants further investigation in the scope of this study.

Looking at these reaction mechanisms it is important to understand that the actual reaction route may be quite different and that the reactions depend on the adsorption energies of the species on the catalyst. Thus for different catalysts these could possibly change.

Table 3: Redox Reaction Mechanism	Table 4: Temkin's Two Step Redox Reaction Mechanism	Table 5: Formate Reaction Mechanism
$H_2O + S \rightleftarrows H_2O \cdot S$	$H_2O + S \rightleftarrows O \cdot S + H_2$	$CO + S \rightleftarrows CO \cdot S$
$H_2O \cdot S + S \rightleftarrows OH \cdot S + H \cdot S$	$O \cdot S + CO \rightleftarrows CO_2 + S$	$H_2O + S \rightleftarrows H_2O \cdot S$
$2OH \cdot S \rightleftarrows H_2O \cdot S + O \cdot S$	$\mathbf{CO + H_2O \rightleftarrows CO_2 + H_2}$	$H_2O \cdot S + S \rightleftarrows OH \cdot S + H \cdot S$
$OH \cdot S + S \rightleftarrows O \cdot S + H \cdot S$		$CO \cdot S + OH \cdot S \rightleftarrows HCOO \cdot S + S$
$2H \cdot S \rightleftarrows H_2 + 2S$		$HCOO \cdot S \rightleftarrows CO_2 + H \cdot S$
$CO + S \rightleftarrows CO \cdot S$		$2H \cdot S \rightleftarrows H_2 + 2S$
$CO \cdot S + O \cdot S \rightleftarrows CO_2 \cdot S + S$		$\mathbf{CO + H_2O \rightleftarrows CO_2 + H_2}$
$CO_2 \cdot S \rightleftarrows CO_2 + S$		

$\mathbf{CO + H_2O \rightleftarrows CO_2 + H_2}$		

(Callaghan, 2006)

2.7 Literature Review

Several studies have been performed using density functional theory (DFT), a molecular modeling method. In DFT the atoms of the surface and adsorbing species are modeled using quantum mechanics. One can therefore model surface adsorption and reactions, obtaining thermodynamic and kinetic data about catalyst surface reactions.

One issue in this field currently is the amount of time and computer capabilities available to the researchers. Due to this many approximations and differences lie in each study. The ones that may be of importance when comparing data include: number of layers and atoms used for the surface, bond distances between particles, whether the surface is relaxed (i.e. are the surface atoms allowed to move), the initial placement of the particles, and the legitimacy and validity of the computer program that was used. Below is a brief summary of previous work in this field.

2.7.1 A Periodic Density Functional Theory Study of the Dehydrogenation of Methanol over Pt(111)

In the paper by Desai et al. (Desai, Neurock, & Kourtakis, 2002), they modeled the dehydrogenation of methanol over the Pt(111) surface using DFT. They modeled seven different intermediates (methanol, methoxide, hydroxymethyl, formaldehyde, formyl, carbon monoxide, and hydrogen), and found that hydroxymethyl is a strong potential reactant intermediate. All C-H bond breaking steps were found to be exothermic, while C-O bond breaking was found to be endothermic.

This paper used a three layer hcp Pt(111) surface for studying the multiple reactions in the dehydrogenation of methanol. They first made sure three layers was enough by studying hydrogen over a three-, four-, and five-layered slab of platinum showing the difference was less than 5 kJ/mol and thus a three layered surface would be sufficient for the studies. They constructed the surface using a distance of 2.81 Å, this number they received from solving for the minimum energy for their structure. This can be compared to the experimental lattice constant of 2.78 Å. To account for the changes in the surface due to adsorption they relaxed the top two layers leaving only the third one held constant.

Their study focused primarily on 7 intermediates: methanol(CH_3OH), methoxide(CH_3O), hydroxymethyl(CH_2OH), formaldehyde(HCHO), formyl(HCO), carbon monoxide(CO_2), and hydrogen(H) with the following relevant data:

Table 6: Desai et al. (Desai, 2002) Primary Intermediates' Adsorption Energies and Sites

Molecule	Adsorption Energy (kJ/mol)	Adsorption site
CH_3OH	-43	Atop
CH_3O	-161	Bridge
CH_2OH	-209	Atop
HCHO	-49	di-σ
HCO	-237	η^2-η^1-C,O
CO	-168	Three-fold hollow
H	-269	Three-fold hollow

The C-H bond-breaking reaction was found to be 80 kJ/mol more favorable than the O-H bond-breaking reaction, partly because the C-H bond is intrinsically weaker than the O-H bond and partly because the product of C-H bond activation, the hydroxymethyl intermediate, is more strongly bound to the Pt surface than the product of O-H bond activation, the methoxide intermediate. The activation barrier to the formation of the hydroxymethyl intermediate was found to be 50 kJ/mol lower than the barrier to the formation of the methoxide intermediate. The dehydrogenation of the hydroxymethyl intermediate to form formaldehyde and surface hydrogen was the thermodynamically least-favored step in the proposed sequence, with an activation barrier of +120 kJ/mol. Experimentally, however, there is no evidence for the formation of a stable hydroxymethyl intermediate.

2.7.2 A Comparative Theoretical Study of the Hydrogen, Methyl, and Ethyl Chemisorption on the Pt(111) Surface

In the study by Papoian, Nørskov, and Hoffmann (Papoian, Nørskov, & Hoffmann, 2000), they examined several relevant species over a Pt (111) surface.

This study set up a simulation on a three-layer Pt (111) slab. They optimized their surface to a bulk distance of 2.83 Å, similar to the experimental value of 2.78 Å.

Their results for H_2 adsorption are listed below:

Table 7 Binding energies (per H_2) for a single monolayer H on Pt (111)

Binding site	atop	bridge	HCP	FCC
Binding Energy	-0.77 eV	-0.71 eV	-0.75 eV	-0.85 eV

They conclude by saying their data agrees well with literature values also strengthening the idea that hydrogen can pass between sites fairly easily but is bonded more strongly to the fcc site.

2.7.3 A Comparison of the Adsorption and Diffusion of Hydrogen on the {111} Surfaces of Ni, Pd, and Pt from Density Functional Theory Calculations

In the work of Watson, Wells, Willock, and Hutchings (Watson, Wells, Willock, & Hutchings, 2001), they modeled hydrogen over several different metal surfaces.

This group used the program VASP (Vienna Ab initio Simulation Program) to conduct their DFT studies on various {111} surfaces. They set up using the calculated equilibrium lattice constant for Pt(111) of 3.990 Å compared to an experimental value of 3.924 Å (Pt).

They conducted simulations over 2 differently sized surfaces, one with 12 metal atoms of three layers with a vacuum gap equivalent to 3 layers introduced to create the surfaces (one each side of the slab). The larger surface contained 20 metal atoms with 5 layers and a vacuum gap of 3 layers.

Table 8. Adsorption energies over Pt (111) for H_2

Rigid Surface	3 layers				5 layers			
Position	atop	bridge	hcp	fcc	atop	bridge	hcp	fcc
E_{ads} (kJ/mol)	-44.8	-42.4	-43.2	-43.9	-40.1	-39	-39.4	-42.7
Relaxed Surface	3 layers				5 layers			
E_{ads}	-49.3	-47.6	-48.1	-47.9	-43.4	-42.5	-43.4	-46

Their calculated adsorption energy for hydrogen yielded around -41 kJ/mol which is in good approximation to microcalorimetric experiments giving -45 kJ/mol. The preferred site being once again the fcc hollow site which has also been observed with low energy recoil scattering.- The calculated Pt-H bond length of 1.88 Å is slightly larger than the experimental value, 1.78 Å.

2.8 Quantum Chemistry

Quantum chemistry applies quantum mechanics to various chemical systems in an attempt to predict the outcome of an experiment. Due to the complexity of the many quantum equations and the number of molecules involved in the system these calculations can expand very quickly and the use of the computers computational power is a necessity. For this project the program CP2K was used which will be explained in further detail in the methodology.

2.9 Quantum Mechanics

Quantum mechanics is a branch of modern physics which attempts to explain interactions between matter and energy at the atomic and subatomic scales. Quantum mechanics provides a description of the dual wave/particle like behaviors and interactions of sub atomic particles. To do this quantum physicists use a mathematical formulation called the wave function. The wave function describes a system in a whole, and solving for a particular position gives a probability of finding the system in that state. The reason for this lies predominantly in the Heisenberg uncertainty principle.

Heisenberg noted in 1927 that in order to know the position or momentum of a particle, it would initially have to be measured yet to measure it changes some of its components. For example: In order to see an object, photons must be bounced off of it. For macroscopic items the impact of a photon will normally have a very little effect and it can be measured accordingly. For a particle when a photon makes contact it is possible that it will change its position or momentum. Due to the nature of photons, if you have a large momentum it will have a small wavelength and vice versa, thus when a large momentum photon is used to measure a particle it will give a good description of the position of the particle yet the photon will effectively change the momentum of the particle. Likewise, when a photon with small momentum and a long wavelength is used the transfer of momentum will be small yet the scattering of the photon will give a poor description of its current position. Due to these issues --and given that we are unable to use classical mechanics to find solutions to such problems--using the probabilities of a system is a better choice.

2.10 Density Functional Theory

Density functional theory is a quantum mechanical method used to model the electronic structures of various structures and phases. The theory gets its name from using functionals, or functions of functions, to determine various properties, in this case electron density. A functional can best be described as a function which is dependent on another function. For example taking the integral over a set area of a function would be a functional. (CP2K Developers Home Page)

Electron density is a measure of the probability of an electron being present at a particular location and is thus a physical characteristic of all molecules (Gotwals & Sendlinge, 2007). DFT is currently one of the newer alternatives to the ab initio method.

Ab initio methods have an advantage in that they will converge to the exact solution yet is given in the non-relativistic solution of the Schrodinger Equation. The main issue with ab initio is the computational cost and time. Due to this many approximate methods were introduced which would give approximate real solutions with little computer power and less time. DFT is one such method that gives a physical overall energy that can be used to analyze a reaction.

Density functional theory is based off of defining the electron density to solve for the ground state energy. Hohenberg and Kohn showed that it was possible to calculate the energy potential (Ev) as a function of the electron density, n(r)(the probability of finding an electron at position r):

$$\mathrm{E_v}[\mathrm{n}(\mathbf{r})] = \int \mathrm{n}(\mathbf{r})\mathrm{v}(\mathbf{r})\mathrm{d}\mathbf{r} + \mathrm{F_{HK}}[\mathrm{n}(\mathbf{r})]$$

where v(r) is the potential at the position r and FHK[n(r)] is a universal functional defined by Levy as

$$\mathrm{F_{HK}}[\mathrm{n}(\mathbf{r})] = \min_{\Psi \to \mathrm{n}(\mathbf{r})} \langle \Psi | \mathcal{T} + \mathcal{V}_{ee} | \Psi \rangle$$

Thus the ground state energy can be found as:

$$\mathrm{E_0} = \min_{\mathrm{n}(\mathbf{r})} \left(\int \mathrm{n}(\mathbf{r})\mathrm{v}(\mathbf{r})\mathrm{d}\mathbf{r} + \mathrm{F_{HK}}[\mathrm{n}(\mathbf{r})] \right)$$

The main issue is currently solving for a precise functional FHK. Due to this, an approximation has been made that results from evaluation of the kinetic part of the functional due to the orbitals. To use these calculation methods practically, the use of common day computing power becomes needed as well as extensive, well-built programs such as CP2K.

CHAPTER 3: METHODOLOGY

The principle goal of this study was to create a method of research that could be used to continue work in density functional theory for fuel cell development. To check our methods we compared the data obtained using this study's computational method with the data generated by other authors and their computational methods. The program used in this paper was the freely available CP2K (Car-Parinello 2000) program used to run molecular simulations based on density functional theory. This chapter explains the various approaches I used in implementing CP2K to obtain results for this study.

3.0 Simulation Setup

To create the simulated catalyst surfaces, I initially found the bulk distances for a Pt(111) surface and a Ru(0001) surface, 2.77 Angstroms and 2.66 Angstroms respectively. Thus each Pt-Pt bond and each Ru-Ru bond will have those distances between each atom. Platinum aligns in a ccp (Cubic Close-Packed) crystal structure and along the (111) surface. Ruthenium aligns in a hcp (Hexagonal Close-Packed) crystal structure and along the (0001) surface. The surfaces were composed of only 2 layers, 19 atoms on top and 12 on bottom which can be seen below:

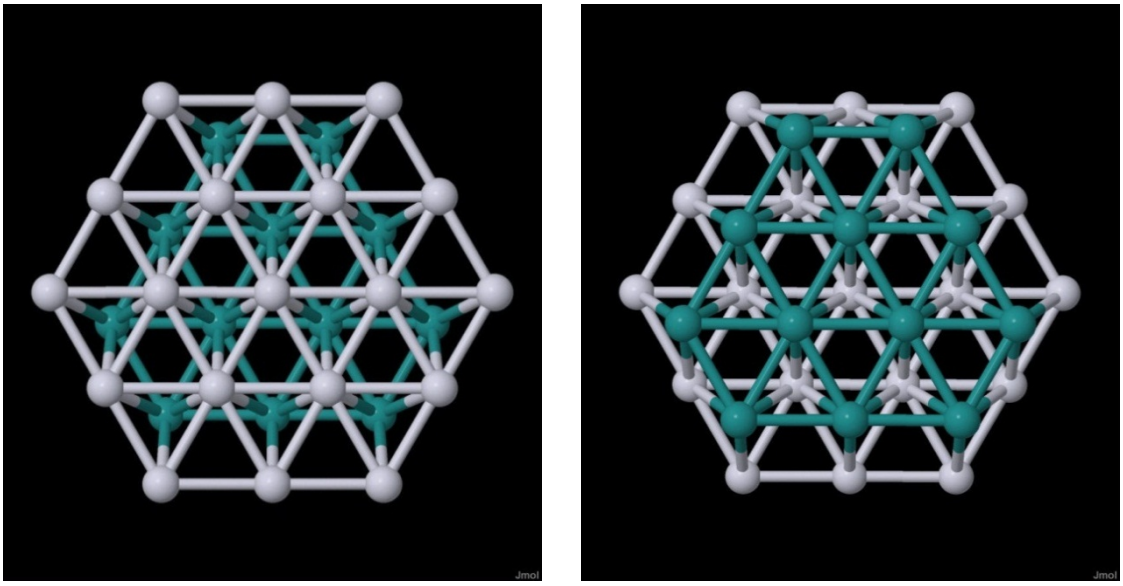


Figure 9: Example Surfaces, top layer (left) and the second layer (right)

I then chose the 4 major reaction sites a molecule could adsorb on:

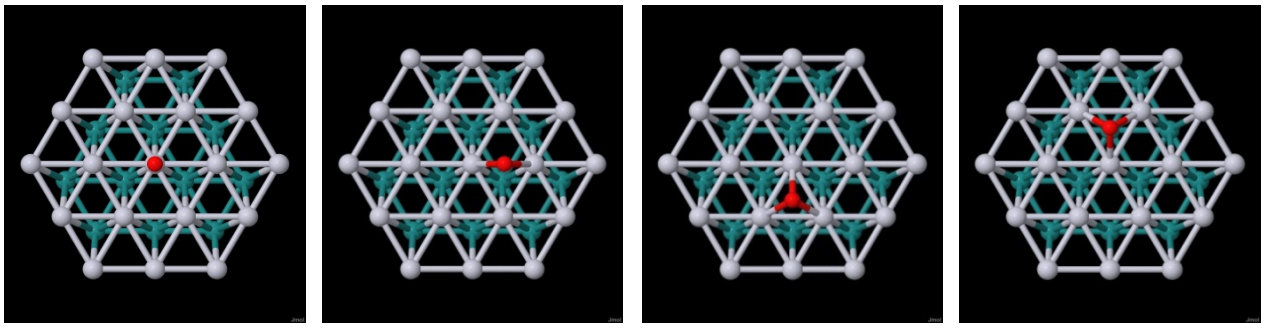


Figure 10: Example Positions, from left to right: top, bridge, fcc, hcp, for adsorption

Decisions were then made concerning the multiple bonding orientations each reactant could take, i.e. along the x axis, y axis or z axis. As shown by the next graphs:

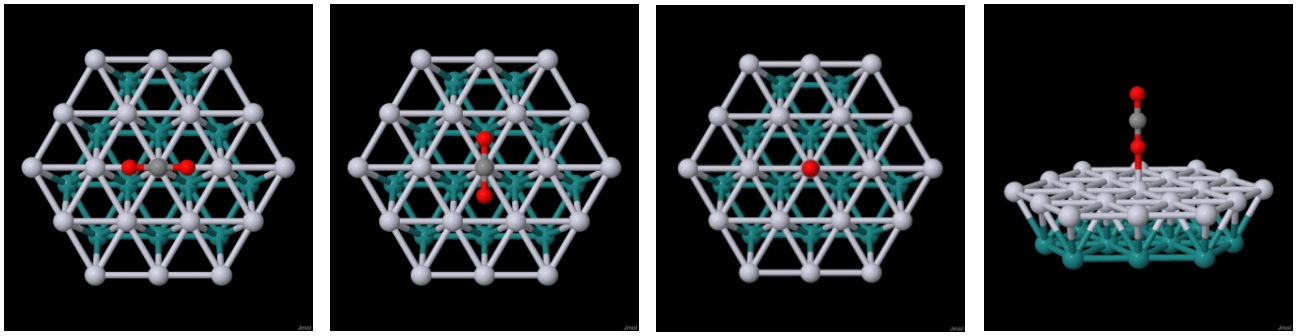


Figure 11: Example Adsorption Configurations, from left to right: x-axis, y-axis, z-axis, and z-axis again from the side view

One last consideration is the possible elements (of each molecule) that could absorb, i.e. for an OH molecule would the hydrogen or oxygen absorb on the surface.

Within the scope of this study it was not all possible to simulate all alignments for each molecule. Looking at all other bonding possibilities, even the remotely possible orientations, could yield interesting reaction insights. The study focused on the common adsorption species in the molecule with the common orientation at the 4 binding sites on the surface.

These criterions resulted in creation of the multiple bond position input files for each molecule along the Platinum and Ruthenium surfaces.

3.1 Computer Simulated Chemical Interactions

With the advancement in computational power, computer simulations have become increasingly popular in the scientific field. These simulations offer a look at how theory can be tested in comparison to experimental values. Many of the simulations allow scientists to study chemical and atomic states that may not be experimentally feasible to study. These simulations are based off of theory from quantum chemistry and thus the equations involved are difficult even for simple systems. With systems involving multiple species these equations could take years for an individual to work out. With the addition of computers it has been reduced to a few days and with such programs using density functional theory it can give an approximate solution even within a few hours. To run these simulations we used the program CP2K to run our simulations.

3.1.1 CP2K and Quickstep

The CP2K program allows density functional theory simulations within the Quickstep module of the program (CP2K Developers Home Page). It utilizes the Gaussian and plane wave (GPW) method, so that the electrons of the atoms are mathematically represented by Gaussian and plane wave functions. The potentials of Goedecker, Teter, and Hutter (GTH) were used to represent core electrons, while double zeta basis functions were used to represent valence electrons. The Perdew, Burke, and Ernzerhof (PBE) exchange correlation functional was used for all calculations and all calculations were spin-polarized. A cluster model was used to represent the metal surfaces.

CHAPTER 4: RESULTS AND DISCUSSIONS

Initial Trials

Initial trials to confirm the validity of CP2K were done by simulating individual compounds and obtaining reaction energies for different reactions. These results are shown below in Table 9. These reaction energies are reasonable, indicating the validity of my approach.

Table 9: Initial reaction trials, theoretical data obtained from the nist website (National Institute of Standards and Technology, 2011)

Reaction (units given in Kj/mol)	Experimental	Theoretical	% Diff
$H_2 + CH_3Br \rightarrow HBr + CH_4$	-80.33	-72.32	9.98
$N_2 + 3H_2 \rightarrow 2NH_3$	-197.74	-118.99	39.83
$H_2CO + HCl + H_2 \rightarrow CH_3Cl + H_2O$	-156.65	-120.34	23.18
$CO_2 + H_2 \rightarrow CO + H_2O$	87.39	99.81	14.21

Following this I began to simulate the adsorption of these molecules on a platinum and ruthenium surface separately giving the following results for adsorption energies.

4.0 Numerical Simulation Results

Table 10: Summary of calculated adsorption energies over the different surfaces

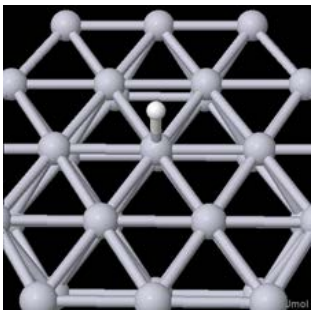
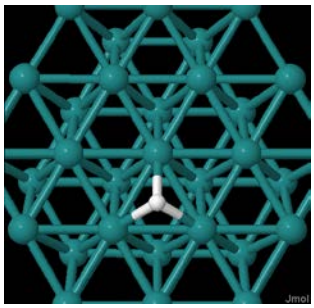
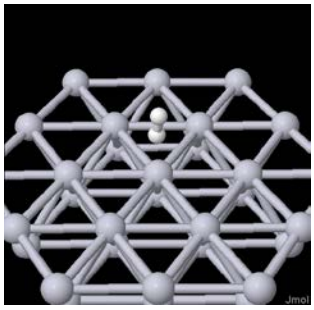
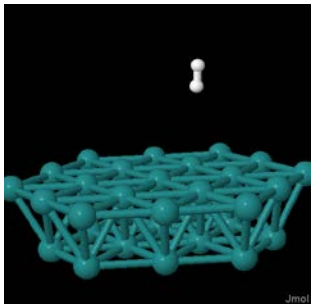
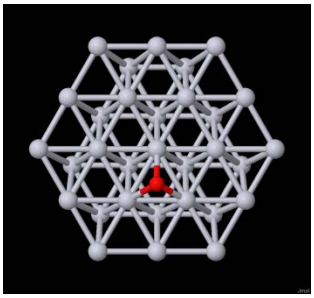
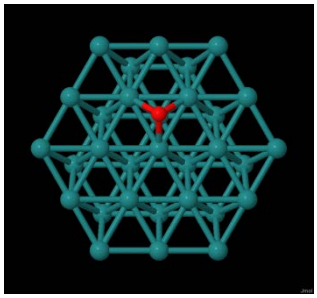
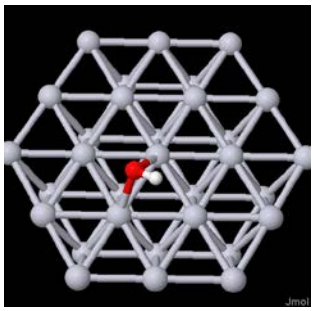
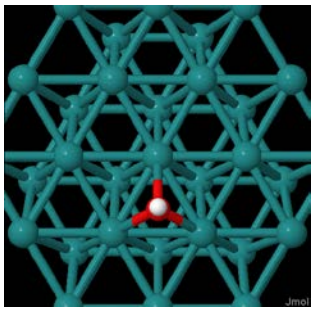
Chemical		Pt (111)		Ru (0001)	
	Adsorption site	E_{Ads} (eV)	Literature Value (eV)	E_{Ads} (eV)	Literature Value (eV)
H	top	-2.754	-2.71[1]	-2.358	-2.48[1]
	bridge	-2.643		-2.652	-2.64[1]
	fcc	-2.700	-2.788[2]	-2.752	-2.79[1]
	hcp	-2.570		-2.676	-2.72[1]
H_2	top	-0.024		-0.003	
	bridge	-0.024		-0.037	
	fcc	-0.030		0.008	
	hcp	-0.023		-0.036	
O	top	-5.348		-6.706	
	bridge	-6.116		-7.176	
	fcc	-6.741		-7.982	
	hcp	-6.355		-8.234	
OH (O Ads)	top	-1.094	-2.31[3]	-1.661	-2.82[6]
	bridge	-1.952	-2.24[3]	-2.716	-3.1[6]
	fcc	-1.601	-1.9[3]	-2.797	-3.21[6]
	hcp	-1.492	-1.8[3]	-2.773	-3.1[6]
OH (H Ads)	top	-0.074		-2.307	
	bridge	-1.932		-2.721	
	fcc	-1.983		-0.457	
	hcp	-0.156		-2.209	
H_2O	top	-0.094	0.291[4]	0.008	0.38[6]
	bridge	0.028	0.123[4]	0.055	0.12[6]
	fcc	-0.002	0.121[4]	-0.016	0.05[6]
	hcp	0.004		0.026	0.04[6]
CO (C Ads)	top	-1.742	-1.631[5]	-1.804	-1.93[3]
	bridge	-1.802	-1.752[5]	-1.694	-1.85[3]
	fcc	-1.958	-1.803[5]	-1.694	-1.91[3]
	hcp	-1.822	-1.798[5]	-1.794	-1.96[3]
CO (O Ads)	top	0.097		0.174	
	bridge	0.104		0.122	
	fcc	0.110		0.185	
	hcp	0.132		0.157	
CO_2 (C Ads)	top	0.016		-0.033	
	bridge	0.075		0.288	
	fcc	0.005		0.517	
	hcp	0.009		0.349	
CO_2 (O Ads)	top	0.128		0.196	
	bridge	0.094		0.150	
	fcc	0.133		0.187	
	hcp	0.092		0.218	
COOH	top	-2.359	-2.34[5]	-1.992	
	bridge	-2.362		-2.343	
	fcc	-2.151		-2.167	
	hcp	-2.370		-2.321	
CH_3OH	top	-0.168	-0.33[1]	-0.117	
	bridge	-0.060		0.000	
	fcc	-0.102		-0.021	
	hcp	-0.071		-0.006	

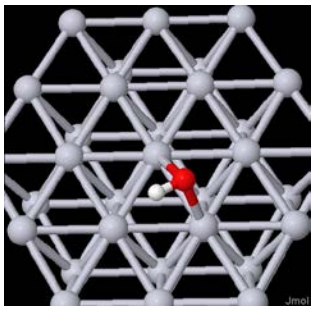
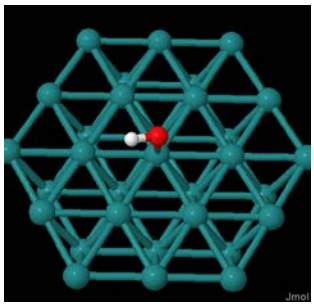
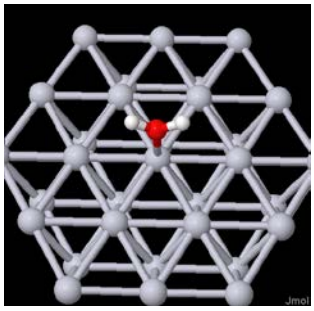
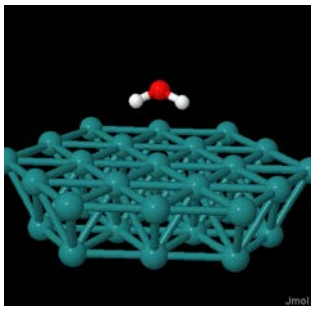
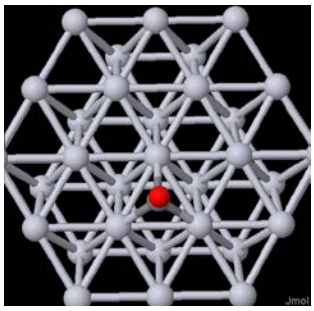
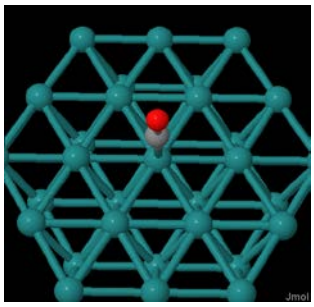
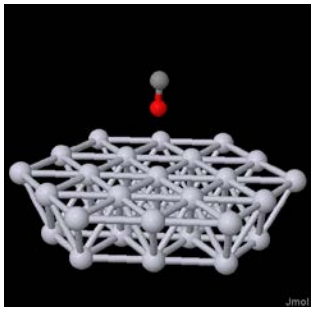
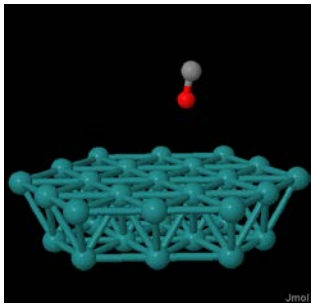
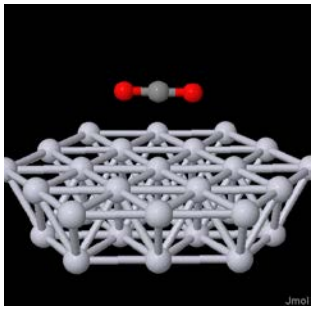
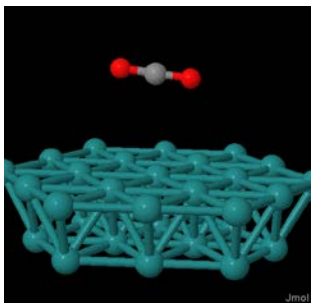
Reference List
1: Greeley, 2003
2: Desai, 2002
3: Koper, 2001
4: Meng, 2004
6: Michaelides, 2002

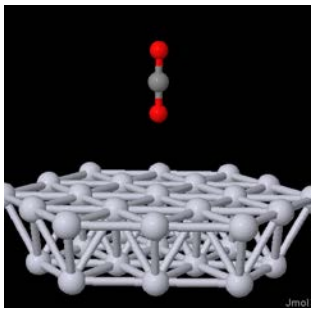
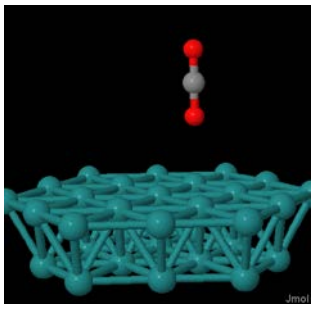
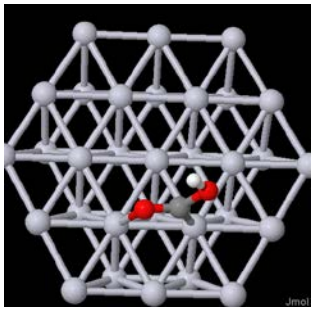
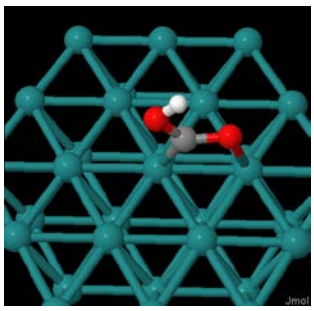
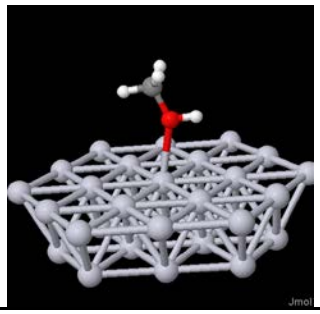
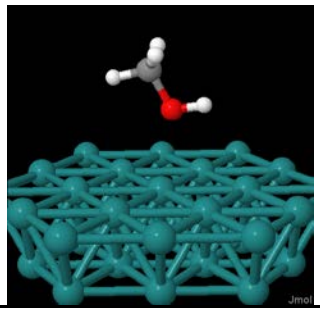
These numbers give us an idea of how probable a specific adsorption mode is. The more negative a number is, the more likely it is to occur. Energies close to zero or positive would be less likely. In the following pictures I give the lowest energies I received from my calculations for

each configuration. Many of the simulations had the molecule move significantly to a different position when it was optimizing the structure to the lowest energy. Some molecules would also move away from the surface due to the higher energies. Below are the pictures which can be referred back to in the following discussions.

Table 11: Images of most stable adsorption geometries over the Pt(111) and Ru (0001) surfaces
Numbers indicate energies in eV

Chemical	Pt (111)		Ru (0001)	
H	top -2.754		fcc -2.752	
H_2	fcc -0.030		bridge -0.037	
O	fcc -6.740		hcp -8.233	
OH (O Ads)	bridge -1.952		fcc -2.797	

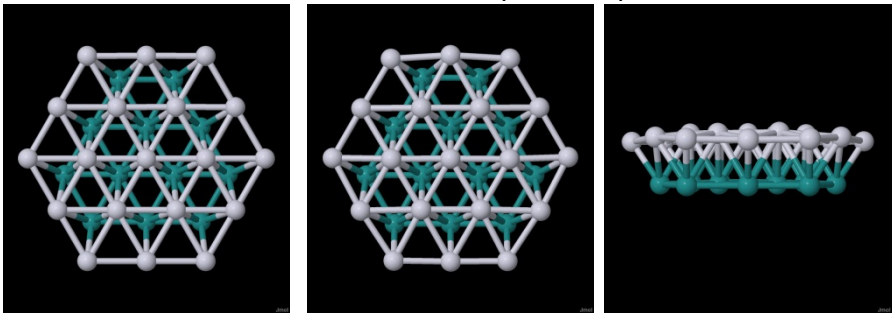
OH (H Ads)	fcc -1.983		bridge -2.721	
H_2O	top -0.094		fcc -0.016	
CO (C Ads)	fcc -1.958		top -1.804	
CO (O Ads)	top 0.097		bridge 0.122	
CO_2 (C Ads)	fcc 0.005		top -0.033	

CO_2 (O Ads)	hcp 0.092		bridge 0.150	
COOH	hcp -2.370		hcp -2.321	
CH_3OH	top -0.168		top -0.117	

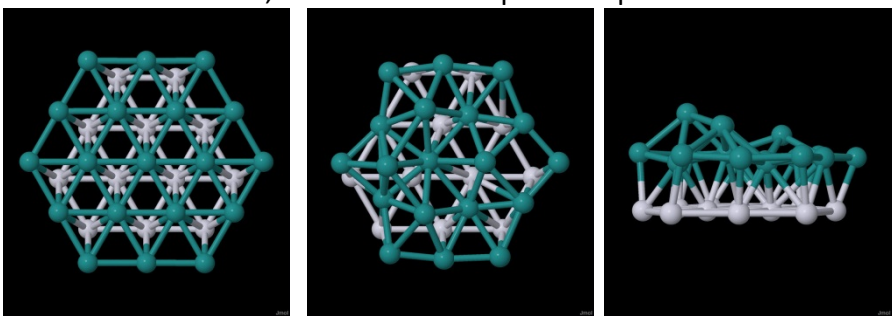
4.1 Mixed Metal Surfaces

I also simulated surfaces with both Pt and Ru. These are shown in figure 14 below. My results indicate significant rearrangement of the surfaces due to the inclusion of two different materials.

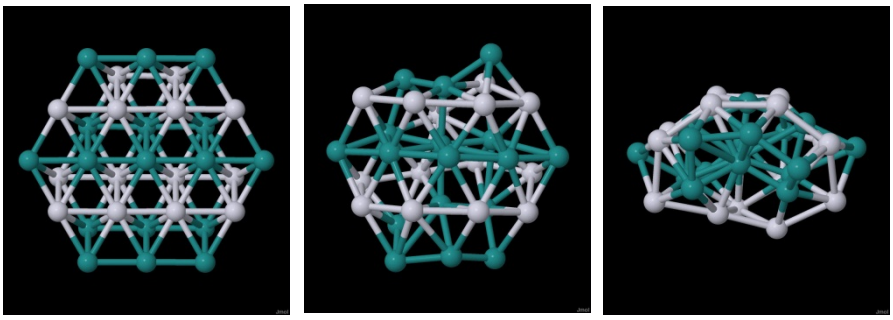
Ruthenium on bottom, Platinum on top with top relaxed:



Platinum on bottom, Ruthenium on top with top relaxed:



Mixed Platinum and Ruthenium all relaxed



Mixed Platinum and Ruthenium all relaxed

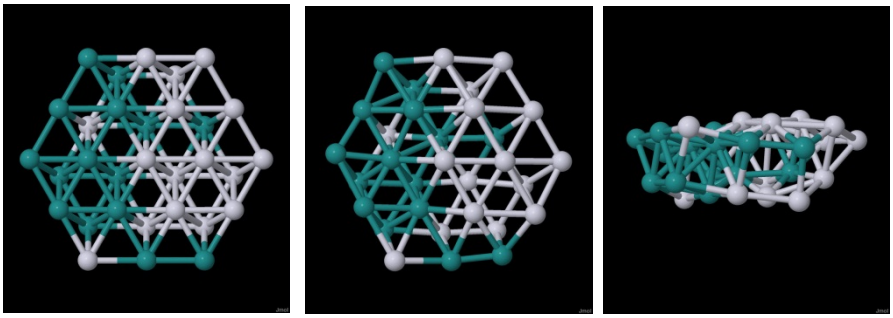


Figure 12: Geometries for mixed metal surfaces

From these figures it can be noted that the process of making a mixed catalyst appears to be very important. If done randomly the surfaces will create hills and valleys so to speak. What

we'd like to see is a smooth surface if anything to make the analysis and calculations much easier. Another reason for a clearer surface is that disordered surfaces as such have a higher chance of breaking apart and in effect destroying the catalyst itself.

4.2 Discussion of Results

4.2.1 Agreement with Catalyst Reaction Sites

As Table 10 shows, our numbers show good agreement with literature values for adsorption energies.

4.2.2 Summary of Results by Reactant

4.2.2a H:

The calculated adsorption energy of -2.75eV was found to prefer the top site. This agrees with Olsen et al. (Olsen, Kroes, & Baerends, 1999).

In the simulations hydrogen only fully adsorbed to the top and hcp sites while in the fcc it moved to the bridge site and along the bridge it began to move closer to the top site. For ruthenium the fcc site gave the best binding energy of -2.75 compared to a literature value of -2.79 eV (Greeley & Mavrikakis, 2004).

4.2.2b O:

Monoatomic oxygen showed the highest adsorption energies, -6.74 eV for platinum and a staggering -8.23 eV for Ruthenium. It appears to bind well at all sites yet specifically at the fcc position for platinum and hcp position for ruthenium.

4.2.2c OH:

OH appears to preferentially adsorb with either the oxygen or hydrogen atom at the top site although O bound to metal is most stable. The best two sites are with the oxygen along the bridge and hydrogen at the fcc site with adsorption energies of -1.95 eV and -1.98 eV.

For ruthenium this number dropped to -2.79eV with O adsorbed at the fcc site.

4.2.2d Water:

Water does not bond very well only at the top site with an energy of -0.09 eV for Pt and endothermic at 0.0079eV for Ru. Likely the initial configuration influenced this result.

4.2.2e CO:

Carbon monoxide binds well at nearly all sites for both Pt and Ru showing the best adsorption energy at -1.96eV at the fcc site for Pt and -1.8 eV at the top site for Ru. It only bonds with the carbon on the surface and not with the O atom.

4.2.2f CO_2:

Carbon dioxide does not bond with Pt but interestingly could bond endothermically at the bridge and hollow sites of Ru.

4.2.2g COOH:

COOH consistently moved such that the carbon and oxygen atoms would be in top positions for both Pt and Ru, and gave a Pt value of -2.37 eV and -2.34 eV for Ru.

4.2.2h Methanol:

Methanol would only bond at the top site of platinum with an energy of -0.17 eV.

4.2.3 Consolidation of Research Information

This study serves to consolidate the DMFC catalyst bonding energies into one single study using a common methodology.

The study also consolidates much of the information concerning DMFC, the surface interactions phenomena, catalyst variables, and the resulting bonding energies.

This may serve as an introductory guide to engineers needing basic information prior to continuing DMFC research and enhancement to this study.

4.2.4 Direction of Study

The information in this study of interactions of a platinum surface and a ruthenium surface within methanol decomposition species can serve to guide catalyst development toward a mixed surface of platinum and ruthenium.

4.3 Result Discrepancies

During the course of validating my numbers with literature values I began to notice nearly every paper had slightly different results due to their initial conditions placed on the system. Most

studies also would only study a couple species at a given time. Then again many species I was unable to find resources for. Possible reasons for the differences between studies include the number of layers of platinum and ruthenium, the method used, the multiplicity defined, and the initial position, distances, orientation, and simulation techniques.

Reported differences in hydroxyl and water adsorption energies between the values obtained in our simulation versus literature values is worthy of further study.

One major issue with a mixed surface such as platinum and ruthenium is due to the different bond lengths, so that the mixed surface would not come from a perfect structure. For example large distortions of atoms can be seen in Section 4.1, showing Pt-Ru surfaces.

CHAPTER 5: RECOMMENDATIONS FOR FURTHER STUDY

The study data and methodology pointed out four areas where these same simulations can possibly be enhanced:

- Relaxed surfaces can be used in the simulation of the catalyst surfaces
- Multi-layered catalyst surfaces could be simulated.
- Better choice of spin multiplicity
- Using an optimized bulk distance

The review of the DMFC literature and technology points to other areas where similar simulation studies can be used to enhance our understanding of the process. These suggested studies would be:

- Water poisoning at start up
- Creation of oxygen on catalyst and subsequent burning of methanol
- Other given geometries of adsorbates
- Mixed coverage simulations (OH and H near reactive site of H_2O)
- Simulations on Pt-Ru bonds and sites
- Creation of proposed ideal Pt-Ru crystal structure

CHAPTER 6: CONCLUSIONS

This study demonstrates the informational requirements and methodology for analyzing the catalytic reactions involved in fuel cells using modern computational methods. The adsorption of several species on catalyst surfaces were simulated using density functional theory as programmed in CP2K. The results agree well with other reported studies, and indicate that Pt and Ru surfaces are both strong catalysts for dissociating methanol in the fuel cell. The simulations both identify issues and provide direction in choosing between different catalysts and creating mixed metal catalysts. This study summarizes and expands the available surface bonding energy data beyond currently published data. A primary finding is that it is critical to make a clear definition and statement of the catalyst variables and a prioritization of these variables when configuring density functional theory simulations.

Initial setup variables, such as surface relaxation, number of surface layers, and reactant location and orientation, affect both the validity of the results and the computation power and convergence time of each simulation. This points to the need for further research to identify the effect of each setup variable, and the magnitude of these effects. Understanding of these effects will allow setup of valid DFT computations with limited computational power and optimal convergence time. This report can serve as a foundation for such a study.

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CHAPTER 8: EXAMPLE INPUT FILE

```
&FORCE_EVAL
 METHOD Quickstep
 &DFT
  #MULTIPLICITY 1
  UKS
  BASIS_SET_FILE_NAME ./GTH_BASIS_SETS_5-12-10
  POTENTIAL_FILE_NAME ./GTH_POTENTIALS_5-12-10
  WFN_RESTART_FILE_NAME x-RESTART.wfn
  &MGRID
   CUTOFF 300
  &END MGRID
  &QS
   WF_INTERPOLATION ASPC
   EXTRAPOLATION_ORDER 3
  &END QS
  &SCF
   EPS_SCF 1.E-6
   SCF_GUESS RESTART
   MAX_SCF 400
   &OT T
    PRECONDITIONER FULL_SINGLE_INVERSE
    MINIMIZER DIIS
    LINESEARCH 3PNT
   &END OT
  &END SCF
  &XC
   &XC_FUNCTIONAL PBE
   &END XC_FUNCTIONAL
  &END XC
  &PRINT
# &TOPOLOGY_INFO
# XYZ_INFO T
# &END TOPOLOGY_INFO
# &V_HARTREE_CUBE
# FILENAME ./rut_elpot
# &END V_HARTREE_CUBE
#  &E_DENSITY_CUBE
#   FILENAME ./HPt13..7-5..4h2o-2
#  &END E_DENSITY_CUBE
# &MO_CUBES
# WRITE_CUBE T
```

Multiplicity: States number of unbonded electrons (in future commenting out forces lowest

Basis and Potential Sets define characteristics of the Elements. To be provided with program and put in same file as input will be run.(Don't need to change)

```
# NHOMO 2
# NLUMO 1
# &END MO_CUBES
  &END PRINT
 &END DFT
&SUBSYS
 &CELL
  ABC 15 15 15
  #UNIT ANGSTROM
 &END CELL
 &COORD
        O        0.0000000000        0.0000000000        0.0000000000
        H        0.7615000000       -0.59870000000       0.0000000000
        H       -0.7615000000       -0.59870000000       0.0000000000
&END COORD
  &KIND H
   BASIS_SET DZVP-MOLOPT-GTH

   POTENTIAL GTH-PBE-q1
  &END KIND
  &KIND O
   BASIS_SET DZVP-MOLOPT-GTH
   POTENTIAL GTH-PBE-q6
  &END KIND
 &END SUBSYS
&END FORCE_EVAL
&GLOBAL
 PROJECT H2O
 RUN_TYPE GEO_OPT
#RUN_TYPE ENERGY
 PRINT_LEVEL LOW
&END GLOBAL
&MOTION
 &GEO_OPT
  MAX_ITER 400
  MAX_FORCE 0.0009725
  OPTIMIZER BFGS
 &END GEO_OPT
 &CONSTRAINT
  &FIXED_ATOMS
   LIST 1 2 3
  &END FIXED_ATOMS
 &END CONSTRAINT
&END MOTION
```

XYZ Coordinates of Species

Element Description: Description of element type to be found in basis and potential sets (If other types will need to add)

Project Name

Allows to fix certain atoms in place (i.e. 1 = O, 2 = H, 3 = H)

CHAPTER 9: EXAMPLE XYZ OUTPUT FILE

Water on a Platinum surface

Number of Atoms

Number of Iterations needed

Overall Energy (in Hartrees)

```
     34
i =       17, E =     -3741.4060196787
Pt         0.0000000000        0.0000000000        0.0000000000
Pt        -2.7700000000        0.0000000000        0.0000000000
Pt         2.7700000000        0.0000000000        0.0000000000
Pt        -5.5400000000        0.0000000000        0.0000000000
Pt         5.5400000000        0.0000000000        0.0000000000
Pt        -1.3850000000       -2.3988903680        0.0000000000
Pt         1.3850000000       -2.3988903680        0.0000000000
Pt        -4.1550000000       -2.3988903680        0.0000000000
Pt         4.1550000000       -2.3988903680        0.0000000000
Pt        -1.3850000000        2.3988903680        0.0000000000
Pt         1.3850000000        2.3988903680        0.0000000000
Pt        -4.1550000000        2.3988903680        0.0000000000
Pt         4.1550000000        2.3988903680        0.0000000000
Pt         0.0000000000       -4.7977807370        0.0000000000
Pt        -2.7700000000       -4.7977807370        0.0000000000
Pt         2.7700000000       -4.7977807370        0.0000000000
Pt         0.0000000000        4.7977807370        0.0000000000
Pt        -2.7700000000        4.7977807370        0.0000000000
Pt         2.7700000000        4.7977807370        0.0000000000
Pt        -1.3850000000       -0.7996301230       -2.2616955290
Pt         1.3850000000       -0.7996301230       -2.2616955290
Pt        -4.1550000000       -0.7996301230       -2.2616955290
Pt         4.1550000000       -0.7996301230       -2.2616955290
Pt         0.0000000000        1.5992602460       -2.2616955290
Pt        -2.7700000000        1.5992602460       -2.2616955290
Pt         2.7700000000        1.5992602460       -2.2616955290
Pt         0.0000000000       -3.1985204910       -2.2616955290
Pt        -2.7700000000       -3.1985204910       -2.2616955290
Pt         2.7700000000       -3.1985204910       -2.2616955290
Pt        -1.3850000000        3.9981506140       -2.2616955290
Pt         1.3850000000        3.9981506140       -2.2616955290
 O        -0.0002630697        0.0004103600        2.2584188800
 H        -0.8035061045       -0.0011067769        2.8077220085
 H         0.8031885616       -0.0013520376        2.8073520974
```

XYZ Positions of Optimized Geometry (Input into Jmol to view positions)

CHAPTER 10: Formulation of Simulations

Base program testing:
Simulation runs on 14 basic compounds were run using the CP2K to verify the program operation. These programs converged between one hour and one day, and resulted in reasonably accurate reaction energies (Refer to Table 9).

Surface Model development
A platinum surface model supplied by Professor Deskins, consisting of 11 platinum atoms on 2 levels, was then added to the simulation. Simulation runs using this surface appeared inadequate in size based upon the literature study.

A broader platinum surface model was obtained from a colleague, consisting of 32 symmetrical atoms on 2 levels. After some initial simulations inspection of the coordinates of the surface, showed that the platinum molecules were not in a perfect alignment, it appears it was ran to move freely by itself and then those coordinates were used for the next simulations. These simulations runs were excluded.

A new surface platinum model was generated with the same alignment and structure. It was seen that the correct structure (111) for platinum was an equilateral pyramid with a bulk distance of 2.77 angstroms between atoms. A coordinate surface model for a perfect platinum crystal was generated using a 2.77 A distance and a 111 frame.

The literature review of Pt/Ru (111) structures showed ruthenium aligned in the same structure as platinum with a bulk distance of 2.66. The coordinate surface model for a ruthenium (111) surface was created.

Ruthenium in fact does not align in a (111) configuration normally and will align in a (0001). A meeting with Prof. Shivkumar, of the WPI material science department, clarified the difference in 0001 and a 111 structure. When simulating only two layers, a 0001 alignment and a 111 alignment are in fact equivalent.

Mixed platinum/Ruthenium surfaces were combined using these two surface models.

Model development:
Early simulations used molecule orientations which were random, based upon an assumption that the program would move each molecule to the lowest energy level achieved. 30 or more simulations on the new surfaces (one day each) and the initial 14 test molecule simulations were run with this assumption.

A graduate student (Neal Rosenthal) determined that the fixed and relaxed molecule assignments were swapped. This required a code review and movement of code from one section to another as well as re-simulating these runs.

During this process I found that on the NIST Chemistry Database website they have compiled the final configurations of many compounds using Density Functional theory. From this point a re-ran many simulations based on these distances.

Simulation Runs:
The following sets of simulations were run:

- 18 Initial basic compounds program verification runs
- 48 simulations on pure platinum
- 48 simulations on pure ruthenium
- 4 mixed surface simulations
- In addition nearly every simulation was ran twice to fix multiple errors and many simulations were ran that were not deemed valuable enough to include in this paper

At this point I had finished many of my simulations and had started putting much of the information together. At this point I had not considered the bridge site in my calculations and was notified of this mistake. Thus I began to run simulations along the bridge sites. I also had begun to notice some molecules which weren't adsorbed in the initial coordinates and thus wanted to rerun them such that they were adsorbed in the beginning just to keep my runs consistent. I also began to formulate new ideas on positions, alignments and studying the other adsorbate agents such as for OH either the oxygen adsorbing or the hydrogen. At this point I also began to add more mixed surface simulations although none with adsorbed species since I first wanted to finish my analysis on pure ruthenium and platinum catalysts such that I could create surfaces that would be of some interest. Around this point I also found an error within the simulation viewer I was using such that I was not actually viewing the final states but only the first iteration and thus upon going the pile of data I was able to find the different states that actually adsorbed. Continuing research I also began to think of possibilities of running multiple species together to solve for the reaction sites that are actually used based on where the precursor would be. Many of this data could not be completed due to time and the computational needs since there are many other professors and students running programs on the same server. Beyond all this I believe the amount of information received was beyond what would normally be expected compared to many papers I've found online.

CHAPTER 11: Input criteria and output results

Following I list all the initial conditions I set for these experiments and the outcomes I received. The coordinates follow x, y and z correspondingly, where the axis is defined as follows:

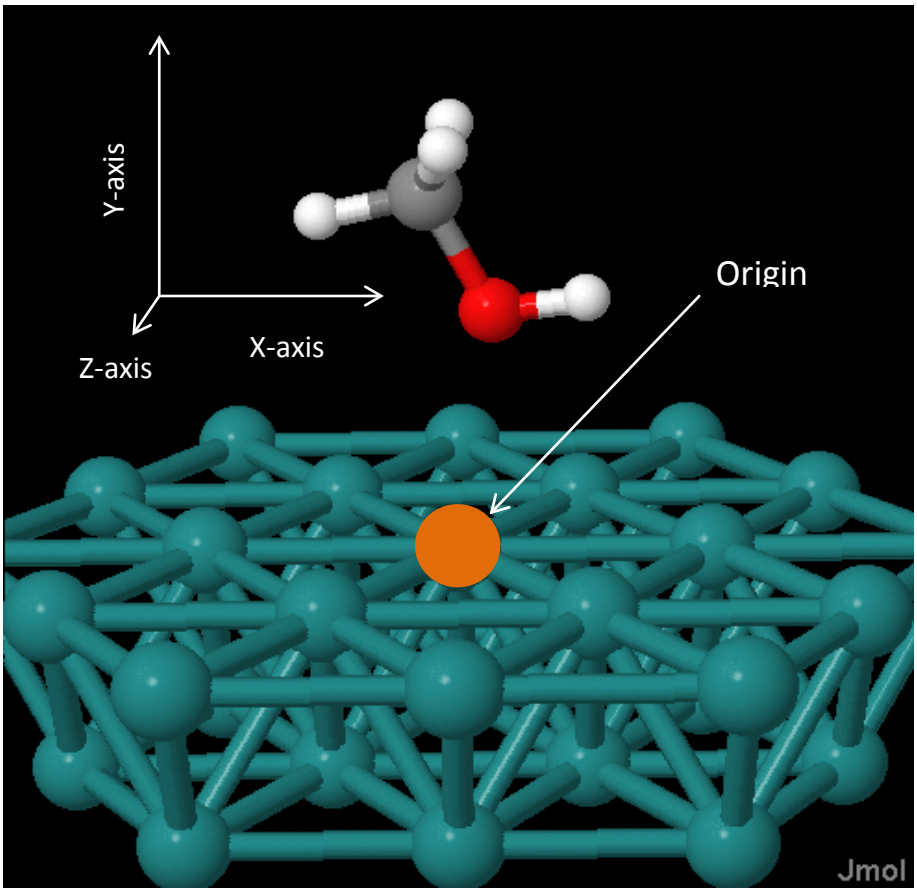

Figure 13: Axis orientation of simulations

Distances are measured in angstroms while energies are given in Hartrees.

11.0 Surfaces:

To model the surfaces mentioned I used and received the following data:

Platinum Surface:
Bulk distance: 2.77
Multiplicity: 3
All atoms held fixed at:

```
Pt          0.0000000000        0.0000000000        0.0000000000
Pt         -2.7700000000        0.0000000000        0.0000000000
Pt          2.7700000000        0.0000000000        0.0000000000
```

```
Pt        -5.5400000000        0.0000000000        0.0000000000
Pt         5.5400000000        0.0000000000        0.0000000000
Pt        -1.3850000000       -2.3988903680        0.0000000000
Pt         1.3850000000       -2.3988903680        0.0000000000
Pt        -4.1550000000       -2.3988903680        0.0000000000
Pt         4.1550000000       -2.3988903680        0.0000000000
Pt        -1.3850000000        2.3988903680        0.0000000000
Pt         1.3850000000        2.3988903680        0.0000000000
Pt        -4.1550000000        2.3988903680        0.0000000000
Pt         4.1550000000        2.3988903680        0.0000000000
Pt         0.0000000000       -4.7977807370        0.0000000000
Pt        -2.7700000000       -4.7977807370        0.0000000000
Pt         2.7700000000       -4.7977807370        0.0000000000
Pt         0.0000000000        4.7977807370        0.0000000000
Pt        -2.7700000000        4.7977807370        0.0000000000
Pt         2.7700000000        4.7977807370        0.0000000000
Pt        -1.3850000000       -0.7996301230       -2.2616955290
Pt         1.3850000000       -0.7996301230       -2.2616955290
Pt        -4.1550000000       -0.7996301230       -2.2616955290
Pt         4.1550000000       -0.7996301230       -2.2616955290
Pt         0.0000000000        1.5992602460       -2.2616955290
Pt        -2.7700000000        1.5992602460       -2.2616955290
Pt         2.7700000000        1.5992602460       -2.2616955290
Pt         0.0000000000       -3.1985204910       -2.2616955290
Pt        -2.7700000000       -3.1985204910       -2.2616955290
Pt         2.7700000000       -3.1985204910       -2.2616955290
Pt        -1.3850000000        3.9981506140       -2.2616955290
Pt         1.3850000000        3.9981506140       -2.2616955290
```

Iterations needed: 2

Calculated Energy: -3724.1803388541

Ruthenium Surface:

Bulk distance: 2.66

Multiplicity: 3

All atoms held fixed at:

```
Ru         0.0000000000        0.0000000000        0.0000000000
Ru        -2.6600000000        0.0000000000        0.0000000000
Ru         2.6600000000        0.0000000000        0.0000000000
Ru        -5.3200000000        0.0000000000        0.0000000000
Ru         5.3200000000        0.0000000000        0.0000000000
Ru        -1.3300000000       -2.3036275740        0.0000000000
Ru         1.3300000000       -2.3036275740        0.0000000000
Ru        -3.9900000000       -2.3036275740        0.0000000000
Ru         3.9900000000       -2.3036275740        0.0000000000
Ru        -1.3300000000        2.3036275740        0.0000000000
Ru         1.3300000000        2.3036275740        0.0000000000
Ru        -3.9900000000        2.3036275740        0.0000000000
Ru         3.9900000000        2.3036275740        0.0000000000
Ru         0.0000000000       -4.6072551480        0.0000000000
Ru        -2.6600000000       -4.6072551480        0.0000000000
Ru         2.6600000000       -4.6072551480        0.0000000000
Ru         0.0000000000        4.6072551480        0.0000000000
Ru        -2.6600000000        4.6072551480        0.0000000000
Ru         2.6600000000        4.6072551480        0.0000000000
Ru        -1.3300000000       -0.7678758580       -2.1718809050
Ru         1.3300000000       -0.7678758580       -2.1718809050
Ru        -3.9900000000       -0.7678758580       -2.1718809050
Ru         3.9900000000       -0.7678758580       -2.1718809050
```

```
Ru          0.0000000000        1.5357517160       -2.1718809050
Ru         -2.6600000000        1.5357517160       -2.1718809050
Ru          2.6600000000        1.5357517160       -2.1718809050
Ru          0.0000000000       -3.0715034320       -2.1718809050
Ru         -2.6600000000       -3.0715034320       -2.1718809050
Ru          2.6600000000       -3.0715034320       -2.1718809050
Ru         -1.3300000000        3.8393792900       -2.1718809050
Ru          1.3300000000        3.8393792900       -2.1718809050
```

Iterations needed: 2

Calculated Energy: -2933.7227185588

11.1 Individual Chemicals

All of the following simulations were run keeping only the individual chemicals for use in calculating the bond energies and for the initial trials. Nearly all of the simulations here had the multiplicity commented out except for two runs which are noted

11.1.1 H:

Initial Position:

```
  H         0.0000000000        0.0000000000        0.0000000000
```

Final Position:

```
  H         0.0000000000        0.0000000000        0.0000000000
```

Iterations needed: 2

Calculated Energy: `-0.4991318928`

11.1.2 H:

Multiplicity: 2

Initial Position:

```
  H         0.0000000000        0.0000000000        0.0000000000
```

Final Position:

```
  H         0.0000000000        0.0000000000        0.0000000000
```

Iterations needed: 2

Calculated Energy: `-0.4991318928`

11.1.3 H_2:

Initial Position:

```
  H        -0.3714000000        0.0000000000        0.0000000000
  H         0.3714000000        0.0000000000        0.0000000000
```

Final Position:

```
  H        -0.3753073388       -0.0000000000       -0.0000000000
  H         0.3753073388        0.0000000000        0.0000000000
```

Iterations needed: 3

Calculated Energy: `-1.1660516211`

11.1.4 O:

Initial Position:

```
O          0.0000000000        0.0000000000        0.0000000000
```

Final Position:

```
O          0.0000000000        0.0000000000        0.0000000000
```

Iterations needed: 2

Calculated Energy: `-15.7518132611`

11.1.5 OH:

Initial Position:

```
O          0.1092000000        0.0000000000        0.0000000000
H         -0.8739000000        0.0000000000        0.0000000000
```

Final Position:

```
O          0.0941588142       -0.0000003063        0.0000003648
H         -0.8911505426        0.0000004529       -0.0000005740
```

Iterations needed: 5

Calculated Energy: `-16.5308319117`

11.1.6 H_2O:

Initial Position:

```
O          0.0000000000        0.0000000000        0.0000000000
H          0.7615000000       -0.5987000000        0.0000000000
H         -0.7615000000       -0.5987000000        0.0000000000
```

Final Position:

```
O         -0.0000000499       -0.0005137630       -0.0000000256
H          0.7650024913       -0.5987995729        0.0000000231
H         -0.7650024337       -0.5987993991        0.0000000975
```

Iterations needed: 4

Calculated Energy: `-17.2222327344`

11.1.7 CO:

Initial Position:

```
O         -0.6502000000        0.0000000000        0.0000000000
C          0.4877000000        0.0000000000        0.0000000000
```

Final Position:

```
O         -0.6511120683        0.0000001959       -0.0000000362
C          0.4879497903       -0.0000002156        0.0000000401
```

Iterations needed: 3

Calculated Energy: `-21.6779617828`

11.1.8 CO_2:

Initial Position:

```
C          0.0000000000        0.0000000000        0.0000000000
O          1.1692000000        0.0000000000        0.0000000000
O         -1.1692000000        0.0000000000        0.0000000000
```

Final Position:

```
C          0.0000509032        0.0000035191       -0.0000014280
O          1.1753178848        0.0000003000       -0.0000001129
O         -1.1754445568        0.0000002815       -0.0000001058
```

Iterations needed: 3

Calculated Energy: `-37.7674282612`

11.1.9 COOH:

Initial Position:

```
O         -1.0654000000        0.0000000000        2.7978000000
H         -0.7637000000        0.0000000000        3.7346000000
C          0.0000000000        0.0000000000        2.0000000000
O          1.1609000000        0.0000000000        2.2720000000
```

Final Position:

```
O         -1.0248965435       -0.0000001334        2.8096589993
H         -0.7123419979        0.0000007238        3.7469883008
C          0.0400400564       -0.0000003918        1.9989360426
O          1.2126250434        0.0000002219        2.2508409813
```

Iterations needed: 22

Calculated Energy: `-38.2721640558`

11.1.10 CH_3OH:

Initial Position:

```
C         -0.0469000000        0.6608000000        0.0000000000
O         -0.0469000000       -0.7576000000        0.0000000000
H         -1.0944000000        0.9749000000        0.0000000000
H          0.4371000000        1.0863000000        0.8933000000
H          0.4371000000        1.0863000000       -0.8933000000
H          0.8762000000       -1.0514000000        0.0000000000
```

Final Position:

```
C         -0.0480939481        0.6685072072        0.0000001813
O         -0.0463611038       -0.7636740832       -0.0000002157
H         -1.1000809558        0.9785004394       -0.0000010375
H          0.4384740827        1.0875002528        0.8972604940
H          0.4384752529        1.0875000877       -0.8972598471
H          0.8787766449       -1.0560327856        0.0000005317
```

Iterations needed: 5

Calculated Energy: `-24.0836473859`

11.1.11 CH_3Br:

Multiplicity: 1

Initial Position:

```
C          0.0000000000        0.0000000000       -1.5399000000
Br         0.0000000000        0.0000000000        0.4244000000
H          0.0000000000        1.0369000000       -1.8711000000
H          0.8980000000       -0.5185000000       -1.8711000000
H         -0.8980000000       -0.5185000000       -1.8711000000
```

Final Position:

```
C          0.0000000199       -0.0000234167       -1.5386254271
Br        -0.0000001649       -0.0000011335        0.4244074425
H          0.0000000517        1.0400100408       -1.8716524225
H          0.9006516203       -0.5200213342       -1.8716562019
H         -0.9006515303       -0.5200213799       -1.8716560845
```

Iterations needed: 4

Calculated Energy: `-20.8874856382`

11.1.12 CH_3Cl:

Initial Position:

```
C          0.0000000000        0.0000000000       -1.1393000000
H          0.0000000000        1.0338000000       -1.4854000000
H          0.8953000000       -0.5169000000       -1.4854000000
H         -0.8953000000       -0.5169000000       -1.4854000000
Cl         0.0000000000        0.0000000000        0.6642000000
```

Final Position:

```
C          0.0000000446       -0.0000056311       -1.1330462382
H         -0.0000000202        1.0360978704       -1.4852917312
H          0.8972568939       -0.5180295941       -1.4852992208
H         -0.8972568950       -0.5180294841       -1.4852992467
Cl        -0.0000000232       -0.0000014037        0.6579980412
```

Iterations needed: 4

Calculated Energy: `-22.4564577518`

11.1.13 CH_4:

Initial Position:

```
C          0.0000000000        0.0000000000        0.0000000000
H          0.6312000000        0.6312000000        0.6312000000
H         -0.6312000000       -0.6312000000        0.6312000000
H         -0.6312000000        0.6312000000       -0.6312000000
H          0.6312000000       -0.6312000000       -0.6312000000
```

Final Position:

```
C         -0.0000007260        0.0000005003        0.0000003690
H          0.6326431248        0.6326442373        0.6326440945
H         -0.6326448235       -0.6326436618        0.6326444492
H         -0.6326451120        0.6326449581       -0.6326441950
H          0.6326414274       -0.6326416840       -0.6326417769
```

Iterations needed: 4

Calculated Energy: `-8.0762682507`

11.1.14 H_2CO:

Initial Position:

```
C          0.0000000000       -0.5289000000        0.0000000000
O          0.0000000000        0.6775000000        0.0000000000
H          0.9376000000       -1.1236000000        0.0000000000
H         -0.9376000000       -1.1236000000        0.0000000000
```

Final Position:

```
C          0.0000000050       -0.5634822783       -0.0000001311
O         -0.0000000038        0.6493557891        0.0000000388
H          0.9469725719       -1.1550821518        0.0000022894
H         -0.9469725727       -1.1550821562       -0.0000023573
```

Iterations needed: 13

Calculated Energy: `-22.8713848216`

11.1.15 HBr:

Initial Position:

```
Br         0.0000000000        0.0000000000        0.0000000000
H          1.4381000000        0.0000000000        0.0000000000
```

Final Position:

```
Br        -0.0012305643       -0.0000000060       -0.0000000002
H          1.4393073527        0.0000000060        0.0000000002
```

Iterations needed: 3

Calculated Energy: `-14.0078669441`

11.1.16 HCl:

Initial Position:

```
H          0.0000000000        0.0000000000        0.0000000000
Cl         1.2896000000        0.0000000000        0.0000000000
```

Final Position:

```
H          0.0003085914       -0.0000000304       -0.0000000137
Cl         1.2892965530        0.0000000304        0.0000000137
```

Iterations needed: 2

Calculated Energy: `-15.5815905651`

11.1.17 N_2:

Initial Position:

```
N          0.5528000000        0.0000000000        0.0000000000
N         -0.5528000000        0.0000000000        0.0000000000
```

Final Position:

```
N          0.5540865868       -0.0000002276       -0.0000001235
N         -0.5540865861        0.0000002279        0.0000001238
```

Iterations needed: 4

Calculated Energy: `-19.9044619290`

11.1.18 NH_3:

Initial Position:

```
N          0.0000000000        0.0000000000        0.1192000000
H          0.0000000000        0.9388000000       -0.2781000000
H          0.8130000000       -0.4694000000       -0.2781000000
H         -0.8130000000       -0.4694000000       -0.2781000000
```

Final Position:

```
N          0.0000000279       -0.0004570200        0.0923247296
H         -0.0000000720        0.9431106086       -0.3014469270
H          0.8170422844       -0.4721741481       -0.3017661659
H         -0.8170424503       -0.4721740810       -0.3017657651
```

Iterations needed: 13

Calculated Energy: `-11.7389661144`

11.2 Chemicals on the Platinum Surface

For all of the following data the positions mentioned are included with the platinum surface mentioned above.

11.2.1 H:

Top:

Multiplicity: 4

Initial Position:

```
H          0.0000000000        0.0000000000        2.0000000000
```

Final Position:

```
H          0.0007085061       -0.0004562187        1.5628776662
```

Number of Iterations: 11

Calculated Energy: `-3724.7806966286`

Bridge:

Multiplicity: 4

Initial Position:

```
H          1.3850000000        0.0000000000        1.5000000000
```

Final Position:

```
H          1.6762126714        0.2529002839        1.1942083500
```

Number of Iterations: 21

Calculated Energy: `-3724.7765896262`

Hcp:

Multiplicity: 4

Initial Position:

```
H          0.0000000000       -1.5992602460        1.0000000000
```

Final Position:

```
H          0.0183806430       -2.1880405096        1.0914848103
```

Number of Iterations: 25

Calculated Energy: -3724.7787037654

Fcc:

Multiplicity: 4

Initial Position:

```
H          0.0000000000        1.5992602460        1.0000000000
```

Final Position:

```
H          0.0020329673        1.6155335062        0.9719807672
```

Number of Iterations: 5

Calculated Energy: -3724.7739007107

11.2.2 H_2:

Top:

Multiplicity: 3

Initial Position:

```
H          0.0000000000        0.0000000000        2.0000000000
H          0.0000000000        0.0000000000        2.7428000000
```

Final Position:

```
H          0.0055255724       -0.0025130641        3.0865569393
H          0.0170100124        0.0087691570        3.8395299597
```

Number of Iterations: 33

Calculated Energy: -3725.3472798743

Bridge:

Multiplicity: 3

Initial Position:

```
H          1.3850000000        0.0000000000        1.5000000000
H          1.3850000000        0.0000000000        2.2428000000
```

Final Position:

```
H          1.5050239380       -0.0055769694        3.1741942496
H          1.5036937343       -0.0266025085        3.9266296379
```

Number of Iterations: 49

Calculated Energy: -3725.3472810784

Hcp:

Multiplicity: 3

Initial Position:

```
H          0.0000000000       -1.5992602460        1.0000000000
```

```
H          0.0000000000       -1.5992602460        1.7428000000
```

Final Position:

```
H         -0.0224832737       -1.8174498022        3.1067312719
H          0.0133562824       -1.9239315391        3.8512197763
```

Number of Iterations: 57

Calculated Energy: `-3725.3474959887`

Fcc:

Multiplicity: 3

Initial Position:

```
H          0.0000000000        1.5992602460        1.0000000000
H          0.0000000000        1.5992602460        1.7428000000
```

Final Position:

```
H          0.0233299000        1.7223508218        3.1011002917
H          0.0004556486        1.8224106044        3.8469732790
```

Number of Iterations: 54

Calculated Energy: `-3725.3472340065`

11.2.3 O:

Top:

Multiplicity: 1

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
```

Final Position:

```
O          0.0000064968       -0.0000177661        1.8641215636
```

Number of Iterations: 6

Calculated Energy: `-3740.1286895387`

Bridge:

Multiplicity: 1

Initial Position:

```
O          1.3850000000        0.0000000000        2.0000000000
```

Final Position:

```
O          1.4031087817        0.0106200857        1.4752514153
```

Number of Iterations: 18

Calculated Energy: `-3740.1569220967`

Hcp:

Multiplicity: 1

Initial Position:

```
O          0.0000000000       -1.5992602460        2.0000000000
```

Final Position:

```
O          -0.0003982800       -1.5967554956        1.3052364349
```

Number of Iterations: 23

Calculated Energy: -3740.1798723622

Fcc:

Multiplicity: 1

Initial Position:

```
O           0.0000000000        1.5992602460        2.0000000000
```

Final Position:

```
O           0.0000859222        1.5954135424        1.3178961697
```

Number of Iterations: 17

Calculated Energy: -3740.1657069371

11.2.4 OH (O Adsorbed):

Top:

Multiplicity: 4

Initial Position:

```
O           0.0000000000        0.0000000000        2.0000000000
H           0.0000000000        0.0000000000        2.9831000000
```

Final Position:

```
O          -0.0017527476        0.0009571113        1.9778362929
H           0.0025149289        0.0005457113        2.9414851260
```

Number of Iterations: 8

Calculated Energy: -3740.7510932441

Bridge:

Multiplicity: 4

Initial Position:

```
O           1.3850000000        0.0000000000        2.0000000000
H           1.3850000000        0.0000000000        2.9831000000
```

Final Position:

```
O           1.4989373967       -0.0860232904        1.6981205325
H           1.5092094617        0.8142368474        2.1013171560
```

Number of Iterations: 47

Calculated Energy: -3740.7826356860

Hcp:

Multiplicity: 4

Initial Position:

```
O           0.0000000000       -1.5992602460        2.0000000000
H           0.0000000000       -1.5992602460        2.9831000000
```

Final Position:

```
O           0.0010276268       -1.5921186752        1.5957343640
H           0.0104622927       -1.5991794919        2.5765094922
```

Number of Iterations: 25

Calculated Energy: -3740.7697297886

Fcc:

Multiplicity: 4

Initial Position:

O	0.0000000000	1.5992602460	2.0000000000
H	0.0000000000	1.5992602460	2.9831000000

Final Position:

O	-0.0008095652	1.5929149379	1.6833847490
H	-0.0078399125	1.5881464104	2.6654289336

Number of Iterations: 20

Calculated Energy: -3740.7657141914

11.2.5 OH (H Adsorbed):

Top:

Multiplicity: 4

Initial Position:

H	0.0000000000	0.0000000000	2.0000000000
O	0.0000000000	0.0000000000	2.9831000000

Final Position:

H	-0.0020367843	0.0015368260	2.1156927344
O	-0.0003927805	-0.0000917785	3.1175483501

Number of Iterations: 11

Calculated Energy: -3740.7135994787

Bridge:

Multiplicity: 4

Initial Position:

H	1.3850000000	0.0000000000	1.3000000000
O	1.3850000000	0.0000000000	2.2831000000

Final Position:

H	1.6473238202	-0.6321592095	2.1732711297
O	1.6905948447	0.2681976731	1.7762841337

Number of Iterations: 73

Calculated Energy: -3740.7818790013

Hcp:

Multiplicity: 4

Initial Position:

H	0.0000000000	-1.5992602460	1.3000000000
O	0.0000000000	-1.5992602460	2.2831000000

Final Position:

H	0.0555678694	-1.9928872834	2.1076029697

```
O          0.8451422363       -1.5003558227        1.7819501266
```

Number of Iterations: 78

Calculated Energy: `-3740.7837540479`

Fcc:

Multiplicity: 4

Initial Position:

```
H          0.0000000000        1.5992602460        1.3000000000
O          0.0000000000        1.5992602460        2.2831000000
```

Final Position:

```
H         -0.0202284362        1.5891003914        1.4643268514
O          0.0043112756        1.5946942427        2.4501208300
```

Number of Iterations: 18

Calculated Energy: `-3740.7166033152`

11.2.6 H_2O:

Top:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
H         -0.7615000000        0.0000000000        2.5987000000
H          0.7615000000        0.0000000000        2.5987000000
```

Final Position:

```
O         -0.0002630697        0.0004103600        2.2584188800
H         -0.8035061045       -0.0011067769        2.8077220085
H          0.8031885616       -0.0013520376        2.8073520974
```

Number of Iterations: 17

Calculated Energy: `-3741.4060196787`

Bridge:

Multiplicity: 3

Initial Position:

```
O          1.3850000000        0.0000000000        2.0000000000
H          0.6235000000        0.0000000000        2.5987000000
H          2.1465000000        0.0000000000        2.5987000000
```

Final Position:

```
O          1.4070818362       -0.0000927149        2.8213885072
H          0.6018871198       -0.0186664631        3.3681610670
H          2.1406619930        0.0251174741        3.4600247115
```

Number of Iterations: 46

Calculated Energy: `-3741.4015360019`

Hcp:

Multiplicity: 3

Initial Position:

```
O          0.0000000000       -1.5992602460        2.0000000000
H         -0.7615000000       -1.5992602460        2.5987000000
H          0.7615000000       -1.5992602460        2.5987000000
```

Final Position:

```
O         -0.0004356053       -1.2160680014        2.8167263243
H         -0.7728235567       -1.5785112242        3.2852649502
H          0.7730944550       -1.5748254866        3.2859865168
```

Number of Iterations: 39

Calculated Energy: -3741.4026539505

Fcc:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        1.5992602460        2.0000000000
H         -0.7615000000        1.5992602460        2.5987000000
H          0.7615000000        1.5992602460        2.5987000000
```

Final Position:

```
O         -0.0010118838        1.2176275643        2.7262272451
H         -0.7711609107        1.5937260545        3.1885493359
H          0.7759652429        1.5762704501        3.1906239380
```

Number of Iterations: 26

Calculated Energy: -3741.4024091225

11.2.7 CO (C Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
C          0.0000000000        0.0000000000        2.0000000000
O          0.0000000000        0.0000000000        3.1379000000
```

Final Position:

```
C          0.0009100703       -0.0007977893        1.8540442762
O         -0.0000011534        0.0001110042        3.0057053277
```

Number of Iterations: 10

Calculated Energy: -3745.9223136877

Bridge:

Multiplicity: 3

Initial Position:

```
C          1.3850000000        0.0000000000        2.0000000000
O          1.3850000000        0.0000000000        3.1379000000
```

Final Position:

```
C          1.4141636114        0.0295375574        1.4836774480
O          1.4033764979        0.0033941742        2.6638556518
```

Number of Iterations: 18

Calculated Energy: -3745.9245127798

Hcp:

Multiplicity: 3

Initial Position:

```
C          0.0000000000       -1.5992602460        2.0000000000
O          0.0000000000       -1.5992602460        3.1379000000
```

Final Position:

```
C         -0.0040645444       -1.6296878018        1.3611379002
O         -0.0000092363       -1.5972456006        2.5523801529
```

Number of Iterations: 24

Calculated Energy: -3745.9302659637

Fcc:

Multiplicity: 3

Initial Position:

```
C          0.0000000000        1.5992602460        2.0000000000
O          0.0000000000        1.5992602460        3.1379000000
```

Final Position:

```
C          0.0043130245        1.6225822716        1.3777309583
O         -0.0002442906        1.6003861903        2.5697495539
```

Number of Iterations: 23

Calculated Energy: -3745.9252551847

11.2.8 CO (O Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
C          0.0000000000        0.0000000000        3.1379000000
```

Final Position:

```
O          0.0000792956        0.0000599765        2.9096631298
C         -0.0012412113       -0.0030593725        4.0488769322
```

Number of Iterations: 47

Calculated Energy: -3745.8547417363

Bridge:

Multiplicity: 3

Initial Position:

```
O          1.3850000000        0.0000000000        2.0000000000
C          1.3850000000        0.0000000000        3.1379000000
```

Final Position:

```
O          1.4041525157       -0.0009011636        2.9115825982
C          1.3902084924        0.0057118706        4.0513185663
```

Number of Iterations: 39

Calculated Energy: -3745.8544697731

Hcp:

Multiplicity: 3

Initial Positions:

```
O          0.0000000000       -1.5992602460        2.0000000000
C          0.0000000000       -1.5992602460        3.1379000000
```

Final Position:

```
O          0.0000516937       -1.5939215837        2.9129781877
C          0.0001810394       -1.6013446987        4.0527175123
```

Number of Iterations: 45

Calculated Energy: `-3745.8542548906`

Fcc:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        1.5992602460        2.0000000000
C          0.0000000000        1.5992602460        3.1379000000
```

Final Position:

```
O          0.0001413293        1.5954190014        2.8237218645
C          0.0012430256        1.6017083194        3.9634200968
```

Number of Iterations: 32

Calculated Energy: `-3745.8534653281`

11.2.9 CO_2 (C Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
O         -1.1692000000        0.0000000000        2.0000000000
C          0.0000000000        0.0000000000        2.0000000000
O          1.1692000000        0.0000000000        2.0000000000
```

Final Position:

```
O         -1.2209044115        0.0000216879        3.2861529172
C         -0.0471127366       -0.0013805140        3.2815452866
O          1.1266634431        0.0006576150        3.2860577765
```

Number of Iterations: 63

Calculated Energy: `-3761.9471646112`

Bridge:

Multiplicity: 3

Initial Position:

```
O          0.2458000000        0.0000000000        2.0000000000
C          1.3850000000        0.0000000000        2.0000000000
O          2.5542000000        0.0000000000        2.0000000000
```

Final Position:

```
O          0.2840979080       -0.0000691953        2.9201964152
```

```
C          1.4549487466        0.0019372192        3.0165746326
O          2.6254328167        0.0010977254        3.1016941593
```

Number of Iterations: 63

Calculated Energy: -3761.9450280087

Hcp:

Multiplicity: 3

Initial Position:

```
O         -1.1692000000       -1.5992602460        2.0000000000
C          0.0000000000       -1.5992602460        2.0000000000
O          1.1692000000       -1.5992602460        2.0000000000
```

Final Position:

```
O         -1.1247287398       -1.5006629863        3.2849134086
C          0.0472134158       -1.4528169279        3.2374838229
O          1.2196957587       -1.4068024827        3.1929023442
```

Number of Iterations: 63

Calculated Energy: -3761.9476008663

Fcc:

Multiplicity: 3

Initial Position:

```
O         -1.1692000000        1.5992602460        2.0000000000
C          0.0000000000        1.5992602460        2.0000000000
O          1.1692000000        1.5992602460        2.0000000000
```

Final Position:

```
O        -1.2179558716        1.4066457539        3.1936501713
C        -0.0455075804        1.4521915363        3.2404802894
O         1.1262209147        1.5006214363        3.2858583837
```

Number of Iterations: 104

Calculated Energy: -3761.9474294161

11.2.10 CO_2 (O Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
C          0.0000000000        0.0000000000        3.1692000000
O          0.0000000000        0.0000000000        4.3384000000
```

Final Position:

```
O         -0.0000406164       -0.0000704683        2.7372971456
C         -0.0000814938       -0.0001337632        3.9107226590
O          0.0000118420       -0.0001341041        5.0808776782
```

Number of Iterations: 43

Calculated Energy: -3761.9430690909

Bridge:

Multiplicity: 3

Initial Position:

```
O          1.3850000000        0.0000000000        2.0000000000
C          1.3850000000        0.0000000000        3.1692000000
O          1.3850000000        0.0000000000        4.3384000000
```

Final Position:

```
O          1.5006260027       -0.0011121013        2.8257074006
C          1.4530307764       -0.0019349641        3.9987172879
O          1.4050053207       -0.0002707035        5.1683029900
```

Number of Iterations: 46

Calculated Energy: `-3761.9443019072`

Hcp:

Multiplicity: 3

Initial Position:

```
O          0.0000000000       -1.5992602460        2.0000000000
C          0.0000000000       -1.5992602460        3.1692000000
O          0.0000000000       -1.5992602460        4.3384000000
```

Final Position:

```
O         -0.0001094116       -1.5941231606        2.7453506784
C         -0.0002385377       -1.5939895367        3.9196760210
O         -0.0000260031       -1.5937609256        5.0898810873
```

Number of Iterations: 39

Calculated Energy: `-3761.9428702342`

Fcc:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        1.5992602460        2.0000000000
C          0.0000000000        1.5992602460        3.1692000000
O          0.0000000000        1.5992602460        4.3384000000
```

Final Position:

```
O         -0.0000164668        1.5940671328        2.8245753704
C          0.0000234107        1.5947438937        3.9986500502
O         -0.0000335028        1.5943547918        5.1694876608
```

Number of Iterations: 43

Calculated Energy: `-3761.9444036040`

11.2.11 COOH:

Top:

Multiplicity: 4

Initial Position:

```
O         -1.0654000000        0.0000000000        2.7978000000
H         -0.7637000000        0.0000000000        3.7346000000
```

```
C          0.0000000000        0.0000000000        2.0000000000
O          1.1609000000        0.0000000000        2.2720000000
```

Final Position:

```
O         -1.0282666457       -0.0001777606        2.7057822319
H         -0.7935642851       -0.0015988461        3.6612406421
C          0.1580105039       -0.0018358206        2.0291909727
O          1.2224933609       -0.0003490914        2.6224599679
```

Number of Iterations: 21

Calculated Energy: `-3762.5392043399`

Bridge:

Multiplicity: 4

Initial Position:

```
O          0.3196000000        0.0000000000        2.7978000000
H          0.6213000000        0.0000000000        3.7346000000
C          1.3850000000        0.0000000000        2.0000000000
O          2.5459000000        0.0000000000        2.2720000000
```

Final Position:

```
O         -0.0992372733        0.0004350278        2.9110419706
H          0.4575159163       -0.0008216242        3.7230104107
C          0.7134023028        0.0007432507        1.8573759322
O          1.9644391857        0.0006530622        2.0624947490
```

Number of Iterations: 48

Calculated Energy: `-3762.5393102453`

Hcp:

Multiplicity: 4

Initial Position:

```
O         -1.0654000000       -1.5992602460        2.7978000000
H         -0.7637000000       -1.5992602460        3.7346000000
C          0.0000000000       -1.5992602460        2.0000000000
O          1.1609000000       -1.5992602460        2.2720000000
```

Final Position:

```
O         -1.2241927341       -1.0367749910        2.6345852095
H         -0.6508040150       -0.9743850040        3.4312867239
C         -0.4990150452       -1.6243651316        1.6615664474
O          0.6643456360       -2.0679053361        1.9808339374
```

Number of Iterations: 65

Calculated Energy: `-3762.5315602228`

Fcc:

Multiplicity: 4

Initial Position:

```
O         -1.0654000000        1.5992602460        2.7978000000
H         -0.7637000000        1.5992602460        3.7346000000
C          0.0000000000        1.5992602460        2.0000000000
O          1.1609000000        1.5992602460        2.2720000000
```

Final Position:

```
O         -1.5976682500        1.6946654715        2.8142289795
H         -1.0748924854        1.5714285521        3.6393505989
C         -0.7422161997        2.0979449173        1.8629919642
O          0.4700284587        2.2522281176        2.1539903584
```

Number of Iterations: 103

Calculated Energy: `-3762.5395935440`

11.2.12 CH_3OH:

Top:

Multiplicity: 3

Initial Position:

```
C         -0.0469000000        0.0000000000        3.6608000000
O         -0.0469000000        0.0000000000        2.2424000000
H         -1.0944000000        0.0000000000        3.9749000000
H          0.4371000000        0.8933000000        4.0863000000
H          0.4371000000       -0.8933000000        4.0863000000
H          0.8762000000        0.0000000000        1.9486000000
```

Final Position:

```
C         -0.0961352814        0.0000747391        3.8381743179
O          0.4715599743        0.0001218487        2.5173627259
H         -1.1837354760       -0.0011348651        3.7090949063
H          0.2024270217        0.9005701520        4.3949289854
H          0.2045717962       -0.9000895361        4.3945830265
H          1.4454623016        0.0261977758        2.5506397367
```

Number of Iterations: 47

Calculated Energy: `-3748.2701423455`

Bridge:

Multiplicity: 3

Initial Position:

```
C          1.3381000000        0.0000000000        3.6608000000
O          1.3381000000        0.0000000000        2.2424000000
H          0.2906000000        0.0000000000        3.9749000000
H          1.8221000000        0.8933000000        4.0863000000
H          1.8221000000       -0.8933000000        4.0863000000
H          2.2612000000        0.0000000000        1.9486000000
```

Final Position:

```
C          1.1977481950       -0.0019813931        4.0813109222
O          1.0159076887        0.0013088633        2.6578643244
H          0.1982511342       -0.0038272153        4.5326114519
H          1.7339805987        0.8962326832        4.4228031443
H          1.7366888428       -0.9002796474        4.4192733466
H          1.8889580056        0.0446339663        2.2100438145
```

Number of Iterations: 37

Calculated Energy: `-3748.2661989196`

Hcp:

Multiplicity: 3

Initial Position:

```
C          -0.0469000000       -1.5992602460        3.3608000000
O          -0.0469000000       -1.5992602460        1.9424000000
H          -1.0944000000       -1.5992602460        3.6749000000
H           0.4371000000       -2.4925602460        3.7863000000
H           0.4371000000       -0.7059602460        3.7863000000
H           0.8762000000       -1.5992602460        1.6486000000
```

Final Position:

```
C          -0.2239452474       -1.5186646288        4.1378676982
O          -0.3800086249       -1.3144274414        2.7236967446
H          -1.2300084794       -1.5308412665        4.5755580323
H           0.2666152789       -2.4786031150        4.3563663379
H           0.3587313626       -0.7043455792        4.5970068191
H           0.4134626553       -1.6516570206        2.2598212951
```

Number of Iterations: 43

Calculated Energy: `-3748.2677451404`

Fcc:

Multiplicity: 3

Initial Position:

```
C          -0.0469000000        1.5992602460        3.3608000000
O          -0.0469000000        1.5992602460        1.9424000000
H          -1.0944000000        1.5992602460        3.6749000000
H           0.4371000000        2.4925602460        3.7863000000
H           0.4371000000        0.7059602460        3.7863000000
H           0.8762000000        1.5992602460        1.6486000000
```

Final Position:

```
C          -0.1810810323        1.5583668796        3.9656527451
O          -0.2863640559        1.4070916452        2.5396912365
H          -1.2031081067        1.5495143266        4.3601893974
H           0.2992843459        2.5111154310        4.2326988871
H           0.3849637742        0.7243531315        4.4085325493
H           0.5798377470        1.6199893528        2.1249031125
```

Number of Iterations: 79

Calculated Energy: `-3748.2665838423`

11.3 Chemicals on the Ruthenium Surface

For all of the following data the positions mentioned are included with the ruthenium surface mentioned above.

11.3.1 H:

Top:

Multiplicity: 4

Initial Position:

```
H           0.0000000000        0.0000000000        2.0000000000
```

Final Position:

```
H          0.0017182774        0.0014986315        1.6289782727
```

Number of Iterations: 10

Calculated Energy: -2934.3084925743

Bridge:

Multiplicity: 4

Initial Position:

```
H          1.3300000000        0.0000000000        1.2000000000
```

Final Position:

```
H          1.3199625316        0.0087816733        1.2347085952
```

Number of Iterations: 4

Calculated Energy: -2934.3193078098

Hcp:

Multiplicity: 4

Initial Position:

```
H          0.0000000000       -1.5357517160        1.2000000000
```

Final Position:

```
H         -0.0007180933       -1.5281255859        1.1265515433
```

Number of Iterations: 6

Calculated Energy: -2934.3229784285

Fcc:

Multiplicity: 4

Initial Position:

```
H          0.0000000000        1.5357517160        1.2000000000
```

Final Position:

```
H         -0.0051685134        1.5269726650        1.1104038374
```

Number of Iterations: 5

Calculated Energy: -2934.3201915896

11.3.2 H_2:

Top:

Multiplicity: 3

Initial Position:

```
H          0.0000000000        0.0000000000        2.0000000000
H          0.0000000000        0.0000000000        2.7428000000
```

Final Position:

```
H          0.0109341808        0.0173246588        3.2794750199
H          0.0055762525        0.0063294120        4.0325928879
```

Number of Iterations: 39

Calculated Energy: -2934.8888901014

Bridge:

Multiplicity: 3

Initial Position:

```
H          1.3300000000        0.0000000000        1.5000000000
H          1.3300000000        0.0000000000        2.2428000000
```

Final Position:

```
H          1.5226825020        0.1602880302        3.4188153506
H          1.5922341067        0.1721114657        4.1683422681
```

Number of Iterations: 75

Calculated Energy: -2934.8901437605

Hcp:

Multiplicity: 3

Initial Position:

```
H          0.0000000000       -1.5357517160        1.2000000000
H          0.0000000000       -1.5357517160        1.9428000000
```

Final Position:

```
H         -0.0251655925       -1.6112127624        3.3009251400
H          0.0158267802       -2.0042261172        3.9418068874
```

Number of Iterations: 54

Calculated Energy: -2934.8884897356

Fcc:

Multiplicity: 3

Initial Position:

```
H          0.0000000000        1.5357517160        1.2000000000
H          0.0000000000        1.5357517160        1.9428000000
```

Final Position:

```
H          0.0068761032        1.5848153336        3.2863605609
H          0.1128961992        1.5395403673        4.0306340622
```

Number of Iterations: 58

Calculated Energy: -2934.8900800308

11.3.3 O:

Top:

Multiplicity: 1

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
```

Final Position:

```
O         -0.0018421299        0.0014416677        1.7673831239
```

Number of Iterations: 33

Calculated Energy: -2949.7209706236

Bridge:

Multiplicity: 1

Initial Position:

```
O          1.3300000000        0.0000000000        2.0000000000
```

Final Position:

```
O          1.3140937713       -0.0158881707        1.4199900495
```

Number of Iterations: 15

Calculated Energy: -2949.7382358611

Hcp:

Multiplicity: 1

Initial Position:

```
O          0.0000000000       -1.5357517160        2.0000000000
```

Final Position:

```
O         -0.0008208216       -1.5048021832        1.3176346373
```

Number of Iterations: 24

Calculated Energy: -2949.7678552737

Fcc:

Multiplicity: 1

Initial Position:

```
O          0.0000000000        1.5357517160        2.0000000000
```

Final Position:

```
O          0.0001270763        1.5044624800        1.3082415752
```

Number of Iterations: 24

Calculated Energy: -2949.7771241213

11.3.4 OH (O Adsorbed):

Top:

Multiplicity: 4

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
H          0.0000000000        0.0000000000        2.9831000000
```

Final Position:

```
O          0.0020187886        0.0012397567        1.9551204018
H          0.0013310577       -0.0098664225        2.9196924079
```

Number of Iterations: 10

Calculated Energy: -2950.3142923279

Bridge:

Multiplicity: 4

Initial Position:

```
O          1.3300000000        0.0000000000        2.0000000000
H          1.3300000000        0.0000000000        2.9831000000
```

Final Position:

```
O          1.3123758159       -0.0951994400        1.6867215998
H          1.2550962789        0.7095277222        2.2432662380
```

Number of Iterations: 45

Calculated Energy: `-2950.3530651832`

Hcp:

Multiplicity: 4

Initial Position:

```
O          0.0000000000       -1.5357517160        2.0000000000
H          0.0000000000       -1.5357517160        2.9831000000
```

Final Position:

```
O          0.0008927143       -1.5022552840        1.5063996555
H          0.0130179953       -1.4089416428        2.4773453576
```

Number of Iterations: 31

Calculated Energy: `-2950.3560509945`

Fcc:

Multiplicity: 4

Initial Position:

```
O          0.0000000000        1.5357517160        2.0000000000
H          0.0000000000        1.5357517160        2.9831000000
```

Final Position:

```
O          0.0002065687        1.5006728453        1.5038128653
H          0.0006421938        1.3998167783        2.4750049726
```

Number of Iterations: 26

Calculated Energy: `-2950.3551775823`

11.3.5 OH (H Adsorbed):

Top:

Multiplicity: 4

Initial Position:

```
H          0.0000000000        0.0000000000        2.0000000000
O          0.0000000000        0.0000000000        2.9831000000
```

Final Position:

```
H         -0.8744760202       -0.3745481172        2.3114847793
O          0.0006806109       -0.0959092104        1.9765380994
```

Number of Iterations: 85

Calculated Energy: `-2950.3380453941`

Bridge:

Multiplicity: 4

Initial Position:

```
H          1.3300000000        0.0000000000        1.2000000000
O          1.3300000000        0.0000000000        2.1831000000
```

Final Position:

```
H          1.2514783069        0.1687287338        2.4666771076
O          1.3115882392        0.5718806265        1.5799938744
```

Number of Iterations: 67

Calculated Energy: `-2950.3532679829`

Hcp:

Multiplicity: 4

Initial Position:

```
H          0.0000000000       -1.5357517160        1.2000000000
O          0.0000000000       -1.5357517160        2.1831000000
```

Final Position:

```
H         -0.0062027011       -1.5367894261        1.2616455948
O          0.0002121282       -1.5019114992        2.2562181948
```

Number of Iterations: 14

Calculated Energy: `-2950.2700551681`

Fcc:

Multiplicity: 4

Initial Position:

```
H          0.0000000000        1.5357517160        1.2000000000
O          0.0000000000        1.5357517160        2.1831000000
```

Final Position:

```
H          0.0067549504        1.9880290784        2.0442568577
O         -0.0005246127        1.0372992164        1.7869086632
```

Number of Iterations: 50

Calculated Energy: `-2950.3344367003`

11.3.6 H_2O:

Top:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
H         -0.7615000000        0.0000000000        2.5987000000
H          0.7615000000        0.0000000000        2.5987000000
```

Final Position:

```
O          0.0008733582       -0.0005834007        2.4454686907
H         -0.7881118664        0.0137491016        3.0161296532
H          0.7882568522       -0.0026400881        3.0186616541
```

Number of Iterations: 38

Calculated Energy: -2950.9446591871

Bridge:

Multiplicity: 3

Initial Position:

O	1.3300000000	0.0000000000	2.0000000000
H	0.5685000000	0.0000000000	2.5987000000
H	2.0915000000	0.0000000000	2.5987000000

Final Position:

O	1.3172034226	-0.0006232343	2.7543333624
H	0.5015023091	0.1274414971	3.2714722234
H	2.0388724786	0.0304357006	3.4074339529

Number of Iterations: 42

Calculated Energy: -2950.9429181019

Hcp:

Multiplicity: 3

Initial Position:

O	0.0000000000	-1.5357517160	1.5000000000
H	-0.7615000000	-1.5357517160	2.0987000000
H	0.7615000000	-1.5357517160	2.0987000000

Final Position:

O	0.0014643372	-0.7443949062	2.9095859094
H	-0.7700616318	-1.2754381136	2.6306003918
H	0.7651513665	-1.2877054234	2.6301561632

Number of Iterations: 50

Calculated Energy: -2950.9455299711

Fcc:

Multiplicity: 3

Initial Position:

O	0.0000000000	1.5357517160	1.5000000000
H	-0.7615000000	1.5357517160	2.0987000000
H	0.7615000000	1.5357517160	2.0987000000

Final Position:

O	0.0020299134	0.8350240931	2.8179814450
H	-0.7747037634	1.3934758583	2.6153384342
H	0.7584958119	1.4168679933	2.6027464300

Number of Iterations: 51

Calculated Energy: -2950.9440029617

11.3.7 CO (C Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
C          0.0000000000        0.0000000000        2.0000000000
O          0.0000000000        0.0000000000        3.1379000000
```

Final Position:

```
C         -0.0046734244       -0.0034449096        1.8897740752
O          0.0002526198        0.0003021319        3.0568528385
```

Number of Iterations: 11

Calculated Energy: `-2955.4669756468`

Bridge:

Multiplicity: 3

Initial Position:

```
C          1.3300000000        0.0000000000        2.0000000000
O          1.3300000000        0.0000000000        3.1379000000
```

Final Position:

```
C          1.3850872825        0.0004300079        1.6017701501
O          1.3153050220       -0.0031821130        2.7899051923
```

Number of Iterations: 20

Calculated Energy: `-2955.4629458647`

Hcp:

Multiplicity: 3

Initial Position:

```
C          0.0000000000       -1.5357517160        2.0000000000
O          0.0000000000       -1.5357517160        3.1379000000
```

Final Position:

```
C          0.1260576393       -1.3892433158        1.5282131645
O          0.0066684081       -1.4972940403        2.7120718975
```

Number of Iterations: 44

Calculated Energy: `-2955.4629395368`

Fcc:

Multiplicity: 3

Initial Position:

```
C          0.0000000000        1.5357517160        2.0000000000
O          0.0000000000        1.5357517160        3.1379000000
```

Final Position:

```
C          0.0147103578        1.5953766654        1.4439627554
O          0.0000098126        1.5921625984        2.6433544830
```

Number of Iterations: 35

Calculated Energy: `-2955.4666223181`

11.3.8 CO (O Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
C          0.0000000000        0.0000000000        3.1379000000
```

Final Position:

```
O          0.0014408771        0.0008446597        2.8217755827
C          0.0036932217       -0.0037079979        3.9614593357
```

Number of Iterations: 40

Calculated Energy: `-2955.3942908635`

Bridge:

Multiplicity: 3

Initial Position:

```
O          1.3300000000        0.0000000000        2.0000000000
C          1.3300000000        0.0000000000        3.1379000000
```

Final Position:

```
O          1.1230307277        0.0025180000        3.1903251315
C          1.3156163440       -0.0701087739        4.3109962896
```

Number of Iterations: 45

Calculated Energy: `-2955.3962132766`

Hcp:

Multiplicity: 3

Initial Position:

```
O          0.0000000000       -1.5357517160        2.0000000000
C          0.0000000000       -1.5357517160        3.1379000000
```

Final Position:

```
O         -0.0000615116       -1.4064746374        2.9168111818
C         -0.0047856308       -1.5473548637        4.0481468066
```

Number of Iterations: 41

Calculated Energy: `-2955.3938694149`

Fcc:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        1.5357517160        2.0000000000
C          0.0000000000        1.5357517160        3.1379000000
```

Final Position:

```
O          0.0016969126        1.4039947031        3.0106100854
C          0.0160236876        1.6652812681        4.1207534227
```

Number of Iterations: 51

Calculated Energy: `-2955.3949225205`

11.3.9 CO_2 (C Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
O          -1.1692000000         0.0000000000         2.0000000000
C           0.0000000000         0.0000000000         2.0000000000
O           1.1692000000         0.0000000000         2.0000000000
```

Final Position:

```
O          -1.3066515554         0.0945533640         3.7513654775
C          -0.1422271277         0.0481352160         3.6034535264
O           1.0248808694        -0.0000525683         3.4728555022
```

Number of Iterations: 107

Calculated Energy: `-2971.4913668574`

Bridge:

Multiplicity: 3

Initial Position:

```
O           0.1608000000         0.0000000000         2.0000000000
C           1.3300000000         0.0000000000         2.0000000000
O           2.4992000000         0.0000000000         2.0000000000
```

Final Position:

```
O           0.1733127427        -0.0014718226         2.9949923618
C           0.9276988116        -0.0105356413         2.0464012661
O           2.2305737727        -0.0005599585         2.0473832648
```

Number of Iterations: 52

Calculated Energy: `-2971.4795588457`

Hcp:

Multiplicity: 3

Initial Position:

```
O          -1.1692000000        -1.5357517160         2.0000000000
C           0.0000000000        -1.5357517160         2.0000000000
O           1.1692000000        -1.5357517160         2.0000000000
```

Final Position:

```
O          -1.1314732922        -1.6927694778         2.1511082437
C          -0.0080539981        -1.2944356643         1.6763472437
O           1.1304576607        -1.7799948208         2.0690831052
```

Number of Iterations: 30

Calculated Energy: `-2971.4711347675`

Fcc:

Multiplicity: 3

Initial Position:

```
O          -1.1692000000         1.5357517160         2.0000000000
C           0.0000000000         1.5357517160         2.0000000000
O           1.1692000000         1.5357517160         2.0000000000
```

Final Position:

```
O          -1.1367821478         1.6900048965         2.0681143066
```

```
C          0.0222721114        1.2695445588        1.6704433529
O          1.1329832502        1.6882329701        2.1528349497
```

Number of Iterations: 29

Calculated Energy: `-2971.4773066199`

11.3.10 CO_2 (O Adsorbed):

Top:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        0.0000000000        2.0000000000
C          0.0000000000        0.0000000000        3.1692000000
O          0.0000000000        0.0000000000        4.3384000000
```

Final Position:

```
O          0.0000135150       -0.0005997802        2.8416698291
C         -0.0001547595       -0.0015469352        4.0147059370
O         -0.0000066010       -0.0003816395        5.1857290196
```

Number of Iterations: 45

Calculated Energy: `-2971.4829282843`

Bridge:

Multiplicity: 3

Initial Position:

```
O          1.3300000000        0.0000000000        2.0000000000
C          1.3300000000        0.0000000000        3.1692000000
O          1.3300000000        0.0000000000        4.3384000000
```

Final Position:

```
O          1.3161473033        0.0017085757        2.8342103923
C          1.3141751553        0.0020477171        4.0080113139
O          1.3124222822        0.0003388322        5.1786215921
```

Number of Iterations: 38

Calculated Energy: `-2971.4846293860`

Hcp:

Multiplicity: 3

Initial Position:

```
O          0.0000000000       -1.5357517160        2.0000000000
C          0.0000000000       -1.5357517160        3.1692000000
O          0.0000000000       -1.5357517160        4.3384000000
```

Final Position:

```
O         -0.0000547643       -1.5021815347        2.8307585202
C         -0.0001245981       -1.5030116534        4.0046860744
O         -0.0000359417       -1.5003950163        5.1752105023
```

Number of Iterations: 44

Calculated Energy: `-2971.4832765613`

Fcc:

Multiplicity: 3

Initial Position:

```
O          0.0000000000        1.5357517160        2.0000000000
C          0.0000000000        1.5357517160        3.1692000000
O          0.0000000000        1.5357517160        4.3384000000
```

Final Position:

```
O         -0.0000331402        1.4990071793        2.8357126574
C          0.0001519548        1.4998111318        4.0099032374
O          0.0001055428        1.4997857511        5.1808298954
```

Number of Iterations: 36

Calculated Energy: `-2971.4821223240`

11.3.11 COOH:

Top:

Multiplicity: 4

Initial Position:

```
O         -1.0654000000        0.0000000000        2.7978000000
H         -0.7637000000        0.0000000000        3.7346000000
C          0.0000000000        0.0000000000        2.0000000000
O          1.1609000000        0.0000000000        2.2720000000
```

Final Position:

```
O         -1.0223314886       -0.0003153223        2.8041546300
H         -0.7368367602        0.0070419304        3.7463657539
C          0.1397394854       -0.0066009453        2.0631983876
O          1.2281100754        0.0014277462        2.6326093876
```

Number of Iterations: 20

Calculated Energy: `-2972.0680935834`

Bridge:

Multiplicity: 4

Initial Position:

```
O          0.2646000000        0.0000000000        2.7978000000
H          0.5663000000        0.0000000000        3.7346000000
C          1.3300000000        0.0000000000        2.0000000000
O          2.4909000000        0.0000000000        2.2720000000
```

Final Position:

```
O          0.0005774910       -0.0010709871        2.9976640885
H          0.6063563099        0.0099806040        3.7739026393
C          0.7718529745       -0.0144040862        1.8938151018
O          2.0385805722        0.0001076458        2.0758927494
```

Number of Iterations: 33

Calculated Energy: `-2972.0809806284`

Hcp:

Multiplicity: 4

Initial Position:

```
O         -1.0654000000       -1.5357517160        2.7978000000
```

```
H          -0.7637000000       -1.5357517160        3.7346000000
C           0.0000000000       -1.5357517160        2.0000000000
O           1.1609000000       -1.5357517160        2.2720000000
```

Final Position:

```
O          -0.9204564329       -0.8273395124        2.8050038395
H          -0.6354413949       -1.3816800002        3.5669155225
C          -0.0094409451       -1.0319065375        1.8141883382
O           0.9296015009       -1.8649223462        2.0753274039
```

Number of Iterations: 57

Calculated Energy: `-2972.0745085005`

Fcc:

Multiplicity: 4

Initial Position:

```
O          -1.0654000000        1.5357517160        2.7978000000
H          -0.7637000000        1.5357517160        3.7346000000
C           0.0000000000        1.5357517160        2.0000000000
O           1.1609000000        1.5357517160        2.2720000000
```

Final Position:

```
O          -1.3123611321        1.3202897281        2.9003178687
H          -0.6894323569        1.2109903868        3.6546890523
C          -0.5846503572        1.7659664246        1.8492010897
O           0.6601278697        1.9709627640        2.0647253619
```

Number of Iterations: 74

Calculated Energy: `-2972.0801699152`

11.3.12 CH_3OH:

Top:

Multiplicity: 3

Initial Position:

```
C          -0.0469000000        0.0000000000        3.6608000000
O          -0.0469000000        0.0000000000        2.2424000000
H          -1.0944000000        0.0000000000        3.9749000000
H           0.4371000000        0.8933000000        4.0863000000
H           0.4371000000       -0.8933000000        4.0863000000
H           0.8762000000        0.0000000000        1.9486000000
```

Final Position:

```
C          -0.3278498717        0.0121362266        3.8808002691
O           0.3744613599       -0.0009174014        2.6242586304
H          -1.3965381943        0.0411189921        3.6392387937
H          -0.0687663681        0.9041806997        4.4717327777
H          -0.1185695884       -0.8938100107        4.4693229316
H           1.3257659992       -0.1471843594        2.7711265203
```

Number of Iterations: 63

Calculated Energy: `-2957.8106700012`

Bridge:

Multiplicity: 3

Initial Position:

```
C          1.2831000000        0.0000000000        3.4608000000
O          1.2831000000        0.0000000000        2.0424000000
H          0.2356000000        0.0000000000        3.7749000000
H          1.7671000000        0.8933000000        3.8863000000
H          1.7671000000       -0.8933000000        3.8863000000
H          2.2062000000        0.0000000000        1.7486000000
```

Final Position:

```
C          1.0249071241        0.0206036857        4.3510656121
O          1.0266405696       -0.0010371758        2.9146409550
H         -0.0250873710        0.0543798543        4.6673874479
H          1.5440310537        0.9099841888        4.7454404698
H          1.4863589408       -0.8826416931        4.7793623415
H          1.8925338021       -0.3245953200        2.6024242343
```

Number of Iterations: 63

Calculated Energy: `-2957.8063647537`

Hcp:

Multiplicity: 3

Initial Position:

```
C         -0.0469000000       -1.5357517160        3.3608000000
O         -0.0469000000       -1.5357517160        1.9424000000
H         -1.0944000000       -1.5357517160        3.6749000000
H          0.4371000000       -2.4290517160        3.7863000000
H          0.4371000000       -0.6424517160        3.7863000000
H          0.8762000000       -1.5357517160        1.6486000000
```

Final Position:

```
C         -0.2129106332       -1.5870622322        4.1619909288
O         -0.0958788851       -1.4991773582        2.7297197519
H         -1.2819984860       -1.6844105527        4.3840690510
H          0.3158136830       -2.4674174982        4.5600407688
H          0.1674447652       -0.6807279772        4.6579965872
H          0.8235871801       -1.2583887788        2.5015911310
```

Number of Iterations: 76

Calculated Energy: `-2957.8071414628`

Fcc:

Multiplicity: 3

Initial Position:

```
C         -0.0469000000        1.5357517160        3.3608000000
O         -0.0469000000        1.5357517160        1.9424000000
H         -1.0944000000        1.5357517160        3.6749000000
H          0.4371000000        2.4290517160        3.7863000000
H          0.4371000000        0.6424517160        3.7863000000
H          0.8762000000        1.5357517160        1.6486000000
```

Final Position:

```
C         -0.2724044545        1.5136196177        4.1715871540
O         -0.2871646050        1.5011962164        2.7323398475
H         -1.3166933621        1.5562021666        4.5036484339
H          0.2616330788        2.3962407952        4.5592122831
H          0.1889236184        0.6028786274        4.5816131659
H          0.5674545652        1.1563102602        2.4027619553
```

Number of Iterations: 113

Calculated Energy: -2957.8065994068

11.4 Mixed Surfaces positions

The following surfaces can be seen in Figure 14

Ruthenium on bottom, Platinum on top with top relaxed:
Multiplicity: 3
Initial Positions:

```
Pt         0.0000000000        0.0000000000        0.0000000000
Pt        -2.7700000000        0.0000000000        0.0000000000
Pt         2.7700000000        0.0000000000        0.0000000000
Pt        -5.5400000000        0.0000000000        0.0000000000
Pt         5.5400000000        0.0000000000        0.0000000000
Pt        -1.3850000000       -2.3988903680        0.0000000000
Pt         1.3850000000       -2.3988903680        0.0000000000
Pt        -4.1550000000       -2.3988903680        0.0000000000
Pt         4.1550000000       -2.3988903680        0.0000000000
Pt        -1.3850000000        2.3988903680        0.0000000000
Pt         1.3850000000        2.3988903680        0.0000000000
Pt        -4.1550000000        2.3988903680        0.0000000000
Pt         4.1550000000        2.3988903680        0.0000000000
Pt         0.0000000000       -4.7977807370        0.0000000000
Pt        -2.7700000000       -4.7977807370        0.0000000000
Pt         2.7700000000       -4.7977807370        0.0000000000
Pt         0.0000000000        4.7977807370        0.0000000000
Pt        -2.7700000000        4.7977807370        0.0000000000
Pt         2.7700000000        4.7977807370        0.0000000000
Ru        -1.3300000000       -0.7678758580       -2.1718809050
Ru         1.3300000000       -0.7678758580       -2.1718809050
Ru        -3.9900000000       -0.7678758580       -2.1718809050
Ru         3.9900000000       -0.7678758580       -2.1718809050
Ru         0.0000000000        1.5357517160       -2.1718809050
Ru        -2.6600000000        1.5357517160       -2.1718809050
Ru         2.6600000000        1.5357517160       -2.1718809050
Ru         0.0000000000       -3.0715034320       -2.1718809050
Ru        -2.6600000000       -3.0715034320       -2.1718809050
Ru         2.6600000000       -3.0715034320       -2.1718809050
Ru        -1.3300000000        3.8393792900       -2.1718809050
Ru         1.3300000000        3.8393792900       -2.1718809050
```

Fixed atoms:

```
  LIST 20 21 22 23 24 25 26 27 28 29 30 31
```

Final Positions:

```
Pt         0.0023133313        0.0112102559        0.1720154644
Pt        -2.6733989567        0.0029334654        0.1539501969
Pt         2.6776671309       -0.0040648477        0.1219370603
Pt        -5.3675548005        0.0472677066       -0.2322655670
Pt         5.3579570555        0.0826158914       -0.2085449245
Pt        -1.3314184514       -2.2862953857        0.1088243533
Pt         1.3706477901       -2.2868239518        0.1504817606
Pt        -4.0831691781       -2.3431543794       -0.0635472707
Pt         4.0899607431       -2.3551069760       -0.0642213623
Pt        -1.3226497967        2.3156014073        0.1164595847
Pt         1.3336568766        2.3122792885        0.1659520596
Pt        -4.0650538204        2.3071904971       -0.2041404992
Pt         4.0504255742        2.3346076486       -0.2195167953
Pt         0.0039861016       -4.6643382570       -0.2111816043
```

```
Pt        -2.5954016119       -4.6244876770       -0.1829344390
Pt         2.5944388078       -4.6384423348       -0.1771908215
Pt        -0.0009767026        4.7136774626       -0.0618101890
Pt        -2.7189899975        4.5515092605       -0.1739304153
Pt         2.7102782606        4.5680622075       -0.1906917639
Ru        -1.3300000000       -0.7678758580       -2.1718809050
Ru         1.3300000000       -0.7678758580       -2.1718809050
Ru        -3.9900000000       -0.7678758580       -2.1718809050
Ru         3.9900000000       -0.7678758580       -2.1718809050
Ru         0.0000000000        1.5357517160       -2.1718809050
Ru        -2.6600000000        1.5357517160       -2.1718809050
Ru         2.6600000000        1.5357517160       -2.1718809050
Ru         0.0000000000       -3.0715034320       -2.1718809050
Ru        -2.6600000000       -3.0715034320       -2.1718809050
Ru         2.6600000000       -3.0715034320       -2.1718809050
Ru        -1.3300000000        3.8393792900       -2.1718809050
Ru         1.3300000000        3.8393792900       -2.1718809050
```

Iterations needed: 29

Calculated Energy: `-3418.3776109492`

Platinum on bottom, Ruthenium on top with top relaxed:

Multiplicity: 3

Initial Positions:

```
Ru         0.0000000000        0.0000000000        0.0000000000
Ru        -2.6600000000        0.0000000000        0.0000000000
Ru         2.6600000000        0.0000000000        0.0000000000
Ru        -5.3200000000        0.0000000000        0.0000000000
Ru         5.3200000000        0.0000000000        0.0000000000
Ru        -1.3300000000       -2.3036275740        0.0000000000
Ru         1.3300000000       -2.3036275740        0.0000000000
Ru        -3.9900000000       -2.3036275740        0.0000000000
Ru         3.9900000000       -2.3036275740        0.0000000000
Ru        -1.3300000000        2.3036275740        0.0000000000
Ru         1.3300000000        2.3036275740        0.0000000000
Ru        -3.9900000000        2.3036275740        0.0000000000
Ru         3.9900000000        2.3036275740        0.0000000000
Ru         0.0000000000       -4.6072551480        0.0000000000
Ru        -2.6600000000       -4.6072551480        0.0000000000
Ru         2.6600000000       -4.6072551480        0.0000000000
Ru         0.0000000000        4.6072551480        0.0000000000
Ru        -2.6600000000        4.6072551480        0.0000000000
Ru         2.6600000000        4.6072551480        0.0000000000
Pt        -1.3850000000       -0.7996301230       -2.2616955290
Pt         1.3850000000       -0.7996301230       -2.2616955290
Pt        -4.1550000000       -0.7996301230       -2.2616955290
Pt         4.1550000000       -0.7996301230       -2.2616955290
Pt         0.0000000000        1.5992602460       -2.2616955290
Pt        -2.7700000000        1.5992602460       -2.2616955290
Pt         2.7700000000        1.5992602460       -2.2616955290
Pt         0.0000000000       -3.1985204910       -2.2616955290
Pt        -2.7700000000       -3.1985204910       -2.2616955290
Pt         2.7700000000       -3.1985204910       -2.2616955290
Pt        -1.3850000000        3.9981506140       -2.2616955290
Pt         1.3850000000        3.9981506140       -2.2616955290
```

Fixed atoms:

```
   LIST 20 21 22 23 24 25 26 27 28 29 30 31
```

Final Positions:

```
Ru        -0.5577438281       -0.0652653486        0.2247408245
Ru        -2.2757259640       -0.2914768170        1.9633839231
Ru         1.8581447146       -0.1199367679        1.0171844643
Ru        -4.3618853598       -0.1722654537        0.2444016298
Ru         5.1123196832       -0.1392903671        0.0431618519
Ru        -0.7204676119       -2.3317569868        1.3499011087
Ru         1.1757551668       -2.1384045104       -0.1790480384
Ru        -2.5718430822       -1.7194943104       -0.1684947945
Ru         3.5623004223       -1.9085409345        0.0252494591
Ru        -0.7041207002        2.1347861710        1.5078394096
Ru         1.1609725072        1.9259883750       -0.0794479203
Ru        -2.6581061719        1.4679576867        0.1549848206
Ru         3.5812499000        1.5753264247        0.1379287701
Ru         0.0901359323       -4.3661300315       -0.0026692839
Ru        -2.2580740721       -4.1224801575        0.1240052456
Ru         2.5353704970       -4.2583137165        0.0911433067
Ru         0.0502852604        4.1410686449       -0.0397469879
Ru        -2.3040689212        3.7931165573        0.2166710696
Ru         2.6652948090        3.8685676648        0.0165148763
Pt        -1.3850000000       -0.7996301230       -2.2616955290
Pt         1.3850000000       -0.7996301230       -2.2616955290
Pt        -4.1550000000       -0.7996301230       -2.2616955290
Pt         4.1550000000       -0.7996301230       -2.2616955290
Pt         0.0000000000        1.5992602460       -2.2616955290
Pt        -2.7700000000        1.5992602460       -2.2616955290
Pt         2.7700000000        1.5992602460       -2.2616955290
Pt         0.0000000000       -3.1985204910       -2.2616955290
Pt        -2.7700000000       -3.1985204910       -2.2616955290
Pt         2.7700000000       -3.1985204910       -2.2616955290
Pt        -1.3850000000        3.9981506140       -2.2616955290
Pt         1.3850000000        3.9981506140       -2.2616955290
```

Iterations needed: 230

Calculated Energy: `-3239.8482495129`

Mixed Platinum and Ruthenium all relaxed

Multiplicity: 3

Initial Positions:

```
Ru         0.0000000000        0.0000000000        0.0000000000
Ru        -2.6600000000        0.0000000000        0.0000000000
Ru         2.6600000000        0.0000000000        0.0000000000
Ru        -5.3200000000        0.0000000000        0.0000000000
Ru         5.3200000000        0.0000000000        0.0000000000
Pt        -1.3300000000       -2.3036275740        0.0000000000
Pt         1.3300000000       -2.3036275740        0.0000000000
Pt        -3.9900000000       -2.3036275740        0.0000000000
Pt         3.9900000000       -2.3036275740        0.0000000000
Pt        -1.3300000000        2.3036275740        0.0000000000
Pt         1.3300000000        2.3036275740        0.0000000000
Pt        -3.9900000000        2.3036275740        0.0000000000
Pt         3.9900000000        2.3036275740        0.0000000000
Ru         0.0000000000       -4.6072551480        0.0000000000
Ru        -2.6600000000       -4.6072551480        0.0000000000
Ru         2.6600000000       -4.6072551480        0.0000000000
Ru         0.0000000000        4.6072551480        0.0000000000
Ru        -2.6600000000        4.6072551480        0.0000000000
Ru         2.6600000000        4.6072551480        0.0000000000
Pt        -1.3850000000       -0.7996301230       -2.2616955290
Pt         1.3850000000       -0.7996301230       -2.2616955290
Pt        -4.1550000000       -0.7996301230       -2.2616955290
Pt         4.1550000000       -0.7996301230       -2.2616955290
```

```
Ru          0.0000000000        1.5992602460       -2.2616955290
Ru         -2.7700000000        1.5992602460       -2.2616955290
Ru          2.7700000000        1.5992602460       -2.2616955290
Ru          0.0000000000       -3.1985204910       -2.2616955290
Ru         -2.7700000000       -3.1985204910       -2.2616955290
Ru          2.7700000000       -3.1985204910       -2.2616955290
Pt         -1.3850000000        3.9981506140       -2.2616955290
Pt          1.3850000000        3.9981506140       -2.2616955290
```

Fixed atoms:

none

Final Positions:

```
Ru          0.0746928833        0.1640204139        1.3461905722
Ru         -2.3518234308        0.3317439307        0.4104907357
Ru          2.5200983685        0.0896391542        0.4734073050
Ru         -4.6672570470        0.4080443181       -0.8138978598
Ru          4.7071611373        0.1715177674       -0.5731271836
Pt         -1.4120111420       -2.0194859938        1.1468573594
Pt          1.2725426441       -2.0637891001        1.1239108546
Pt         -3.5688024160       -1.8866739812       -0.3147776225
Pt          3.4005934010       -2.1671848898       -0.4598764136
Pt         -1.3128202515        2.3618740279        1.7643140317
Pt          1.5011632929        2.2696580048        1.6604621882
Pt         -3.4830585706        2.6236475001        0.1607298513
Pt          3.4572357605        2.4259501522       -0.2696633884
Ru          0.1856489546       -3.9961646405       -0.0959029580
Ru         -2.1618618379       -4.2157196324       -0.3068819088
Ru          2.0563495657       -4.2030667146       -1.4414060765
Ru         -0.1200049625        3.1161693424       -0.2893661905
Ru         -1.8485412118        3.5122520736       -1.6464787399
Ru          1.8339676465        4.4158496050        0.2215288227
Pt         -1.1862813818       -0.5370659594       -3.3617681893
Pt          1.3161993132       -0.0847794330       -4.0086148553
Pt         -3.8251091816       -0.9365190543       -2.8511098143
Pt          3.7756595063       -0.5482283630       -2.8358451458
Ru         -0.2586858316        0.6665092394       -1.0130616022
Ru         -2.6030377710        1.1715847785       -1.9173438177
Ru          1.9835212634        0.9131611660       -1.7640779556
Ru         -0.2652321179       -1.8969807617       -1.2312979857
Ru         -2.1553171540       -2.8160693632       -2.2401463000
Ru          1.7025907371       -2.0872357307       -2.3699315948
Pt         -0.3684886150        2.0585284464       -3.2816903932
Pt          1.6525960825        3.3804622562       -2.1600969774
```

Iterations needed: 264

Calculated Energy: `-3290.9884636171`

Mixed Platinum and Ruthenium all relaxed

Multiplicity: 3

Initial Positions:

```
Pt          0.0000000000        0.0000000000        0.0000000000
 Ru         -2.6600000000        0.0000000000        0.0000000000
 Pt          2.6600000000        0.0000000000        0.0000000000
 Ru         -5.3200000000        0.0000000000        0.0000000000
 Pt          5.3200000000        0.0000000000        0.0000000000
 Ru         -1.3300000000       -2.3036275740        0.0000000000
 Pt          1.3300000000       -2.3036275740        0.0000000000
 Ru         -3.9900000000       -2.3036275740        0.0000000000
 Pt          3.9900000000       -2.3036275740        0.0000000000
 Ru         -1.3300000000        2.3036275740        0.0000000000
```

```
 Pt          1.3300000000        2.3036275740        0.0000000000
 Ru         -3.9900000000        2.3036275740        0.0000000000
 Pt          3.9900000000        2.3036275740        0.0000000000
 Ru          0.0000000000       -4.6072551480        0.0000000000
 Pt         -2.6600000000       -4.6072551480        0.0000000000
 Ru          2.6600000000       -4.6072551480        0.0000000000
 Pt          0.0000000000        4.6072551480        0.0000000000
 Ru         -2.6600000000        4.6072551480        0.0000000000
 Pt          2.6600000000        4.6072551480        0.0000000000
 Ru         -1.3850000000       -0.7996301230       -2.2616955290
 Pt          1.3850000000       -0.7996301230       -2.2616955290
 Ru         -4.1550000000       -0.7996301230       -2.2616955290
 Pt          4.1550000000       -0.7996301230       -2.2616955290
 Ru          0.0000000000        1.5992602460       -2.2616955290
 Pt         -2.7700000000        1.5992602460       -2.2616955290
 Ru          2.7700000000        1.5992602460       -2.2616955290
 Pt          0.0000000000       -3.1985204910       -2.2616955290
 Ru         -2.7700000000       -3.1985204910       -2.2616955290
 Pt          2.7700000000       -3.1985204910       -2.2616955290
 Ru         -1.3850000000        3.9981506140       -2.2616955290
 Pt          1.3850000000        3.9981506140       -2.2616955290
```

Fixed atoms:

none

Final Positions:

```
Pt          0.0235453896        0.1133112013        0.6645929016
 Ru         -2.3564403064        0.1698412870       -0.3742379766
 Pt          2.6497068047        0.0856816305        0.7424224646
 Ru         -4.8056817200        0.4186070421       -0.1028451166
 Pt          5.2290350894        0.0821226336       -0.1814850326
 Ru         -1.0985933637       -2.0347290652       -0.3533395290
 Pt          1.3030383996       -2.1832992492        0.4982833599
 Ru         -3.5345907619       -1.9510252435        0.1201599201
 Pt          4.0095256309       -2.2489547312        0.3810968060
 Ru         -1.3255415944        2.3496308900        0.2910200409
 Pt          1.3211008750        2.4172770765        0.6333131345
 Ru         -3.6420834617        2.4016764436       -0.7557421516
 Pt          3.9481818201        2.3313710701       -0.1800696460
 Ru          0.3181029964       -4.3772656900       -0.3578506965
 Pt         -2.1704021759       -4.3159648876        0.2858382508
 Ru          2.5905130521       -4.1484388333       -0.5693732585
 Pt         -0.0259877104        4.6656730498       -0.0541316440
 Ru         -2.6706185474        4.5007991132       -0.1690022313
 Pt          2.6183975302        4.5452772826       -0.4579442910
 Ru         -1.4389612779       -0.9901211375       -2.5629392689
 Pt          1.1354391203       -0.8374666242       -2.7238046391
 Ru         -3.9832105765       -0.8983279331       -2.0798639214
 Pt          3.6370515641       -1.0287827137       -1.8903565183
 Ru         -0.2592756479        1.1339109212       -1.7778639713
 Pt         -2.6769343832        1.3120255804       -2.8914270388
 Ru          2.2826265138        1.1683191281       -1.6489902265
 Pt         -0.1685323816       -3.2855020576       -2.5242297909
 Ru         -2.7857862948       -3.0682460047       -2.0209131941
 Pt          2.4425402948       -3.1765376607       -2.8113215342
 Ru         -1.4326110414        3.3980108029       -1.9374163854
 Pt          1.1327986842        3.3410658855       -2.2011231824
```

Iterations needed: 202

Calculated Energy: `-3341.9454350896`