Catalytic Methane Dissociative Chemisorption over Pt(111): Surface Coverage Effects and Reaction Path Description

Inara Colon-Diaz
University of Massachusetts Amherst

Follow this and additional works at: https://scholarworks.umass.edu/masters_theses_2

Recommended Citation
https://scholarworks.umass.edu/masters_theses_2/143

This Campus-Only Access for Five (5) Years is brought to you for free and open access by the Dissertations and Theses at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Masters Theses by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
Catalytic Methane Dissociative Chemisorption over Pt(111):
Surface Coverage Effects and Reaction Path Description

A Thesis Presented

By

INARA COLÓN- DÍAZ

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

February 2015

Chemistry
Catalytic Methane Dissociative Chemisorption over Pt(111):
Surface Coverage Effects and Reaction Path Description

A Thesis Presented

By

INARA COLÓN- DÍAZ

Approved as to style and content by:

[Signatures of审批人员]

Bret Jackson, Chair
Ricardo Metz, Member
Craig T. Martin, Department Head
Chemistry Department
DEDICATION

To my dear Mother and Tim.
ACKNOWLEDGMENTS

I would like to thank my advisor, Bret Jackson, for his patience, support and his admirable enthusiasm for science. I would also like to thank my peers Azar Farjamnia and Han Guo for their help and wisdom. I would like to thank my committee member, Rick Metz, for his curiosity and helpful suggestions.

I would like to thank the United States Department of Energy for their funding and support of this project, in the much-needed effort to advance this area of science. I am also greatly thankful for the support provided by Northeast Alliance for Graduate Education and the Professoriate (NEAGEP).

I want to thank all the people in the Department of Chemistry that made this experience possible. And finally, I am especially grateful for my dear family and friends, for their unconditional love, encouragement and understanding.
Density functional theory calculations were performed to study the dissociative chemisorption of methane over Pt(111) with the idea of finding the minimum energy path for the reaction and its dependence on surface coverage. Two approaches were used to evaluate this problem; first, we used different sizes of supercells (2x2, 3x3, 4x4) in order to decrease surface coverage in the absence of pre-adsorbed H and CH₃ fragments to calculate the energy barriers of dissociation. The second approach uses a 4x4 unit cell and surface coverage is simulated by adding pre-absorbed H and CH₃ fragments. Results for both approaches show that in general the height of the dissociation barriers increases as the surface coverage increases, although the first approach yields slightly lower barriers due to the fact that all repeatable images of the incident molecule are approaching the surface simultaneously. Using the reaction path formulation we were able to compute the potential energy surface for CH₄ dissociation. Our results suggest that excitation of the symmetric stretch and bend modes will likely increase the probability for reaction.
TABLE OF CONTENTS

ACKNOWLEDGMENTS.............................................................................................................iv

ABSTRACT...........................................................................................................................v

LIST OF TABLES......................................................................................................................vii

LIST OF FIGURES...................................................................................................................viii

CHAPTER

I. METHANE CATALYTIC DISSOCIATIVE CHEMISORPTION

   A. Introduction..................................................................................................................1
   B. Previous Work...............................................................................................................3

II. ENERGETICS OF DISSOCIATION AND COVERAGE EFFECTS

   A. Surface Coverage Effects on Reaction Pathways.........................................................12
   B. Maximum Surface Coverage.......................................................................................21

III. REACTION PATH DESCRIPTION OF MODE SELECTIVE CHEMISTRY

   A. Close-Couple Reaction Path Formulation...................................................................27

REFERENCES.........................................................................................................................39
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Relative energies, $E_p$ and $E_b$, for the reaction over Pt(111) at $\Theta = 1/2$, $1/9$, $1/16$ ML and geometries for the transition states</td>
<td>16</td>
</tr>
<tr>
<td>2. Computed vibrational frequencies for the TS at $\Theta = 1/4$, $1/9$, $1/16$ ML and the nine asymptotic (gas phase) CH$_4$ frequencies [12]</td>
<td>18</td>
</tr>
<tr>
<td>3. Layer effects on the geometry and energy barrier ($E_b$) of the TS at $1/4$, $1/9$, $1/16$ ML</td>
<td>19</td>
</tr>
<tr>
<td>4. Relative product state energies ($E_p$) with increasing surface coverage in terms of CH$_3$ and H fragments and reaction sites</td>
<td>23</td>
</tr>
<tr>
<td>5. Relative energy for the TS, $E_b$, for the reaction over Pt(111) at $\Theta = 1/16$, $2/16$, $3/16$, $4/16$ ML and geometries for the transition states</td>
<td>24</td>
</tr>
<tr>
<td>6. Relative product state energies ($E_a$) of systems in Fig. 13, comparing lower energy sites for the H fragments</td>
<td>26</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>State-resolved reaction probabilities for the dissociative chemisorption of CH(_4) on Ni(111) at various surface temperatures.[7]</td>
</tr>
<tr>
<td>2.</td>
<td>Ni(111) ((T_{surf} = 475)K) and Pt(111) ((T_{surf} = 600)K) comparison of (2\nu_3) and laser-off reactivity of CH(_4).[3]</td>
</tr>
<tr>
<td>3.</td>
<td>Calculated transition state geometry for methane dissociation on Ni(111) (top). Distortion from the equilibrium geometry is observed by the elongation of the reactive C—H bond and its deviation from the C(_3) axis of the spectator methyl group, puckering of the Ni atom is also observed.[10]</td>
</tr>
<tr>
<td>4.</td>
<td>CH(_4) state-resolved reactivity as a function of translational energy, portraying results for the four vibrational states and the ground state over Pt(110)-(1x2).[4]</td>
</tr>
<tr>
<td>5.</td>
<td>Comparison of RAIR spectra for chemisorption products of (a) CHD(_3), (b) CH(_2)D(_2), and (c) CH(_3)D on Pt(111) at (T_s = 150) K, for activation by translational and thermal vibrational energy supplied by nozzle heating to (T_n = 700) K (bottom-black traces); for quantum state specific IR pumping of a C—H stretch normal mode vibration (a) CHD(_3)((\nu_1)), (b) CH(_2)D(_2)((\nu_6)), and (c) CH(_3)D((\nu_4)) in a molecular beam using (T_n = 294) K (top-red traces).[6]</td>
</tr>
<tr>
<td>6.</td>
<td>Lines represent the minimum energy path (MEPs) for CH(_4) dissociation over Ni(111), for the listed values of Q. The points are the DFT energies for the reactant, product and transition state.[24]</td>
</tr>
<tr>
<td>7.</td>
<td>Pt(111) (from left to right) 2x2, 3x3 and 4x4 surface unit cells. A 2x2 unit cell corresponds to four atoms per layer and (\Theta = 1/4)ML, the 3x3 unit cell has nine atoms per layer and (\Theta = 1/9)ML, lastly, the 4x4 unit cell has 16 atoms per layer and (\Theta = 1/16)ML</td>
</tr>
<tr>
<td>8.</td>
<td>Side and top view of the Pt(111)/CH(_4) system at the Reactant state (a) the distance from the methane carbon (Z(_c)) and a platinum atom of the top most layer is 8.00Å, while the distance of the hydrogen (Z(_h)) that points directly to the platinum atom is 6.90 Å; (b) shows the top view of methane over the platinum slab.</td>
</tr>
<tr>
<td>9.</td>
<td>Reactant state configurations for CH(_4) over the Pt(111) surface (left). The product state is generated by dissociation of the reactive C—H bond along the bridge (right). The CH(_3)(ads) and the H(ads) remains at the top sites.</td>
</tr>
</tbody>
</table>
10. Surface coverage effects on methane dissociative chemisorption. Reaction pathways at Θ = 1/4, 1/9, 1/16 ML..................................................................................................................17

11. Energy differences at the TS as a function of the number of layers of the Pt(111) slab at the three proposed surface coverages...........................................................................................................20

12. 4x4 Pt(111) slab top most layer with one pre-absorbed CH₃ + H fragment and one newly dissociated methane on reaction site 2............................................................................................................22

13. Reaction sites explored in search of maximum coverage and effects of site blocking by pre-absorbed H and CH₃ fragments.................................................................22

14. Reaction sites 5 to be explored in search of saturation of the metal surface. Methyl fragments will be adsorbed at reaction sites 1, 2, 3 and 4. H fragments will be placed at the fcc or hcp hollows.................................................................25

15. Product state at reaction site 5 having CH₃ at reaction sites 1, 2, 3 and 4 (a). H fragments are placed at the fcc holes (pink). (b) Product state at reaction site 5 having CH₃ fragments at reaction sites 1, 2, 3 and 4. H fragments are distributed between the fcc holes (pink) and the hcp holes (green)...........................................................................................................25

16. D2 configuration at the TS; Pt(111)bridge site bound by fcc (red) and hcp (green) holes. ..........................................................................................................................................................28

17. Representation of the F1 configuration at high separation from the Pt(111) surface. CH₄ is placed at a top site while the non-reactive hydrogen atoms point to fcc hollows.................................................................................................................................29

18. Diagram for the initial guess of methane dissociation (F1 configuration) over Pt(111).........................................................................................................................................................31

19. Graphical representation of the four moving images along reaction path, depicting the top and side view of CH₄ as the C—H dissociates over Pt(111)........................................32

20. Diagram for the 48 images describing the reaction path of methane dissociation over Pt(111).................................................................................................................................33

21. Plot of the nine highest energy frequencies as a function of position along the reaction path ..............................................................................................................................................34

22. Curvature coupling elements for the symmetric modes 1’-8’ ..........................................................................................................................................................................................35

23. Mode-mode couplings between symmetric mode 3’ and symmetric modes 1’-6’ ......................................................................................................................................................35
24. Mode-mode couplings between symmetric mode 4’ and symmetric modes 1’-6’...36

25. Mode-mode couplings between symmetric mode 5’ and symmetric modes 1’-6’...37

26. Mode-mode couplings between symmetric mode 6’ and symmetric modes 1’-6’...37
CHAPTER I

METHANE CATALYTIC DISSOCIATIVE CHEMISORPTION

A. Introduction

In view of the pressing need to find viable fuel alternatives to the combustion of hydrocarbons, hydrogen (H₂) has become a real contender. A virtually emission-free combustion and diverse sources for domestic production have made hydrogen a target of several areas of investigation. With this in mind, public and private sectors are focusing their resources to produce hydrogen in a safe, clean and efficient way. Nowadays, 95% of the H₂ produced in the United States is done through the process of steam reforming [33], where high temperature water vapor interacts with natural gas (methane, CH₄) in a two-step reaction [Eqs. 1 and 2]. This process involves mainly the use of a supported heterogeneous nickel (Ni) catalyst. Although nickel has proven to be a good catalyst for this reaction, it is not free of challenges. Industrial conditions generate problems such as sulfur poisoning, carbon formation, decrease in activity and sintering [30], but most importantly production of H₂ with nickel as a catalyst still requires a considerable energy input because steam reforming is an endothermic process. Due to these challenges and the reduction of the process efficiency, other catalysts are explored to reduce or eliminate some of the shortcomings of catalytic steam reforming. One such catalyst that deserves our attention is platinum (Pt). Since more experimental and theoretical data points to the superior catalytic properties of platinum, it is imperative that an exhaustive assessment be performed.
\[ CH_4 (g) + H_2O(g) \leftrightarrow 3H_2(g) + CO(g) \quad \Delta H_{298}^0 = 206kJ/mol \quad (1) \]

\[ CO (g) + H_2O (g) \rightarrow CO_2 (g) + H_2(g) \quad \Delta H_{298}^0 = -41kJ/mol \quad (2) \]

As mentioned before, natural gas steam reforming is a two-step reaction, where the rate-limiting step is the dissociative chemisorption of CH\(_4\) over the metal catalyst. Taking this into account, it is necessary to understand several aspects of the interaction between the reacting species and the catalytic metal and how these may affect the energy barrier of the reaction. Due to the industrial relevance of steam reforming over metal surfaces, a vast amount of information based on theoretical and experimental studies is available. This will allow us to compare our calculations of the reactivity of CH\(_4\) dissociative chemisorption over platinum surfaces to previous studies. Comparative analysis of the results will help us reveal a more detailed mechanistic and energetic picture of the reactive efficiency of platinum on steam reforming of CH\(_4\).
B. Previous Work

The mechanism by which CH$_4$ dissociates over a metal surface, such as Ni and Pt, is complex and not entirely understood. Theoretical and molecular beam studies have shed some light on the dynamics of C—H bond cleavage during chemisorption of the gas molecule. Through these studies, they have shown reactivity dependence on translational energy, molecular vibrational state and substrate temperature [5, 7, 15, 16, 22, 34], but the magnitude of these effects varies from metal to metal (Figs. 1 and 2).

![Figure 1. State-resolved reaction probabilities for the dissociative chemisorption of CH$_4$ ($v_3, v = 1$) on Ni(111) at various surface temperatures.][7]
Fig. 2. Ni(111) (T_{surf} = 475K) and Pt(111) (T_{surf} = 600K) comparison of 2ν3 and laser-off reactivity of CH₄.

Fig. 1 by Campbell et. al. [7] shows how surface temperature (T_{surf}) effects are most noticeable at translational energies lower than 50kJ/mol for temperatures lower than 300K. In Fig. 2 we can observe that at high T_{surf} reactivity decreases as the translational energy of the incident molecule decreases. Some suggestion for this trend is tunneling and distributions of effective barriers along the translational energy coordinate. Pairing this experimental result with results from calculations done by Jackson’s group [24] on Ni suggests that there is a broad distribution of barrier heights corresponding to different types of lattice distortion encountered by the colliding molecules. The sharp decline in S₀ at lower T_{surf} (<300K) seems to be
dictated by tunneling along the minimum energy path (MEP). Fig. 2 also shows the contribution of vibrational motion to CH₄ reactivity over Pt and Ni by comparing the results of the laser-off and excitation of the first overtone of the antisymmetric stretch (2ν₃) measurements [3]. From the previous figure we can observe that in general Pt is more reactive than Ni, and that excitation of 2ν₃ seems to be more effective on the Ni surface than on Pt.

Figure 3. Calculated transition state geometry for methane dissociation on Ni(111) (top). Distortion from the equilibrium geometry is observed by the elongation of the reactive C—H bond and its deviation from the C₃ axis of the spectator methyl group, puckering of the Ni atom is also observed [10]. Calculated transition state for methane dissociation over Pt(111) in the absence of puckering motion(bottom).
Since methane dissociation reaction requires distortion of the molecule from its equilibrium geometry in order to access the transition state (TS) (Fig. 3, bottom image comes from my calculations over Pt(111)), vibrational energy ($E_{\text{vib}}$) should have a key role on its activation. There exists good agreement that the activation chemistry of methane over Ni surfaces is both mode-specific and bond-selective [1, 3, 7, 16, 19, 31, 34]. Moreover, molecular-beam reactivity studies using deuterated isotopologues of CH$_4$ over Ni have provided clear results of such phenomena. Recent studies of the dynamics of methane dissociation over Pt surfaces also point to mode-specificity and bond-selectivity. The results on Pt by Bisson et al. [3] are particularly interesting. They measured the reaction probability of CH$_4$ over Pt(110)-(1x2) as a function of the molecular translational energy for four different vibrational eigenstates that consisted of combinations of C—H stretch and bend excitations. They characterized the four prepared eigenstates as pure bend ($2\nu_2 + \nu_4$), stretch/bend ($\nu_1 + \nu_4, \nu_3 + \nu_4$) and pure stretch ($2\nu_3$). The results of this study reveals that activation of CH$_4$ depends on the combination of the stretch/bend states as opposed to a pure bend or pure stretch states (Fig. 4).
Figure 4. CH$_4$ state-resolved reactivity as a function of translational energy, portraying results for the four vibrational states and the ground state over Pt(110)-(1x2) [4].

It was determined from previous vibrational mode-selective studies that not only the energy applied to a prepared vibrational state, but also its identity, contributes to the reaction probability for CH$_4$ dissociation. Of similar importance is the study of bond-selective reactivity since the identity of the reaction product can be determined by selective vibrational excitation.
Figure 5. a–c: Comparison of RAIR spectra for chemisorption products of (a) CHD$_3$, (b) CH$_2$D$_2$, and (c) CH$_3$D on Pt(111) at $T_S = 150$ K, for activation by translational and thermal vibrational energy supplied by nozzle heating to $T_n = 700$ K (bottom-black traces); for quantum state specific IR pumping of a C–H stretch normal mode vibration (a) CHD$_3$(ν$_1$), (b) CH$_2$D$_2$(ν$_6$), and (c) CH$_3$D(ν$_4$) in a molecular beam using $T_n = 294$ K (top-red traces)[6].
Chen et al. studied vibrational bond-selectivity on the dissociative chemisorption of three deuterated isotopologues of methane (CHD$_3$, CH$_2$D$_2$ and CH$_3$D) over Pt(111). They used reflection adsorption infrared spectroscopy (RAIRS) to detect the selective dissociation of the C—H over the C—D bond by excitation of the infrared active C—H symmetric normal mode (Fig. 5). Even though the applied vibrational energy was approximately the same for the three species (≈ 36 kJ/mol), the vibrational amplitude is distributed through an increasing number of C—H bonds providing at least a single quantum C—H stretch excitation for each isotopologue. The results of this study is that C—H cleavage is completely bond-specific and the dominant pathway for dissociation in the three partially deuterated methane isotopologues over Pt(111) when state-specific C—H stretch excitations occur.

Reactions such as methane dissociative chemisorption over metal lattices are of great interest for better understanding gas/surface interactions. Electronic structure studies [25,26] over various Ni and Pt surfaces have shown that this reaction exhibits both site-specific reactivity and site-specific binding of the methyl (CH$_3$(ads)) and hydrogen (H(ads)) fragments. The reaction takes place over one of the surface metal atom for all nickel and platinum crystal structures studied. As dissociation of CH$_4$ occurs, CH$_3$(ads) and H(ads) are chemisorbed onto the surface; on Ni(100) and Ni(111) the methyl group moves away from over the metal atom towards the bridge and the fcc hollow respectively. On the other hand, methyl fragments remain over the metal atom and only reorientation is observed on both Pt(100) and Pt(111). Hydrogen also translates to a more energetically favorable site over the lattice as it binds to it. Hydrogen moves to the hollows on Ni(100),
Ni(111) and Pt(111), but moves to a bridge site on Pt(100) [26]. A thorough theoretical study of all possible TS configurations over different Ni and Pt crystal structures shows the minimum energy path for methane dissociation is directly over a metal atom [21, 25, 26], with a single H atom pointing toward the surface. The rotational orientation of the (non-reacting) methyl group seems to have no effect on the barrier, as these H atoms point away from the metal surface. Likewise, the azimuthal orientation of the reactive C—H bond has a negligible effect on the barrier [5]. In addition, some of these studies provide evidence that collision of the molecule with the metal lattice generates motion of the struck metal atom. There exist two competing motions, recoil, which displaces the atom into the bulk of the lattice and puckering, which moves the atom away from the surface plane. Calculations on Ni(111), where Q represents the degree of freedom for lattice motion normal to the surface, show that puckering has a bigger effect on lowering the reaction barrier than recoil (Fig. 6) [24].
Figure 6. Lines represent the minimum energy path (MEPs) for CH$_4$ dissociation over Ni(111), for the listed values of Q. The points are the DFT energies for the reactant, product and transition state[24].

Subsequent calculations on Ni and Pt using a quantum model to determine the effects of lattice motion on the dissociation of methane suggests that recoil occurs in both Ni(111) and Pt(111), while puckering is fastest on Ni than on Pt due to the heavier nature of the Pt atoms[25].
CHAPTER II
ENERGETICS OF DISSOCIATION AND COVERAGE EFFECTS

A. Surface Coverage Effects On Reaction Pathways

Electronic structure calculations in search of the MEP and its TS at different surface coverages for methane dissociative chemisorption over the Pt(111) surface, will allow the construction of the potential energy surfaces. The Climbing Image-Nudge Elastic Band (CI-NEB) method will be used for this purpose, along with the DFT-based Vienna \textit{Ab initio} Simulation Package (VASP), developed at the Institutfür Materialphysik of the Universit"{a}t of Wien [17]. This package uses a plane wave basis set; the nonlocal exchange-correlation effects are treated within the generalized gradient approximation (GGA) [27] using the Perdew–Burke–Ernzerhof (PBE) [28,29] exchange-correlation functional. Fully nonlocal optimized projector augmented-wave (PAW) [2,18] potentials are used to treat the interaction between the ionic cores and the electrons. The energy cut-off ($E_{\text{cut}}$) for the plane wave basis set is 400eV throughout all calculations, where all plane-waves with kinetic energy smaller than $E_{\text{cut}}$ are included in the basis set. The Pt(111) slab is modeled as an asymmetric supercell with periodic boundary conditions, where a large vacuum space, corresponding to six layers, separates the substrate from its repeated image. The Pt(111) substrate is modeled using four layer supercells with hexagonal 2x2, 3x3 and 4x4 arrays of surface unit cells (Fig.7).
Figure 7. Pt(111) (from left to right) 2x2, 3x3 and 4x4 surface unit cells. A 2x2 unit cell corresponds to four atoms per layer and Θ = 1/4ML, the 3x3 unit cell has nine atoms per layer and Θ = 1/9ML, lastly, the 4x4 unit cell has 16 atoms per layer and Θ = 1/16ML.

All calculations are performed using the platinum equilibrium lattice constant 3.978Å. The Brillouin zone is sampled using a Γ-centered grid of k-points, and for each unit cell a different set of k-points is used. As we increase the unit cell size from 2x2 to 3x3 to 4x4 we reduce the k-points from 8x8x1 to 6x6x1 to 4x4x1, respectively. For the total-energy calculations of the reactant and product states the metal slabs and adsorbates are held fixed (Fig. 8).
Figure 8. Side and top view of the Pt(111)/CH₄ system at the Reactant state (a). At this state the distance from the methane carbon (Z_c) and a platinum atom of the top most layer is 8.00 Å, while the distance of the hydrogen (Z_h) that points directly to the platinum atom is 6.89 Å; (b) shows the top view of methane over the platinum slab.

Using the optimized geometry of the RS and PS (Fig. 9a and 9b) at different surface coverages (\( \Theta = 1/4, 1/9, 1/16 \) ML) the reaction pathways were generated by the CI-NEB method. Total energy calculations were also carried out for the zero of energy (ZE), which consist of the methane molecule and the Pt(111) slab at infinite separation. We consider the calculation converged when all forces were equal to or smaller than 0.01 eV/Å. For all the systems we were able to obtain a true first order saddle point, successfully finding a TS for the reaction.
Figure 9. Reactant state configurations for CH₄ over the Pt(111) surface (left). The product state is generated by dissociation of the reactive C—H bond along the bridge (right). The CH₃(ads) and the H(ads) remain at the top sites.

Relative energies for the product state (Eₚ) and transition state (E₇) [Eq. 3 and 4], as functions of the surface coverage, are listed in Table 1. TS state geometries are also listed in this table.

\[
E_p = E_{PS} - E_{ZE} \tag{3}
\]

\[
E_b = E_{TS} - E_{ZE} \tag{4}
\]

Where \( E_{PS} \) is the absolute energy of the product state, \( E_{TS} \) is the absolute energy of the transition state and \( E_{ZE} \) is the absolute zero of energy.
$Z^c$ and $Z^h$ are the distance of the methane carbon and dissociating hydrogen atoms respectively, from the platinum surface at the TS. $r_{C-H}$ is the C-H bond length and $\theta$ is the polar orientation angle of the C-H bond with respect to the surface normal. In Fig. 10 we compare the reaction pathway of the systems. Results for the calculations on the three systems show that as we lower the surface coverage on Pt(111), both the product state ($E_p$) and the transition state ($E_b$) energies decrease. Since the molecule and all of its repeated images are dissociating at the same time, an explanation for higher barriers as $\Theta$ increases is most likely related to repulsion due to charge transfer between the gas particle and the metal.

Table 1. Relative energies, $E_p$ and $E_b$, for the reaction over Pt(111) at $\Theta = 1/4$, 1/9, 1/16ML and geometries for the transition states.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>$Z^c$ (Å)</th>
<th>$Z^h$ (Å)</th>
<th>$r_{C-H}$ (Å)</th>
<th>$\theta$ (deg)</th>
<th>$E_p$ (eV)</th>
<th>$E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x2 (1/4ML)</td>
<td>2.270</td>
<td>1.240</td>
<td>1.498</td>
<td>136.55</td>
<td>0.307</td>
<td>0.934</td>
</tr>
<tr>
<td>3x3 (1/9ML)</td>
<td>2.266</td>
<td>1.230</td>
<td>1.526</td>
<td>137.22</td>
<td>0.226</td>
<td>0.894</td>
</tr>
<tr>
<td>4x4 (1/16ML)</td>
<td>2.266</td>
<td>1.235</td>
<td>1.508</td>
<td>136.88</td>
<td>0.188</td>
<td>0.856</td>
</tr>
</tbody>
</table>
Figure 10. Surface coverage effects on methane dissociative chemisorption. Reaction pathways at Θ = 1/4, 1/9, 1/16 ML.

In order to ensure the correctness of the TS found by the Cl-NEB method [9], we performed a normal mode analysis. Normal mode calculations are performed using VASP, which calculates the Hessian matrix via a central difference approach, using atomic displacements of 0.015Å. Symmetrization is turned off and the plane wave energy cut-off ($E_{cut}$) is increased to 800eV for the 2x2 and 3x3 systems. However, due to the large size of the 4x4 system, $E_{cut}$ is kept at 400eV. Results of the vibrational analysis of the TSs are shown in Table 2. There are fifteen computed frequencies for each one of the systems and nine asymptotic gas phase frequencies of CH$_4$. The first nine frequencies correspond to the following vibrational modes: triply degenerate anti-symmetric stretch (v3), the symmetric stretch (v1), the doubly degenerated bend (v2) and the triply degenerated bend (v4).
As we compare the calculated and asymptotic vibrational frequencies of CH₄ we observe mode softening, especially in the symmetric stretch. This is consistent with experimental and theoretical studies that point to mode specificity in the dissociation of the C-H bond. Having found a stable transition state for CH₄ dissociation over Pt(111) at various surface coverages, we performed an energy minimization calculation of the fixed geometry of such states. This calculation will ensure that we have the lowest energy conformation for the transition state. We also explored the effect of a thicker Pt(111) slab on the transition state energy (Eₜ).

The original system was composed of four layers of platinum and a vacuum space corresponding to 5 layers. We conserved the system setup by increasing the z-

Table 2. Computed vibrational frequencies for the TS at Θ = 1/4, 1/9, 1/16 ML and the nine asymptotic (gas phase) CH₄ frequencies [12].

<table>
<thead>
<tr>
<th>Frequencies</th>
<th>2x2(1/4ML)</th>
<th>3x3(1/9ML)</th>
<th>4x4(1/16ML)</th>
<th>CH₄ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>f1 (cm⁻¹)</td>
<td>3114</td>
<td>3111</td>
<td>3118</td>
<td>3099</td>
</tr>
<tr>
<td>f2 (cm⁻¹)</td>
<td>3089</td>
<td>3082</td>
<td>3094</td>
<td>3099</td>
</tr>
<tr>
<td>f3 (cm⁻¹)</td>
<td>2991</td>
<td>3017</td>
<td>3018</td>
<td>3097</td>
</tr>
<tr>
<td>f4 (cm⁻¹)</td>
<td>1581</td>
<td>1582</td>
<td>1585</td>
<td>2980</td>
</tr>
<tr>
<td>f5 (cm⁻¹)</td>
<td>1403</td>
<td>1409</td>
<td>1401</td>
<td>1513</td>
</tr>
<tr>
<td>f6 (cm⁻¹)</td>
<td>1392</td>
<td>1396</td>
<td>1393</td>
<td>1512</td>
</tr>
<tr>
<td>f7 (cm⁻¹)</td>
<td>1156</td>
<td>1165</td>
<td>1164</td>
<td>1288</td>
</tr>
<tr>
<td>f8 (cm⁻¹)</td>
<td>879</td>
<td>896</td>
<td>891</td>
<td>1288</td>
</tr>
<tr>
<td>f9 (cm⁻¹)</td>
<td>790</td>
<td>804</td>
<td>794</td>
<td>1287</td>
</tr>
<tr>
<td>f10 (cm⁻¹)</td>
<td>422</td>
<td>424</td>
<td>419</td>
<td>...</td>
</tr>
<tr>
<td>f11 (cm⁻¹)</td>
<td>292</td>
<td>378</td>
<td>298</td>
<td>...</td>
</tr>
<tr>
<td>f12 (cm⁻¹)</td>
<td>143</td>
<td>214</td>
<td>132</td>
<td>...</td>
</tr>
<tr>
<td>f13 (cm⁻¹)</td>
<td>132</td>
<td>138</td>
<td>121</td>
<td>...</td>
</tr>
<tr>
<td>f14 (cm⁻¹)</td>
<td>30</td>
<td>58</td>
<td>48</td>
<td>...</td>
</tr>
<tr>
<td>f15 (cm⁻¹)</td>
<td>981i</td>
<td>973i</td>
<td>982i</td>
<td>...</td>
</tr>
</tbody>
</table>
component lattice vector of the periodic box. We use normal precision (ENCUT= 400 eV) and a 0.001 energy cut-off.

Table 3. Layer effects on the geometry and energy barrier ($E_b$) of the TS at 1/4, 1/9, 1/16 ML

<table>
<thead>
<tr>
<th>Coverage, $\theta$</th>
<th>Layer</th>
<th>Transition State Geometry</th>
<th>TS Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Z_{C+}$ (Å)</td>
<td>$Z_{H\dagger}$ (Å)</td>
</tr>
<tr>
<td>1/4ML</td>
<td>4</td>
<td>2.270</td>
<td>1.240</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.270</td>
<td>1.240</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.270</td>
<td>1.240</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.270</td>
<td>1.240</td>
</tr>
<tr>
<td>1/9ML</td>
<td>4</td>
<td>2.266</td>
<td>1.230</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.266</td>
<td>1.230</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.266</td>
<td>1.230</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.266</td>
<td>1.230</td>
</tr>
<tr>
<td>1/16 ML</td>
<td>4</td>
<td>2.266</td>
<td>1.235</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.266</td>
<td>1.235</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.266</td>
<td>1.235</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.266</td>
<td>1.235</td>
</tr>
</tbody>
</table>

Table 3 shows how the energy and geometry of the TS varies with the number of layers, for coverages of 1/4, 1/9 and 1/16ML. As we increase the number of layers the barrier decreases without any change to the TS state geometry. The average energy difference between calculations performed with a five layer Pt(111) slab and calculations using a 4 layer slab is -90meV, while the average energy difference between the 4 and 6 layer slab is 32meV (Fig.11). This sharp energy difference between the 4 and 5 layer slabs might have various explanations, such as the
stacking sequence of the layers, the need to further increase the number of layers in order to reduce quantum surface effects (QSE) which are less visible as the thickness of the slab increases and the use of a bigger k-point grid.

![Energy differences at the TS as a function of the number of layers of the Pt(111) slab at the three proposed surface coverage.](image)

Figure 11. Energy differences at the TS as a function of the number of layers of the Pt(111) slab at the three proposed surface coverage.
B. Maximum Surface Coverage

The study featured in the previous section shows an increase in $E_0$ due to surface coverage based on an unrealistic situation where all the methane is dissociated at the same time. Having this in mind, we will consider methane dissociation in the presence of pre-adsorbed CH$_3$ and H fragments. In order to determine the saturation point or maximum surface coverage on a Pt(111) catalyst for the chemical dissociation of methane, we study the system at different levels of CH$_3$ +H surface coverage. We selected the 4x4 Pt(111) lattice to perform these calculations to minimize the repulsion between the methane in the repeated images. The first system (2/16ML) consists of methyl and hydrogen fragments adsorbed on the lattice surface. The methyl will remain over the top site where dissociation occurred, but placed in the lowest energy configuration with each hydrogen pointing towards a fcc hollow, as well as the hydrogen fragment (Fig. 12). The dissociation of the new incoming methane was evaluated at three possible sites as shown in Fig. 13 (Reaction site 2, 3, 4). Each site is evaluated independently, then we use the product state energies ($E_p$), as shown on Table 4 to determine the lowest energy site for the next system (3/16ML). This system has two adsorbed methyl-hydrogen fragments and the incident molecule will be evaluated at reacting sites 3 and 4. Based on the same evaluating criteria we choose the lowest product state energy site to generate the third system (4/16ML≈1/4ML). The system has three methyl-hydrogen fragments adsorbed onto the surface and reaction site 3 available for the incoming gas particle.
Figure 12. 4x4 Pt(111)slab top most layer with one pre-adsorbed CH$_3$ + H fragment and one newly dissociated methane on reaction site 2. The pre-absorbed fragments are in the configurations of highest adsorption energy and we are still using the D2 configuration for the dissociating CH$_4$.

Figure 13. Reaction sites explored in search of maximum coverage and effects of site blocking by pre-adsorbed H and CH$_3$ fragments.
Cl-NEB calculations of these systems have been performed in order to trace how $E_b$ changes as $\Theta$ increases; in addition we can observe the site blocking effects by the methyl-hydrogen adsorbates on the dissociation barrier. All system and reacting sites will be explored as we expect the energy barrier of the methane dissociation to increase, as more methyl-hydrogen fragments are adsorbed onto the platinum surface. Table 5 reports the energies and geometry of the dissociating methane at the transition state. The case of 1/16ML coverage is the original system of a CH$_4$ dissociating over a bare surface. We further explore energy barriers for dissociation with systems with pre-adsorbed fragments and multiple reaction sites, taking into account that carbon atoms should be placed at least two lattice spaces apart, and the H atoms occupy hollow sites adjacent to the carbons. As expected, an increase in the dissociation barrier is observed as surface coverage increases due to the presence of pre-adsorbed CH$_3$ and H fragments. Focusing on the reaction sites with the lowest $E_p$, as shown in Table 4, there is a 42 meV increase in the barrier from 1/16 to 2/16 ML coverage and a 25meV increase from 2/16 to 3/16 ML coverage. Finally, the 4/16 ML

Table 4. Relative product state energies ($E_p$) with increasing surface coverage in terms of CH$_3$ and H fragments and reaction sites (Fig. 4)

<table>
<thead>
<tr>
<th>Coverage, $\Theta$</th>
<th>Reaction Site 1</th>
<th>Reaction Site 2</th>
<th>Reaction Site 3</th>
<th>Reaction Site 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16</td>
<td>0.188</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2/16</td>
<td>CH$_3$-H (ads)</td>
<td>0.229</td>
<td>0.382</td>
<td>0.320</td>
</tr>
<tr>
<td>3/16</td>
<td>CH$_3$-H (ads)</td>
<td>CH$_3$-H</td>
<td>0.477</td>
<td>0.340</td>
</tr>
<tr>
<td>4/16</td>
<td>CH$_3$-H (ads)</td>
<td>CH$_3$-H</td>
<td>CH$_3$-H</td>
<td>0.433</td>
</tr>
</tbody>
</table>
coverage yielded a similar energy barrier as for the 3/16 ML coverage. Interestingly the energy barrier at 4/16 ML coverage is in good agreement with the energy barrier obtained for the system with 1/4 ML coverage and a 2x2 supercell.

In order to determine the saturation coverage it is imperative to find a stable product state at a fifth reaction site (Fig. 14). We explored two possible systems, the first with all the hydrogen fragments in the fcc hollows (Fig. 15a) while the second has half the hydrogen fragments in the hcp hollows (Fig. 15b). The product energies of these systems, as they appear in Table 6, lead us to infer that the energy barrier for this reaction is exceedingly large.

Table 5. Relative energy for the TS, \( E_{\text{ts}} \), for the reaction over Pt(111) at \( \Theta = 1/16, 2/16, 3/16, 4/16 \) ML and geometries for the transition states.

<table>
<thead>
<tr>
<th>Rxn. Site</th>
<th>Coverage</th>
<th>( Z^T_C ) (Å)</th>
<th>( Z^T_H ) (Å)</th>
<th>( r_{C-H} ) (Å)</th>
<th>( \theta ) (deg)</th>
<th>( E_b ) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/16ML</td>
<td>2.266</td>
<td>1.235</td>
<td>1.508</td>
<td>136.88</td>
<td>0.856</td>
</tr>
<tr>
<td>2</td>
<td>2/16ML</td>
<td>2.266</td>
<td>1.237</td>
<td>1.575</td>
<td>137.00</td>
<td>0.898</td>
</tr>
<tr>
<td>3</td>
<td>2/16ML</td>
<td>2.267</td>
<td>1.235</td>
<td>1.588</td>
<td>136.78</td>
<td>0.943</td>
</tr>
<tr>
<td>4</td>
<td>2/16ML</td>
<td>2.267</td>
<td>1.228</td>
<td>1.599</td>
<td>135.99</td>
<td>1.041</td>
</tr>
<tr>
<td>3</td>
<td>3/16ML</td>
<td>2.269</td>
<td>1.231</td>
<td>1.602</td>
<td>136.48</td>
<td>0.992</td>
</tr>
<tr>
<td>4</td>
<td>3/16ML</td>
<td>2.268</td>
<td>1.229</td>
<td>1.595</td>
<td>136.00</td>
<td>0.923</td>
</tr>
<tr>
<td>4</td>
<td>4/16ML</td>
<td>2.270</td>
<td>1.231</td>
<td>1.595</td>
<td>136.37</td>
<td>0.919</td>
</tr>
</tbody>
</table>
Figure 14. Reaction sites 5 to be explored in search of saturation of the metal surface. Methyl fragments will be adsorbed at reaction sites 1, 2, 3 and 4. H fragments will be placed at the fcc or hcp hollows.

Figure 15. Product state at reaction site 5 having CH$_3$ at reaction sites 1, 2, 3 and 4 (a). H fragments are placed at the fcc holes (pink). (b) Product state at reaction site 5 having CH$_3$ fragments at reaction sites 1, 2, 3 and 4. H fragments are distributed between the fcc holes (pink) and the hcp holes (green).
Table 6. Relative product state energies ($E_p$) of systems at Fig. 13, comparing lower energy sites for the H fragments.

<table>
<thead>
<tr>
<th>System</th>
<th>fcc hollows</th>
<th>fcc/hcp hollows</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Energy ($E_a$) eV</td>
<td>2.618</td>
<td>1.729</td>
</tr>
</tbody>
</table>

The results of these calculations on the saturation limits for the surface coverage is the ideal point of start to determine whether increasing the translational energy and exciting vibrational modes of the incident $\text{CH}_4$ molecule will help surpass the saturation limit by allowing the dissociation of molecule at sites previously labeled as blocked by the adsorbed $\text{CH}_3$ and H fragments. Another possibility is that a dissociating methane molecule may induce an Rideal-Eley reaction, where the dissociating H atom carries excess energy and moves on the surface to meet an adsorbed H atom, resulting in desorption away from the surface as $\text{H}_2$ molecules, opening up surface sites for subsequent methane dissociation.
CHAPTER III

REACTION PATH DESCRIPTION OF MODE SELECTIVE CHEMISTRY

A. Close-Coupled Reaction Path Formulation

Transition state theory calculations have benefited from the use of the well-known reaction path Hamiltonian (RPH) [20,22].

\[
H = \sum_{k=1}^{14} \left[ \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2 \right] + V_0(s) + \frac{1}{2} \left[ p_s - \sum_{k=1}^{14} \sum_{j=1}^{14} Q_k P_j B_{k,j}(s) \right]^2 \left[ 1 + \sum_{k=1}^{15} Q_k B_{k,15}(s) \right]^{-2} \tag{5}
\]

Here \( s \) is the reaction coordinates, \( Q_k \) are the normal vibration coordinates, \( p_s, P_k \) are the momenta conjugate to \( s \), \( Q_k \) and the vibrationally nonadiabatic coupling are given by,

\[
B_{k,j}(s) = \sum_{i=1}^{15} \frac{dL_{i,k}}{ds} L_{i,j}(s) \tag{6}
\]

Here \( L_{i,k} \) are the normal-mode eigenvectors. We will examine the dissociation of CH\(_4\) over Pt(111) through the use of the RPH. In order to compute the terms that define our Hamiltonian from first principles, we assume that the potential energy surface is harmonic about the reaction path and we include all 15 molecular DOF. The first step is to locate the minimum energy path (path of steepest descent from the transition state to the reactant and product states). For this we will use the previously implemented CI-NEB method for 6 points across the reaction path. Mass-weighted Cartesian coordinates \( \{x_i\}, i = 1, \ldots, 15 \) will be used to describe the location of the five CH\(_4\) atoms over the rigid Pt(111) metal surface. The distance along the reaction path is given by \( s \), where \( (ds)^2 = \sum_{i=1}^{15} (dx_i)^2 \); \( s = 0 \) at the transition state, while reactant and product states correspond to large negative and
positive values of $s$, respectively. For this part of the study we choose to represent our system as a five layer, 3x3 supercell with a vacuum space between repetitive images of approximately six layers. As a continuation of the previous studies we initially used the D2 methane configuration, but had problems due to a lack of symmetry with respect to the platinum lattice. This lack of symmetry along the reaction path is due to the dissociation of the C—H bond along the bridge site, which is bounded by fcc (red) and hcp (green) hollows (Fig.16).

Figure 16. D2 configuration at the TS; Pt(111)bridge site bound by fcc (red) and hcp (green) hollow.

After considering different configurations previously calculated by this group, we selected the F1 geometry [25]. This configuration has all of the non-reacting
hydrogen atoms at fcc hollows (Fig.17), while the C—H dissociation occurs along the Y-axis at a fcc hollow site, eliminating the asymmetric effects of the different hollows on the Pt(111) slab.

Figure 17. Representation of the F1 configuration (top and side view) at high separation from the Pt(111) surface. CH₄ is placed at a top site while the non-reactive hydrogen atoms point to fcc hollows.

As previously mentioned, we started our CI-NEB calculations with a minimum of six images, where the end positions represent the energy minimized reactive state (RS) and product state (PS), in which all CH₄ degrees of freedom will remain constrained.
In order to decrease the computational cost of the calculation we moved CH$_4$ closer to the metal surface (reactive state), allowing us to use fewer moving images. As in the previous reaction path calculations a plane wave basis set was used by VASP; the nonlocal exchange-correlation effects are treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. Fully nonlocal optimized projector augmented-wave (PAW) potentials are used to treat the interaction between the ionic cores and the electrons. The energy cut-off ($E_{\text{cut}}$) for the plane wave basis set is 400eV throughout all calculations, the Brillouin zone sampling uses a $\Gamma$-centered grid of 6x6x1 $k$-points and we consider the calculation converged when all forces were equal or smaller than 0.01eV/Å. As we can see on the reaction path diagram in Fig. 18, image 1 is lower in energy than the initial guess for the RS, similarly image 4 is lower in energy than the PS guess. Image 1 and 4 were further analyzed and confirmed to be true minima. In Fig. 19 we show the four points that comprise the reaction path for the F1 methane configuration with representations of the molecule at each point. The energy barrier for the TS is 0.825eV, the CH$_4$ center of mass is at a distance of 2.24 Å from the top site Pt atom, the dissociating C—H bond is stretched to 1.52 Å, and the bond polar orientation angle normal to the Pt surface is 132.2 °. The TS geometries obtained by this calculation are consistent with calculations previously performed by this group (25).
Figure 18. Diagram for the initial guess of methane dissociation (F1 configuration) over Pt(111).

Then, using VASP's NEB (no climbing image) routine we found the relaxed geometries of CH$_4$ for 48 points $s$ along the reaction path (Fig. 20), the total energy, $V_0(s)$, and we performed a normal-mode analysis. This approach calculates the Hessian matrix via central difference with atomic displacements of 0.015Å. The symmetrization is turned off and the plane wave energy cut-off ($E_{\text{cut}}$) is set at 600eV. The results of these calculations allowed us to compute the normal vibrational coordinates $\{Q_k\}$, and the frequencies $\{\omega_k(s)\}$, $k = 1, \ldots, 14$ describing motion orthogonal to the reaction path at a point $s$, and the mode couplings.
Figure 19. Graphical representation of the four moving images along reaction path, depicting the top and side view of CH$_4$ as the C—H dissociates over Pt(111).
Figure 20. Diagram for the 48 images describing the reaction path of methane dissociation over Pt(111).

As we added more points we created a highly detailed reaction path starting with the molecule far above the surface where nine of the frequencies are non-zero, continuing with the areas before and after the TS, and ending at the PS where complete dissociation of the C—H bond was obtained. In Fig. 21 we plot the nine frequencies along the RP, where symmetric frequencies are labeled 1’-6’ and the anti-symmetric frequencies are labeled 1”-3”. We also labeled the four vibrational modes $\nu_3$ (anti-symmetric stretch), $\nu_1$ (symmetric stretch), $\nu_2$ (doubly degenerate bend) and $\nu_4$ (triply degenerate bend). We can observe how the interaction with the Pt surface softens the $\nu_1$ symmetric stretch (3’) as well as some modes of the $\nu_2$ (4’) and $\nu_4$ (5’, 6’) bends, and this softening plays a role in lowering the effective barrier height. Avoided crossings between the symmetrical modes 3’ and modes 4’, 5’ and 6’ occur as s goes from -0.5 to -0.1 amu$^{1/2}$Å.
The symmetric modes couple to each other as well as to the adiabatic ground state, while the anti-symmetric modes only couple to each other. In order to properly describe the energy transfer occurring throughout the dissociative reaction we have calculated the curvature coupling elements, $B_{kF}$, and the mode-mode coupling elements, $B_{kj}$. The next several figures show plots for the curvature couplings (Fig. 22) and the couplings for modes 3’, 4’, 5’ and 6’ (Fig. 23-25). The energy transfer possible between the reaction curvature and the symmetric modes and vice versa as shown in Fig. 22 points toward large effects due to molecular translation and more subtle effects due to the bend modes. In Fig. 23 the larger effects are from the couplings between the symmetric stretch (3’) and the bend (4’).
Figure 22. Curvature coupling elements for the symmetric modes 1’-8’.

Figure 23. Mode-mode couplings between symmetric mode 3’ and symmetric modes 1’-6’.
Larger effects due to mode couplings between the symmetric stretch 3' and the 4' bend and between the later and the 5' bend can be observed in Fig. 24. Figures 25 and 26 show large coupling between the 5' and 6' bend modes.

**Figure 24.** Mode-mode couplings between symmetric mode 4' and symmetric modes 1'-6'.

**Figure 25.** Mode-mode couplings between symmetric mode 5' and symmetric modes 1'-6'.
Finally, based on the RPH, an attempt to implement a full quantum mechanical polyatomic reactive scattering calculations, including all non-adiabatic couplings, will be pursued. The parametric dependence of the vibrational states on $s$ leads to non-adiabatic transitions that depend upon the momentum and kinetic energy of the molecule. Taking this into account, we can try to determine how energy initially allocated on a stretch or bend vibration of the methane molecule generates bond dissociation at the TS. Our wave packet evolves on vibrational adiabatic potentials and couples to other vibrationaly adiabatic states by means of the non-adiabatic couplings. Standard wave-packet techniques will be used to compute the reactive flux, which is Fourier transformed to give state- and energy-resolved reaction probabilities [11]. We would like to apply our close-coupled formulation of the RPH

Figure 26. Mode-mode couplings between symmetric mode 6’ and symmetric modes 1’-5’.
and compute dissociative sticking probabilities of \( \text{CH}_4 \) over Pt(111) by including all 15 molecular DOFs and any effects due to changes in surface temperature. Hopefully this will allow us to find agreement with comparative experimental data.
REFERENCES