The Dissociative Chemisorption of Methane and Its Isotopologues on Metal Surfaces

Han Guo

Follow this and additional works at: https://scholarworks.umass.edu/dissertations_2

Part of the Materials Chemistry Commons, and the Physical Chemistry Commons

Recommended Citation
Guo, Han, "The Dissociative Chemisorption of Methane and Its Isotopologues on Metal Surfaces" (2018). Doctoral Dissertations. 1348.
https://scholarworks.umass.edu/dissertations_2/1348

This Open Access Dissertation 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 Doctoral Dissertations by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
The Dissociative Chemisorption of Methane and Its Isotopologues on Metal Surfaces

A Dissertation Presented

by

Han Guo

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

September 2018

Chemistry
© Copyright by Han Guo 2018

All Rights Reserved
The Dissociative Chemisorption of Methane and Its Isotopologues on Metal Surfaces

A Dissertation Presented

by

Han Guo

Approved as to style and content by:

__________________________
Bret Jackson, Chair

__________________________
Scott Auerbach, Member

__________________________
Ricardo Metz, Member

__________________________
Nathaniel Whitaker, Outside Member

__________________________
Richard Vachet, Head of Chemistry Department
ACKNOWLEDGMENTS

I would like to thank my advisor, Professor Bret Jackson, for his patient guidance and continuous support. He has taught me not only scientific knowledge but also how to do research, which makes me enjoy my role as a young scientist. I want to thank Professor Scott Auerbach for his thoughtful advises. His insightful questions always inspire me to think more about my work. I would also like to thank my other committee members Professor Ricardo Metz and Professor Nathaniel Whitaker.

I enjoyed very much working in the CRUNCH lab. Thanks to Azar Farjamnia for being such a kind and helpful friend. Thanks to my other officemates Bojana Dragicevich, Qinfang Sun and Hongbo Shi for fruitful discussions and making our lab a friendly place to work.

My parents and grandparents have been my greatest source of support throughout my life. Through all my difficulties, they were always there to give me love and strength. I would like to offer my special thanks to my husband, Lian Duan, for his love, patience and understanding. I also want to thank my friends for their kindness and being there whenever I needed them.
The dissociative chemisorption of small molecules on metal surfaces is an important step in many heterogeneous catalytic processes, and has received considerable scientific attention. In this thesis, a quantum approach based on the reaction path Hamiltonian is used to explore the dissociative chemisorption of methane and its deuterated isotopologues on several metal surfaces.

The theoretical approach is described in Chapter 2. This approach treats all 15 degrees of freedom of the methane molecule, and includes the effects of lattice motion, allowing us to examine the translational and vibrational enhancements, mode- and bond-selectivity and the surface temperature dependence observed in experiments.

In Chapter 3, this approach is used to explore the dissociation of CH₄, CHD₃ and CH₂D₂ on Ni(111). The symmetric stretch mode is found to be more effective at promoting dissociation of CH₄ and CHD₃ than the antisymmetric stretch mode, while for CH₂D₂ the
two modes have similar efficacies. This mode specificity has also been observed for C-H stretch overtone and combination states of different symmetry. In addition, the dissociation of methane isotopologues shows bond selective behavior. With our model, mode specificity and bond selectivity is explained in terms of mode softening, the nonadiabatic couplings and symmetry in vibrationally adiabatic normal modes.

The dissociative chemisorption of methane on Pt(111) is examined in Chapter 4, where the computed sticking probabilities and vibrational efficacies are compared between reactions on Pt(111) and Ni(111). The variation in reactivity with surface temperature is investigated with our improved treatment of lattice motion. In addition, to achieve quantitative agreement with experiment, a semi-empirical specific reaction parameter density functional with van der Waals corrections is used and the results are compared with those using the PBE functional.

Finally, the effect of surface defects, i.e. step sites, is investigated in Chapter 5. Different reaction paths have been located for CH₄ dissociation on the stepped Pt(211) and Ni(211) surfaces. For both surfaces, dissociation along the step edge dominates the total sticking at all but the highest incident energies, due to the lower activation energy.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGMENTS</th>
<th>iv</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Molecule-Surface Interactions</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1 Adsorption</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2 Dynamics of Molecule-Surface Interactions</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Major Experimental and Theoretical Results</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Outline</td>
<td>11</td>
</tr>
<tr>
<td>1.5 References</td>
<td>13</td>
</tr>
<tr>
<td>2. THEORIES AND METHODS</td>
<td>19</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Computational Model and Electronic Structure Calculations</td>
<td>20</td>
</tr>
<tr>
<td>2.3 Reaction Path Hamiltonian (RPH) Model</td>
<td>21</td>
</tr>
<tr>
<td>2.4 Close Coupled Wave Packet Approach</td>
<td>26</td>
</tr>
<tr>
<td>2.5 Sticking Probability</td>
<td>30</td>
</tr>
<tr>
<td>2.5.1 Averaging over Impact Sites and Reaction Pathways</td>
<td>31</td>
</tr>
<tr>
<td>2.5.2 Rotational Treatment</td>
<td>33</td>
</tr>
<tr>
<td>2.5.3 Effects of Lattice Motion</td>
<td>34</td>
</tr>
<tr>
<td>2.6 References</td>
<td>39</td>
</tr>
<tr>
<td>3. DISSOCIATIVE CHEMISORPTION OF METHANE AND ITS ISOTOPOLOGUES ON Ni(111)</td>
<td>43</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>43</td>
</tr>
<tr>
<td>3.2 Computational Model and Electronic Structure Calculations</td>
<td>44</td>
</tr>
<tr>
<td>3.3 Mode- and Bond-Selectivity in the Dissociation of CHD₃ on Ni(111)</td>
<td>47</td>
</tr>
<tr>
<td>3.3.1 Effects of Mode Softening and Nonadiabatic Couplings</td>
<td>48</td>
</tr>
<tr>
<td>3.3.2 Sticking Probability</td>
<td>57</td>
</tr>
<tr>
<td>3.3.3 Summary</td>
<td>66</td>
</tr>
</tbody>
</table>
3.4 Mode- and Bond-Selectivity in the Dissociation of CH$_2$D$_2$ on Ni(111) ............................................................ 68
3.5 Reactivity of Overtone Excited CH$_4$ on Ni(111) .................... 79
3.6 Conclusion ........................................................................ 88
3.7 References ......................................................................... 90

4. DISSOCIATIVE CHEMISORPTION OF METHANE ON PT(111) .......................................................... 94
4.1 Introduction ........................................................................ 94
4.2 Computational Model and Electronic Structure Calculations .... 95
4.3 Normal Mode Analysis ...................................................... 100
4.4 Dissociative Sticking Probability ........................................ 107
4.5 Sticking Probability Using the Specific Reaction Parameter (SRP)
   Functional ......................................................................... 118
   4.5.1 Transition State and Minimum Energy Path Using the SRP
         Functional ...................................................................... 118
   4.5.2 Normal Mode Analysis ............................................... 120
   4.5.3 Reaction Probabilities Using the SRP and PBE
         Functionals ...................................................................... 124
4.6 Conclusion ........................................................................ 128
4.7 References ......................................................................... 130

5. DISSOCIATIVE CHEMISORPTION OF METHANE ON STEPPED SURFACES ................................................................ 134
5.1 Introduction ........................................................................ 134
5.2 Computational Model and Electronic Structure Calculations .... 135
5.3 Adsorption of H and CH$_3$ ................................................ 137
5.4 Reaction Paths and Transition States on Pt(211) and Ni(211) .... 141
5.5 Scattering Dynamics for Methane Dissociation on Pt(211) .... 147
   5.5.1 Normal Mode Analysis .............................................. 148
   5.5.2 Rotational Treatment and Impact Site Averaging .......... 149
   5.5.3 Effects of Lattice Motion .......................................... 152
   5.5.4 Dissociative Sticking Probability for CH$_4$ on Pt(211) .... 154
5.6 Scattering Dynamics for Methane Dissociation on Ni(211) .... 156
   5.6.1 Normal Mode Analysis .............................................. 157
   5.6.2 Dissociative Sticking Probability for CH$_4$ on Ni(211) .... 162
5.7 Conclusion ........................................................................ 165
5.8 References ......................................................................... 166

BIBLIOGRAPHY ....................................................................... 169
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1 The molecule-lattice coupling constants ( \alpha ) and ( \beta ) for the dissociative chemisorption of methane on different surfaces.</td>
<td>36</td>
</tr>
<tr>
<td>Table 3.1 Activation energies for CHD(_3) dissociation on Ni(111).</td>
<td>52</td>
</tr>
<tr>
<td>Table 3.2 The increase in barrier height relative to the minimum barrier site for CH(_4) and CHD(_3) dissociation on Ni(111).</td>
<td>58</td>
</tr>
<tr>
<td>Table 3.3 Vibrational efficacies, ( \eta ), for the ( \nu_1 ), ( \nu_2 ) and ( \nu_4 ) states at ( S_0 = 10^{-4} ).</td>
<td>66</td>
</tr>
<tr>
<td>Table 3.4 Activation energies for CH(_2)D(_2) dissociation on Ni(111).</td>
<td>71</td>
</tr>
<tr>
<td>Table 3.5 Vibrational efficacies, ( \eta ), for the ( \nu_6 ), ( \nu_1 ), ( \nu_8 ) and ( \nu_2 ) states at ( S_0 = 10^{-4} ).</td>
<td>78</td>
</tr>
<tr>
<td>Table 3.6 Composition, as a percent, of the C-H stretch overtone and combination eigenstates of CH(_4), in terms of the normal mode basis set of Ref. 54.</td>
<td>82</td>
</tr>
<tr>
<td>Table 4.1 Activation energies for CH(_4) dissociation on Pt(111) and Ni(111).</td>
<td>102</td>
</tr>
<tr>
<td>Table 4.2 Vibrational efficacies ( \eta ) from theory and experiment (expt.) and Sudden Vector Projection overlaps ( \gamma ) for CH(_4) dissociation on Pt(111) and Ni(111). Results are shown for the stretch states.</td>
<td>111</td>
</tr>
<tr>
<td>Table 4.3 Vibrational efficacies ( \eta ) from theory and experiment (expt.) and Sudden Vector Projection overlaps ( \gamma ) for CH(_4) dissociation on Pt(111) and Ni(111). Results are shown for the bending states.</td>
<td>115</td>
</tr>
<tr>
<td>Table 4.4 Transition state data for CH(_4) on Pt(111) using the SRP and PBE functionals.</td>
<td>119</td>
</tr>
<tr>
<td>Table 5.1 The adsorption energy ( E_{ads} ), relative to the energy where the H atom is infinitely far from the surface, for H on Pt(211) and Ni(211).</td>
<td>140</td>
</tr>
<tr>
<td>Table 5.2 The adsorption energy ( E_{ads} ) relative to the energy where CH(_3) is infinitely far from the surface, for CH(_3) on Pt(211) and Ni(211).</td>
<td>141</td>
</tr>
<tr>
<td>Table 5.3 Transition state data for methane dissociation on Pt(211) and Pt(111).</td>
<td>144</td>
</tr>
</tbody>
</table>
Table 5.4 Transition state data for methane dissociation on Ni(211) and Ni(111).................................................................146

Table 5.5 The increase in barrier height relative to the minimum barrier sites on Pt(211)...............................................................151

Table 5.6 The increase in barrier height relative to the minimum barrier sites on Ni(211).................................................................162
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1</td>
<td>One-dimensional potential for the dissociative chemisorption of a diatomic molecule on a metal surface. The horizontal axis is the distance of the molecule from the surface.</td>
</tr>
<tr>
<td>Figure 1.2</td>
<td>Two-dimensional PESs for the reaction of an atom with a diatomic molecule (A + BC → AB + C), where the contour lines represent the potential energy, r₁ is the distance between A and B, and r₂ is the distance between B and C. (a) and (b) represent a PES with an early barrier, while (c) and (d) represent a PES with a late barrier. This figure is taken from Ref. 42.</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Schematic representation of a 3×3 four-layer supercell.</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Unit region for averaging over impact sites on (111) surfaces. The metal bond length is a.</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Total energy along the MEPs for dissociative chemisorption of methane on Ni(111) for three values of Q, the displacement of the lattice atom perpendicular to the surface plane. The curves are shifted along s so that the three corresponding initial states, with the same distance of the carbon atom above the surface, have the same value of s.</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Transition state (left panel) and product state (right panel) configurations for the dissociation of CH₄ on Ni(111). Only the topmost lattice layer is shown. Eₜ and Eₚ are the energies for the transition state and the product state, respectively, relative to the energy where methane is infinitely far above the surface.</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Reaction path for methane dissociation on Ni(111).</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Four possible orientations of CHD₃ at the TS on Ni(111). Carbon, deuterium, hydrogen and nickel atoms are represented by gray, blue, white and green colors, respectively.</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Energies of the normal modes along the reaction path for CH₄ and CHD₃ dissociation on Ni(111).</td>
</tr>
</tbody>
</table>
Figure 3.5 Single-site rigid-lattice reaction probabilities for (A) the symmetric C-H cleavage configuration and (B) the symmetric C-D cleavage configuration of CHD$_3$ dissociation on Ni(111). Results are shown for the ground state (gs) and four excited states, with several levels of nonadiabatic couplings: adiabatic (solid lines), $B_{q,15}$ only (filled circles), $B_{q,k}$ only (open circles), and full coupling (xxx). ..........53

Figure 3.6 $B_{q,15}$ couplings for symmetric C-H cleavage (left panel) and symmetric C-D cleavage (right panel) of CHD$_3$ on Ni(111). ..........54

Figure 3.7 $B_{q,k}$ couplings for symmetric C-H cleavage (left panel) and symmetric C-D cleavage (right panel) of CHD$_3$ on Ni(111). ..........55

Figure 3.8 $B_{q,k}$ couplings for symmetric C-D cleavage of CHD$_3$ on Ni(111) in the entrance channel..........................................................57

Figure 3.9 Dissociative sticking probabilities for CHD$_3$ initially in the ground state (gs) and the 1’ excited state at 90 K. Results are shown for symmetric C-H cleavage (sym C-H cleavage), symmetric C-D cleavage (sym C-D cleavage) and asymmetric C-D cleavage (asym C-D cleavage). .................................................................60

Figure 3.10 Dissociative sticking probabilities for CHD$_3$ initially in the ground state (gs), the 2’, 3’ and 1” excited states at 90 K. Results are shown for symmetric C-H cleavage (sym C-H cleavage) and symmetric C-D cleavage (sym C-D cleavage)..................................................61

Figure 3.11 Dissociative sticking probability for either C-H or C-D cleavage. Results are shown for molecules initially in the ground state (gs) or one of the vibrationally excited states.................................63

Figure 3.12 C-H:C-D cleavage ratio for molecules initially in the ground state (gs) or one of the vibrationally excited states. The lines are from our calculations, and the circles are from the QCT studies by Guo et al.$^{14}$ ........................................................................................................65

Figure 3.13 Total dissociative sticking probability for CHD$_3$ dissociation on Ni(111) at 90 K. Results are shown for molecules initially in the ground state (gs), three excited states and the laser-off state. Circles are experimental data (exp) from Utz et al.$^{17}$ .......................66

Figure 3.14 Six possible orientations of CH$_2$D$_2$ at the TS on Ni(111). Carbon, deuterium, hydrogen and nickel atoms are represented by gray, blue, white and green colors, respectively........................................68
Figure 3.15 Energies of the normal modes along the reaction path for CH\(_2\)D\(_2\) dissociation on Ni(111). ................................................................. 70

Figure 3.16 B_{q,k} couplings for symmetric C-H cleavage (top left), asymmetric C-H cleavage (top right), symmetric C-D cleavage (bottom left) and asymmetric C-D cleavage (bottom right) of CH\(_2\)D\(_2\) on Ni(111). ................................................................. 72

Figure 3.17 Effects of the B_{v_6,v_1} coupling on P0 for symmetric C-H cleavage. (A) B_{q,k} couplings in the entrance channel. (B) Single-site rigid-lattice reaction probability for symmetric C-H cleavage of CH\(_2\)D\(_2\) on Ni(111). The dotted lines represent P_0 computed with B_{v_6,v_1} = 0 for s < -2.5 amu\(^{1/2}\) Å. ................................................................. 73

Figure 3.18 Single-site rigid-lattice reaction probability for symmetric C-D cleavage of CH\(_2\)D\(_2\) on Ni(111). ................................................................. 74

Figure 3.19 Dissociative sticking probability for either C-H or C-D cleavage of CH\(_2\)D\(_2\) on Ni(111) at 95 K. Results are shown for molecules initially in the ground state (gs) or one of the vibrationally excited states................................................................. 76

Figure 3.20 C-H:C-D cleavage ratio for CH\(_2\)D\(_2\) initially in the ground state (gs) or one of the vibrationally excited states on Ni(111). ............ 77

Figure 3.21 Total dissociative sticking probability for CH\(_2\)D\(_2\) dissociation on Ni(111) at 95 K. Results are shown for molecules initially in the ground state and four excited states................................................................. 78

Figure 3.22 Total sticking probabilities for CH\(_2\)D\(_2\) on Ni(111) at 95 K. Lines are theoretical results for molecules in the ground, v_1 or v_6 state, and open black circles represent vibrational-state-average theoretical S_0 under “laser-off” conditions. Triangles are experimental measurements from the Utz group (unpublished data)......................................................................................................... 79

Figure 3.23 Level diagram of the C-H stretch overtone states v_1 + v_3-F\(_2\), 2v_3-F\(_2\), 2v_3-A_1 and 2v_3-E prepared by double resonance excitation. The excitation path for all four overtone states starts from v = 0, J = 1 using the v_3 = 1, J = 0 level as intermediate state. This diagram is from Ref. 5. The symmetric C-H stretch overtone state 2v_1-A_1 is included in the diagram but could not be prepared in the study of Ref. 5................................................................. 80
Figure 3.24 Dissociative sticking probability for CH$_4$ dissociation on Ni(111) at 475 K. Results are shown for the ground, single-quantum and two-quantum normal mode states. .................................................. 84

Figure 3.25 The dissociative sticking probability for the $v_3 + 2v_2$ normal mode state estimated from single-quantum and two-quantum states by shifting the curves. ................................................................. 86

Figure 3.26 Dissociative sticking probabilities for the computed $S_0$ (solid lines) and the estimated $S_0$ (dotted lines) for several normal mode states................................................................. 86

Figure 3.27 Sticking probabilities for the three symmetry components of the $2v_3$ eigenstate and the $v_1 + v_3$-F$_2$ state. The lines represent the theoretical results, and the circles are the experimental data. 5 ...... 87

Figure 4.1 Transition state (left panel) and product state (right panel) configurations for the dissociation of CH$_4$ on Pt(111). Only the topmost Pt layer is shown. $E_b$ and $E_p$ are the energies for the transition state and the product state, respectively, relative to the energy where methane is infinitely far above the surface. .......... 96

Figure 4.2 Reaction path for methane dissociation on Pt(111).......................... 97

Figure 4.3 The root-mean-square displacement $Q_{rms}$ as a function of the surface temperature $T_s$, using the Debye model with $\theta_D = 140$ K$^{36,38}$ (solid lines) and the old model (dotted lines). Results are compared with the AIMD results reported in Ref. 16. .................. 100

Figure 4.4 Energies of the normal modes along the reaction path for CH$_4$ dissociation on Pt(111). ................................................................. 101

Figure 4.5 Curvature couplings for CH$_4$ dissociation on Pt(111) (solid lines) and Ni(111) (dotted lines)................................................................. 103

Figure 4.6 $B_{q,k}$ couplings for CH$_4$ dissociation on Pt(111) (solid lines) and Ni(111) (dotted lines)................................. 104

Figure 4.7 Single-site rigid-lattice reaction probabilities for CH$_4$ on Pt(111) and Ni(111). Results are shown for molecules in the ground state (gs) or four excited stretch states................................. 105

Figure 4.8 $B_{q,k}$ couplings for CH$_4$ dissociation on Pt(111) in the entrance channel ................................................................. 106
Figure 4.9 Computed dissociative sticking probabilities (lines) for CH₄ dissociation on Pt(111) at 600 K. Results are compared with the experimental data (circles) from Ref. 9.................................108

Figure 4.10 Computed dissociative sticking probabilities (lines) for CH₄ dissociation on Ni(111) at 475 K. Results are compared with the experimental data (circles) from Ref. 9 and 42.........................108

Figure 4.11 Dissociative sticking probabilities for CH₄ dissociation on Pt(111) at 600 K. Results are shown for the ground state (gs), the ν₃, ν₁, ν₂ and ν₄ excited states and the components of the ν₂ and ν₄ bending states............................................................113

Figure 4.12 Dissociative sticking probabilities for CH₄ dissociation on Ni(111) at 475 K. Results are shown for the ground state (gs), the ν₃, ν₁, ν₂ and ν₄ excited states and the components of the ν₂ and ν₄ bending states............................................................113

Figure 4.13 Dissociative sticking probabilities for CHD₃ dissociation on Pt(111) at 120 K and 500 K. Our calculations (lines) are compared with the AIMD results (circles) from Ref. 33.........................116

Figure 4.14 Computed ground-state sticking probability (lines) as a function of the surface temperature, $T_s$, for CH₄ dissociation on Pt(111) at four incident energies $E_i = 0.42, 0.48, 0.62$ and 1.27 eV. The experimental data (symbols) are from Ref. 55 and 56..............117

Figure 4.15 The total energy, $V_0$, along the MEP for methane dissociation on Pt(111), using both the PBE and SRP functionals. $V_0$ is plotted as a function of the distance along the path, $s$, and the distance of the carbon atom above the surface plane, $Z_C$, (in the inset)..............120

Figure 4.16 Energies of the eight symmetric normal modes along the reaction path for CHD₃ dissociation on Pt(111), using the SRP (solid lines) and PBE (dotted lines) functionals. ....................................................121

Figure 4.17 B_{q,k} couplings for symmetric C-H cleavage of CHD₃ on Pt(111) in the curve-crossing region, using the SRP (solid lines) and PBE (dotted lines) functionals.................................................122

Figure 4.18 B_{q,k} couplings for symmetric C-H cleavage of CHD₃ on Pt(111) in the entrance channel, using the SRP (solid lines) and PBE (dotted lines) functionals.................................................122
Figure 4.19 $B_{q,k}$ couplings for symmetric C-H cleavage of CHD$_3$ on Pt(111) in the curve-crossing region, using the SRP (solid lines) and PBE (dotted lines) functionals.................................................................123

Figure 4.20 $B_{q,15}$ couplings for symmetric C-H cleavage of CHD$_3$ on Pt(111) in the entrance channel, using the SRP (solid lines) and PBE (dotted lines) functionals.................................................................124

Figure 4.21 Single-site rigid-lattice reaction probability, $P_0$, for C-H cleavage of CHD$_3$. The molecules are initially in the ground state or the 1$\nu_1$ excited state. Results are shown for four combinations of couplings and MEPs. ........................................................................................................125

Figure 4.22 Single-site rigid-lattice reaction probability, $P_0$, for C-H cleavage of CHD$_3$. The molecules are initially in one component of the $\nu_4$ state or the $\nu_2$ state. Results are shown for four combinations of couplings and MEPs. ........................................................................................................126

Figure 4.23 Dissociative sticking probabilities, $S_0$, for CHD$_3$ dissociation on Pt(111) at 500 K, computed using the SRP (solid lines) and PBE (dotted lines) functionals. The molecules are initially in the ground state or one of the single-quantum excited states..............................127

Figure 4.24 Dissociative sticking probabilities, $S_0$, for CHD$_3$ dissociation on Pt(111) at 500 K. The RPH calculations are compared with the AIMD calculations and the experimental data from Ref. 17.......128

Figure 5.1 Schematic representation of the terrace, step and kink sites on a vicinal surface. .........................................................................................................................134

Figure 5.2 Schematic presentation of the bare relaxed surfaces: (A) Pt(211), (B) Ni(211)..................................................................................................................136

Figure 5.3 Adsorption sites on the (211) surface. Only the topmost layer of the 3$\times$2 unit cell is shown. .................................................................................................137

Figure 5.4 Schematic illustration of the interaction between the $\sigma$ bonding orbital and the metal $d$ band.$^{23}$ ..................................................................................139

Figure 5.5 Transition state configurations for the dissociation of CH$_4$ on Pt(211). Only three rows of the topmost metal layer are shown. The geometries are optimized with the PBE functional. The barrier height $E_b$ is given for each configuration. ............................................143
Figure 5.6 Transition state configurations for the dissociation of CH$_4$ on Ni(211). Only the topmost metal layer is shown. The geometries are optimized with the SRP functional. The barrier height $E_b$ is given for each configuration.

Figure 5.7 Reaction paths for CH$_4$ dissociation on Pt(211) and Pt(111), using the PBE functional.

Figure 5.8 Energies of the normal modes for the L (left panel) and N (right panel) paths on Pt(211). Results are computed using the PBE functional.

Figure 5.9 $B_{q,k}$ couplings for the L (left panel) and N (right panel) paths on Pt(211). Results are computed using the PBE functional.

Figure 5.10 Unit regions for averaging over impact sites near the step, terrace, and corner atoms on Pt(211).

Figure 5.11 Transition states for the dissociation of methane on the Pt(211) step sites. Only three rows of the topmost metal layer are shown. The arrows indicate the directions and magnitudes of the largest of the $\beta$-type couplings, in units of eV/Å.

Figure 5.12 Computed contributions to the total dissociative sticking probability of methane from the L, M, N and terrace (T) paths. Results are shown for methane initially in the ground state (gs) or the 1$\nu_3$ excited state at $T_s = 120$ K, using the PBE functional.

Figure 5.13 A comparison of theoretical sticking probabilities for CH$_4$ initially in the ground state (gs) or the 1$\nu_3$ excited state on Pt(211) at $T_s = 120$ K with those obtained from experiments. Results are shown for the step sites (solid lines) and the terrace sites (dashed lines) using the SRP functional. LO represents $S_0$ under laser-off conditions.

Figure 5.14 Reaction paths for methane dissociation on Ni(211) using the SRP functional.

Figure 5.15 Energies of the normal modes for the P (left panel) and Q (right panel) paths on Ni(211). Results are computed using the SRP functional.

Figure 5.16 $B_{q,k}$ couplings for the P (left panel) and Q (right panel) paths in curve-crossing region on Ni(211). Results are computed using the SRP functional.
Figure 5.17 Left panel: state-resolved reaction probabilities along the Q MEP in the entrance channel. Results are shown for molecules initially in the state 2 with a collision energy of 0.9 eV. Right panel: $B_{q,k}$ couplings for the Q path in the entrance channel on Ni(211). All the results are computed using the SRP functional...161

Figure 5.18 Single-site rigid-lattice reaction probabilities for the P (left panel) and Q (right panel) paths on Ni(211). Results are shown for molecules initially in the ground state (gs), and the $v_1$ and $v_3$ excited states, using the SRP functional.........................161

Figure 5.19 Computed contributions to the total dissociative sticking probability of methane from the P, Q and terrace (T) paths. Results are shown for the ground state (gs), and two excited states at $T_e = 500$ K..........................163
CHAPTER 1
INTRODUCTION

1.1 Introduction

The interaction of gas-phase molecules with metal surfaces plays a key role in heterogeneous catalysis, such as the well-known Haber-Bosch process for ammonia production. Another important catalytic process is the steam reforming of natural gas, known as the major industrial method to convert hydrocarbons into syngas, which can be further transformed to higher value chemicals. In this process, methane reacts with high-temperature steam on the surface of a metal catalysis, typically Ni-based, and produces hydrogen, carbon monoxide, and a small amount of carbon dioxide. The rate-limiting step of steam methane reforming is the dissociative chemisorption of methane on metal surfaces.\(^1\) This reaction has received considerable attention, not only because of its industrial importance, but also for its scientific role as a prototypical system for molecule-surface reactions.\(^1\)–\(^4\) The dissociative chemisorption of methane exhibits many interesting dynamical behavior. However, high-level calculations have only become possible very recently.

Experiments have shown that, when the methane molecule collides with a surface, it either dissociates to form chemisorbed H and CH\(_3\) fragments on the surface, or scatters non-reactively back into the gas phase.\(^5\) According to electronic structure studies based on density functional theory (DFT), the barriers to dissociation are about 0.5-1.0 eV on different metal surfaces.\(^6\)–\(^12\) Energy- and vibrational-state-resolved measurements of reactivity show that methane dissociation can be promoted by both the incident translational energy and vibrational excitation of the methane, and this behavior is
nonstatistical\textsuperscript{3,4} with mode-specificity\textsuperscript{13–22} and bond-selectivity\textsuperscript{15,16,18,23–26} being observed. It is also found that the probability for dissociative sticking depends on the surface temperature.\textsuperscript{2–4} In addition, while most studies were performed for reaction on flat surfaces, practical catalysts are likely to have defect sites, such as steps and kinks, on the surface. DFT studies show that the barriers to dissociation are different on flat surfaces and at defect sites,\textsuperscript{9,27–32} consistent with experimental observation that methane dissociation is more reactive on stepped surfaces.\textsuperscript{9,33}

In this work, we use a quantum mechanical approach based on the reaction path Hamiltonian (RPH)\textsuperscript{34,35} to study the dissociative chemisorption of methane and its isotopologues on different metal surfaces. We attempt to understand several aspects of the reaction dynamics: mode- and bond- selectivity, the surface temperature dependence of reactivity and the effects of defect sites.

1.2 Molecule-Surface Interactions

1.2.1 Adsorption

After a molecule collides with a surface, it can either stick to the surface or return to the gas phase. There are two ways for the molecule to bind with the surface. First, the incident molecule can molecularly adsorb onto the surface through weak van der Waals forces involving the polarization of the adsorbate and the surface. This is known as physisorption. The binding energy for physisorption is usually less than 0.3 eV,\textsuperscript{36} and the attractive interaction with the surface is almost uniform across the surface plane. Thus, physisorbed molecules can move freely on the surface.
On the other hand, chemisorption involves electron transfer and the formation of a chemical bond between the adsorbate and the surface. Thus, binding is much stronger for chemisorption relative to physisorption, with an adsorption energy larger than 1.0 eV.\textsuperscript{36} For chemisorption, some incident molecules remain intact upon binding to the surface, known as molecular chemisorption, while others involve bond breaking within the adsorbates and the adsorption of the resulting products. The latter is referred to as dissociative chemisorption. Unlike physisorption, due to the formation of chemical bonds, chemisorption is highly directional, with adsorbates binding at specific sites. Thus, the potential energy surfaces (PESs) are highly corrugated, and chemisorbed molecules are mostly immobile on the surface.

For chemisorption, as a molecule approaches a surface, the orbitals of the molecule interact with the atomic orbitals of the metal. The adsorbate-surface interaction can be described by many models, such as the \textit{d}-band model proposed by Hammer and Nørskov.\textsuperscript{37–39} This model suggests that the strength of the adsorbate-surface interaction and the barrier to dissociation can be determined by the degree of filling of the antibonding adsorbate-metal \textit{d} states, and the degree of orbital overlap between the metal \textit{d} band and the adsorbate (or the size of the coupling matrix element).

\textbf{1.2.2 Dynamics of Molecule-Surface Interactions}

Molecule-surface scattering processes have received considerable scientific attention. There are different types of scattering events: elastic scattering, inelastic scattering and reactive scattering. In elastic scattering, no energy is exchanged within the incident molecule and the surface, while in inelastic scattering, energy flows among different degrees of freedom (DOF) in the system. A special case of inelastic scattering is trapping
or sticking, in which the incident molecule loses enough energy, and is temporarily bound to the surface or becomes adsorbed onto the surface. The molecule can return to the gas phase after a residence time, which is known as desorption. Reactive scattering involves the cleavage of old bonds and the formation of new bonds.

In this study we focus on the dissociative chemisorption process, which is the first and rate-limiting step in many molecule-surface reactions. The binding of an adsorbate can be described by a multidimensional potential energy surface. Figure 1.1 shows a one-dimensional potential for the dissociative chemisorption of a diatomic molecule on a metal surface. The gas-phase molecule dissociates as it collides with the surface, leaving chemisorbed products on the surface. As bond cleavage is involved, most dissociative chemisorption processes are activated, where the molecule has to overcome an activation barrier as it approaches the surface. Thus, molecules with low energies will reflect off the activation barrier.

**Figure 1.1** One-dimensional potential for the dissociative chemisorption of a diatomic molecule on a metal surface. The horizontal axis is the distance of the molecule from the surface.
There are two possible pathways for dissociative chemisorption, known as direct chemisorption and precursor mediated (indirect) chemisorption. For direct chemisorption, a molecule with sufficient energy overcomes the activation barrier, and simply sticks to the surface upon its first encounter with the surface. In this process, the sticking probability increases with increasing incident translational energy. On the other hand, a molecule can first lose some incident energy and become trapped on the surface. Then if the trapped molecule can obtain enough energy to overcome the barrier, it will dissociate and become chemisorbed on the surface. This mechanism is known as precursor mediated chemisorption.

Energy deposited in different degrees of freedom of the reactant can help to surmount the reaction barrier, and the efficacies for promoting reaction are in general not the same for vibrational and translation excitation. Polanyi proposed a set of rules, which relate the relative efficacy of vibrational and translation excitation and the shape of the PES.\textsuperscript{41,42} Figure 1.2\textsuperscript{42} shows two-dimensional PESs for the reaction of an atom with a diatomic molecule ($A + BC \rightarrow AB + C$), where the contour lines represent the potential energy, and the two axes are the intramolecular distances. Polanyi distinguished two types of PES based on the position of the transition state (TS), which is at the top of the barrier. For a PES with an early barrier, the TS is located in the entrance channel, where the B-C bond has not been stretched, and excitation of the B-C stretch is less effective at promoting reaction than adding the same amount of translational energy. On the other hand, for a late-barrier PES, the TS is in the product channel, and vibrational excitation is more effective than translational excitation.
This idea can be generalized to molecule-surface reactions. However, for the
dissociative chemisorption of polyatomic molecules, such as methane, the vibrational
efficacies can be different for excitation of different modes, and the reaction dynamics are
much more complicated. Thus, a high- or full-dimensional PES is needed, and it remains a
challenge to accurately model the dynamics of polyatomic molecule-surface reactions.

**Figure 1.2** Two-dimensional PESs for the reaction of an atom with a diatomic molecule
\((A + BC \rightarrow AB + C)\), where the contour lines represent the potential energy, \(r_1\) is the
distance between A and B, and \(r_2\) is the distance between B and C. (a) and (b) represent a
PES with an early barrier, while (c) and (d) represent a PES with a late barrier. This figure
is taken from Ref. 42.
1.3 Major Experimental and Theoretical Results

During the last few decades, both experimental and theoretical studies have made significant progress in understanding molecule-surface reaction dynamics.\textsuperscript{3,4,43} In experiments, laser excitation and molecular beam techniques provide experimental capabilities to prepare incident molecules in a select vibrational state with well-defined and tunable translational energy. Energy- and state-resolved measurements of gas-surface reactivity provide insight into the role of translational energy, and allow the observation of the mode- and bond- selective behavior in the dissociative chemisorption of methane on metal surfaces.

Juurlink et al. reported the first state-resolved experiments of methane dissociation on Ni(100).\textsuperscript{44} They used infrared laser excitation to prepare CH\textsubscript{4} in the \(1\nu_3\) antisymmetric stretch state, and found that molecules in the \(1\nu_3\) state are up to 1600 times more reactive than those in the ground state, but the \(\nu_3\) excitation is slightly less effective in promoting reactivity than the same amount of translational energy. Another state-resolved study by Smith et al. revealed that vibrational excitation of the \(\nu_3\) stretch is more effective than translational energy on Ni(111).\textsuperscript{45} They found that molecules in the ground state require 45 kJ/mol of translational energy to obtain the same reactivity enhancement provided by 36 kJ/mol of the \(\nu_3\) excitation. On the other hand, Maroni et al. reported that on Ni(100) the reactivity of CH\textsubscript{4} in the \(1\nu_1\) symmetric stretch state is about an order of magnitude higher than that of methane excited to the \(1\nu_3\) antisymmetric stretch state reported by Juurlink et al.,\textsuperscript{44} even though there is a bit less vibrational energy in the \(\nu_1\) state.\textsuperscript{46} In addition, Beck et al. measured the state-resolved sticking probability for CH\textsubscript{2}D\textsubscript{2} dissociation on Ni(100).\textsuperscript{22} They reported that the sticking probability with two quanta of excitation in one C-H bond
was much greater than that with one quantum in each of two C-H bonds. This can be explained by the localization of vibrational energy in a single C-H bond. For bending states, the $3\nu_4$ bending overtone state was found to be significantly less effective than the $\nu_3$ antisymmetric stretch state at promoting dissociative chemisorption on Ni(111) and Ni(100). More recently, Hundt et al. measured the state-resolved sticking probability of CH$_4$ prepared in all three vibrational symmetry components of the $2\nu_3$ overtone vibration as well as in the $\nu_1 + \nu_3$ combination vibration, and observed different reactivities for these states.

All of these studies show mode specificity in the dissociative chemisorption of methane on metal surfaces, where the nature of the vibrational mode, not just its vibrational energy, determines the sticking probability. This mode-specific behavior is often expressed in terms of a vibrational efficacy

$$\eta = \frac{\Delta E_i}{\Delta E_\nu} = \frac{E_i(\text{gs}, S_0) - E_i(\nu, S_0)}{\Delta E_\nu}$$  \hspace{1cm} (1.1)$$

where $\Delta E_i$ is the increase in incident translational energy necessary to give the same $S_0$ as increasing the vibrational energy by $\Delta E_\nu$. $E_i(\nu, S_0)$ and $E_i(\text{gs}, S_0)$ are the translation energies giving a sticking probability of $S_0$ for an initial vibrational state $\nu$ and the ground state (gs), respectively.

In addition to mode specificity, bond selectivity has also been observed in the dissociation of partially deuterated methane isotopologues on metal surfaces. Killelea et al. reported that, for the dissociation of CHD$_3$ on Ni(111), excitation of the $\nu_1$ C-H stretch selectively promotes C-H cleavage with a C-H:C-D cleavage ratio larger than 30:1. Similarly, excitation of a C-H stretch mode leads to highly selective cleavage of a C-H bond for CHD$_3$, CH$_2$D$_2$ and CHD$_3$ dissociation on Pt(111).
Mode specificity and bond selectivity observed in these experiments excludes the possibility of statistical models$^{48-50}$ correctly describing the reaction dynamics, which assume complete intramolecular vibrational energy redistribution (IVR) and treat different forms of energy equally.

Earlier molecular beam experiments also showed surface temperature effects for methane dissociation on Pt(111)$^{51}$ and Ni(100)$^{52}$. However, in these experiments, vibrationally excited molecules in the molecular beam contribute to the total sticking probabilities, and the experiments were unable to distinguish the contributions from different vibrational states. Recent state-resolved studies showed a modest surface temperature dependence at higher incident energies but a stronger dependence at lower energies on Ni(111)$^{53,54}$.

Finally, experiments observed different reactivities for methane dissociation on smooth surfaces and on stepped surfaces. Abild-Pedersen et al. measured the reactivity of CH$_4$ dissociation on a stepped Ni surface$^9$. They found the intrinsic sticking probabilities on the step sites to be two orders of magnitude higher than those on the terrace sites at 500 K. For Pt surfaces, Gee et al. performed molecular beam experiments on the Pt(533) surface, and found that the activation barrier to dissociation is about 0.3 eV lower on the steps of Pt(533) than on the planar Pt(111) surface.$^{33}$

In addition to significant advances made in experiments, theoretical studies have provided a detailed mechanistic understanding of the reaction dynamics. As noted, the statistical models, proposed by Harrison et al., assume complete randomization of the initial internal energy within the incident molecule by rapid IVR before dissociation occurs.$^{48-50,55,56}$ While these models are able to fit the measured sticking probabilities
reasonably well, using several adjustable parameters, they cannot treat the mode- and bond-selective behavior.

To properly treat mode specificity and bond selectivity in the dissociation of methane, an accurate 15-dimensional PES is needed. Some earlier studies used pseudo-diatomic or low-dimensional models to treat the reaction dynamics.\textsuperscript{57–66} Halonen \textit{et al.} used a 4-dimensional model based on a local mode Hamiltonian to explore the behavior of the C-H stretch modes, and found that the symmetric stretch fundamental correlates adiabatically with the vibrational energy localized in the reactive C-H bond, while the antisymmetric stretch amplitude becomes localized in the CH\textsubscript{3} group.\textsuperscript{66} Jackson and co-workers used a sudden approach to incorporate the effects of lattice motion into theoretical models, which can explain the surface temperature dependence.\textsuperscript{7,67–70}

Recently, high- or full-dimensional PESs for methane dissociation on surfaces were reported by several groups. Jiang \textit{et al.} reported a 12-dimensional global PES, fitted to a large number of DFT points, for CH\textsubscript{4} dissociation on Ni(111),\textsuperscript{19} and they used the quasi-classical trajectory (QCT) method on this PES to investigate mode- and bond- selective chemistry in the dissociation of CH\textsubscript{4}, CHD\textsubscript{3} and CH\textsubscript{2}D\textsubscript{2} on Ni(111).\textsuperscript{23} Their results were in qualitative agreement with available experiments at energies above the activation barrier. In other two QCT studies, global PESs based on reactive force fields have been developed for methane dissociation on Ni(111) and Pt(111).\textsuperscript{71,72}

On the other hand, the DFT-based \textit{ab initio} molecular dynamics (AIMD) method has been used in molecule-surface scattering calculations.\textsuperscript{20,26,28,73–76} The Kroes group performed AIMD studies for the dissociative chemisorption of CHD\textsubscript{3} on Ni(111) and Pt(111).\textsuperscript{28,74–76} In their studies, they fitted exchange-correlation functionals to molecular
beam experiments using AIMD calculations, based on the specific reaction parameter (SRP) approach. Their results were able to reproduce several experiments within chemical accuracy at large collision energies.

Finally, to treat the mode selective behavior, the Guo group proposed the Sudden Vector Projection (SVP) model, in which the efficacy of a vibrational mode for promoting reaction is approximately proportional to the overlap between the corresponding vibrational wave function of the reactant and the wave function at the TS.\textsuperscript{23,77}

While these classical methods can give accurate results at high collision energies, the results are problematic at energies below the activation barriers, where most state-resolved experiments are performed, because they cannot treat quantum effects correctly. In our study, we used a quantum model based on the RPH, which treats all 15 degrees of freedom of the methane molecule and includes the effects of lattice motion.

1.4 Outline

In this thesis, we focus on the dissociative chemisorption of methane and its partially deuterated isotopologues on metal surfaces. In Chapter 2, we describe our theoretical models and computational details, including the quantum approach used to compute the single-site rigid-lattice reaction probability, as well as the sudden models to include lattice motion effects, correct the rotational treatment, and average over impact sites. In Chapter 3, we examine the dissociation of CH\textsubscript{4}, CH\textsubscript{2}D\textsubscript{2} and CHD\textsubscript{3} on Ni(111). Mode specificity and bond selectivity observed in this reaction is explained in terms of symmetry, mode softening and the nonadiabatic couplings. We also investigate mode specificity observed for the C-H stretch overtone and combination states of different symmetry. In Chapter 4, we investigate CH\textsubscript{4} dissociation on Pt(111). The results are compared with those on
Ni(111). We also compare the vibrational efficacies for the bending and stretch states. Surface temperature effects are discussed in this chapter. In addition, we compare the results computed using the SRP and PBE functionals. The dissociation of CH$_4$ on the stepped Pt(211) and Ni(211) surfaces is examined in Chapter 5. In this chapter, we first locate the MEPs on these stepped surfaces, and then perform scattering calculations to study the effects of defect sites.
1.5 References

(16) Hundt, P. M.; Ueta, H.; van Reijzen, M. E.; Jiang, B.; Guo, H.; Beck, R. D. J.


115 (26), 13027–13034.


(32) Bengaard, H. S.; Nørskov, J. K.; Sehested, J.; Clausen, B. S.; Nielsen, L. P.; 


(36) Kolasinski, K. W. In Surface Science: Foundations of Catalysis and Nanoscience; 
John Wiley & Sons, 2008; p 128.


(43) Beck, R. D.; Utz, A. L. In Dynamics of Gas-Surface Interactions Atomic-level 
Understanding of Scattering Processes at Surfaces; Dâiez Muiâno, R., Busnengo, 


(76) Nattino, F.; Migliorini, D.; Kroes, G. J.; Dombrowski, E.; High, E. A.; Killelea, D.

CHAPTER 2
THEORIES AND METHODS

2.1 Introduction

In our study, a quantum mechanical approach based on the reaction path Hamiltonian (RPH)\textsuperscript{1,2} is used to simulate reactive scattering processes, and compute the state-resolved sticking probability $S_0(E_i, \nu, T_s)$ for molecules with an incident translational energy $E_i$ and a vibrational state $\nu$ at a surface temperature $T_s$. This model has been used to examine methane dissociation on Ni(100)\textsuperscript{3,4}, Ni(111)\textsuperscript{4–7} and Pt(110)-(1 × 2)\textsuperscript{5,8} surfaces, and successfully explained the effects of incident translational energy and vibrational excitation and the variation in $S_0$ with surface temperature.

Our approach has some unique advantages. First, we treat all 15 degrees of freedom of the methane molecule. This allows us to explore behaviors like bond selectivity and mode specificity of the molecular vibrational modes. Second, with this quantum mechanical approach, we can treat quantum effects rigorously, e.g., the large amount of vibrational zero point energy (ZPE) and the tunneling effects. In addition, in our method, the molecular wave function is expanded in vibrationally adiabatic eigenstates, which allows us to observe the evolution of each vibrational mode as the molecule moves along the reaction path. To compare directly with molecular beam experimental data, we also consider the effects of lattice motion, average results over different impact sites and correct the rotational treatment, if necessary.

In this chapter, we first describe the quantum approach for computing the rigid-lattice reaction probability for a single impact site, $P_0$. Then, we present methods to average $P_0$ over impact sites, correct the rotational treatment, and include the lattice motion effects.
2.2 Computational Model and Electronic Structure Calculations

We perform total energy calculations and frequency calculations using the Density Functional Theory (DFT)-based Vienna *ab initio* simulation package (VASP), developed at the Institut für Materialphysik of the Universität Wien.\(^9\)–\(^13\) This package uses a plane wave basis set. Our calculations are adequately converged for the plane wave expansion truncated at 400 eV for total energy calculations and 600 eV for frequency calculations. The interactions between the ionic cores and the electrons are described by fully nonlocal optimized projector augmented-wave (PAW) potentials\(^9,14\), and exchange-correlation effects are treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional\(^15,16\), unless otherwise specified. However, the calculations for dissociative chemisorption of methane with the PBE functional generally achieve only semiquantitative agreement with experiments.\(^3,6,17\) The reactivity computed for the vibrationally adiabatic ground state is usually overestimated at all energies compared with that measured in molecular beam experiments, while the vibrational efficacy for the C-H stretch mode is underestimated. An explanation for this is that the PBE functional tends to overbind and underestimate the dissociating bond length at the transition state (TS).\(^18,19\) Furthermore, the PBE functional ignores the van der Waals interaction, which affects the molecule in the entrance channel. To achieve more quantitative agreement with experiments, we use the specific reaction parameter (SRP) functional, developed by the Kroes group\(^18\)–\(^20\), for some systems. A more detailed discussion on the SRP functional can be found in Section 4.5.

In this study, an asymmetric slab supercell with periodic boundary conditions is used to represent the metal as a series of infinite slabs, with a large vacuum space between the
slabs. An example of a 3×3 four-layer supercell is shown in Figure 2.1. The Brillouin zone is sampled by an 8×8×1 Γ-centered grid of k points. The convergence with respect to the number of k points can be found in earlier studies.\textsuperscript{21,22} The bare surface structure is obtained by truncating the bulk structure of a perfect crystal, and relaxing the two topmost metal layers, with the remaining layers fixed at their bulk positions. For most metal surfaces, the outermost surface layer experiences inward relaxation.

![Figure 2.1](image.png)

**Figure 2.1** Schematic representation of a 3×3 four-layer supercell.

### 2.3 Reaction Path Hamiltonian (RPH) Model

The Hamiltonian for methane on a rigid metal surface can be written,

\[
H = K + V = -\frac{\hbar^2}{2} \sum_{i=1}^{15} \frac{\partial^2}{\partial x_i^2} + V(x_1, x_2, ..., x_{15}),
\]

(2.1)

where the \( x = \{x_i\}, i = 1, 2, ..., 15 \) are the mass-weighted Cartesian coordinates of the methane nuclei, \( K \) describes the kinetic energy and \( V \) is the potential energy operator. Generally, an accurate potential energy surface (PES) is needed to perform dynamical (scattering) calculations. For the dissociative sticking of methane, a 15-dimensional PES
is needed to describe different motions of the molecule. In practice, developing such PESs is computationally expensive even on a rigid metal surface. Some earlier dynamical studies used pseudo-diatomic or low-dimensional models to treat the molecule.\textsuperscript{5,8,21–35} However, these dynamical models were not able to treat all nine vibrational modes and bond selectivity. Recently, high-dimensional classical models have been used for polyatomic reaction dynamics. Quasi-classical trajectory (QCT) methods have provided accurate results at high collision energies and surface temperatures,\textsuperscript{36–38} but are incapable of treating quantum effects and can be problematic at lower energies. The DFT-based ab initio molecular dynamics (AIMD) approach\textsuperscript{17–19}, in which the potential energy is calculated on the fly, has similar limitations.

The RPH approach\textsuperscript{1,2} has been used in several dynamical studies before.\textsuperscript{39–44} Jackson and coworkers have applied it in fully quantum mechanical scattering calculations.\textsuperscript{3–8} In this method, the PES is constructed near the minimum energy path (MEP) with a harmonic approximation for molecular degrees of freedom perpendicular to motion along the reaction path. Under most experimental conditions, where collision energies are near or below the rigid-lattice barrier height, this approximation is reasonable, as the reaction is only possible along or close to the MEPs and over lattice atoms that are puckered out of the surface plane.

To construct our PES, we first locate the reaction path or the MEP, which can be described as the union of steepest descent paths from the saddle point to the reactant and product states. First, we perform total energy calculations to locate two local minima on the PES, i.e., the reactant state (molecularly physisorbed state) and the product state (dissociative chemisorbed state), with the lattice atoms fixed at their bare relaxed surface
positions. There can be different product configurations on the PES, and the TS and the MEP can depend on the choice of the product state. In our study, we compute the MEPs for different product states. The TS between the reactant and product states is searched with the climbing image-nudged elastic band (CI-NEB) method, and dozens of other points are interpolated along the MEP with the nudged elastic band (NEB) method. Both the CI-NEB and the NEB are chain-of-states methods, in which a string of images represents the reaction path and is relaxed to the MEP via a force projection scheme.

The distance along the MEP is given by the reaction coordinate, \( s \), where \( (ds)^2 = \sum_{i=1}^{15} (da_i(s))^2 \), and \( s = 0 \) at the TS. The \( \alpha(s) = \{a_i(s)\}, i = 1, 2, ..., 15 \) describe the configuration of the molecule on the MEP at a point \( s \), in terms of the mass-weighted Cartesian coordinates. At several points along \( s \), we compute the total energy, \( V_0(s) \), relative the energy of the molecule and the bare relaxed surface at infinite separation. The total energy calculations are considered converged when all forces are smaller than 0.005 eV/Å, unless otherwise specified.

At these points, we also compute the Hessian matrix, \( \bar{K} \), the matrix of the second derivatives of the potential energy with respect to the atomic positions, via a finite difference approach with atomic displacements of 0.015 Å. To compute the Hessian, a very accurate evaluation of the forces is necessary, requiring increased convergence conditions for the electronic energies and an additional support grid in VASP. The potential energy for any general point \( x \) near the \( \alpha(s) \) can be written

\[
V(x) = V_0(s) + \sum_{i=1}^{15} \frac{\partial V(x)}{\partial x_i} |_{x=\alpha}(x_i - a_i) + \frac{1}{2} \sum_{i=1}^{15} \frac{\partial^2 V(x)}{\partial x_i \partial x_j} |_{x=\alpha}(x_i - a_i)(x_j - a_j) + \cdots
\]

(2.2)
where \( V_0(s) = V(a) \) is the potential energy for the configuration \( a \) at \( s \), and \( K_{i,j} = \frac{\partial^2 V(x)}{\partial x_i \partial x_j} \) are the elements of the Hessian matrix. Note that the linear term in Eq. 2.2 is nonzero except for the local minima and the saddle points. To get rid of this term, we define 14 normal vibrational coordinates \( \{ Q_k(s) \} \), \( k = 1, 2, \ldots, 14 \), describing displacements orthogonal to the reaction path at a point \( s \), by diagonalizing the force-projected Hessian \( \overline{K}^p(s) \), ¹

\[
\overline{K}^p(s) = (1 - \overline{P}(s)) \cdot \overline{K}(s) \cdot (1 - \overline{P}(s))
\]

where the projector \( \overline{P}(s) \) is a 15×15 matrix, whose elements are

\[
P_{i,j}(s) = L_{i,15}(s)L_{j,15}(s)
\]

and the \( \{ L_{i,15} \} \) is the normalized gradient vector, describing motion along the reaction path. It can be computed from the first derivative of the reaction path \( a(s) \) with respect to \( s \), \( \frac{da(s)}{ds} \), the direction along the reaction path.

The diagonalization of \( \overline{K}^p \) gives 14 normal mode eigenvectors \( \{ L_{i,k} \}, k = 1, 2, \ldots, 14 \), with nonzero eigenvalues \( \{ \omega_k^2(s) \} \), which provide the frequencies \( \omega_k(s) \) for motion orthogonal to the reaction path. It also has one zero eigenvalue corresponding to motion along the reaction path. We write our PES in the reaction path coordinates \( s \) and \( \{ Q_k(s) \} \), within the harmonic approximation for motion orthogonal to the reaction path, as

\[
V = V_0(s) + \frac{1}{2} \sum_{k=1}^{14} \omega_k^2(s)Q_k^2(s)
\]

The transformation between the mass-weighted Cartesian coordinates \( x_i \) and our reaction path coordinates is defined by

\[
x_i(s) = a_i(s) + \sum_{k=1}^{14} L_{i,k}(s)Q_k(s)
\]
Given the transformation in Eq. 2.6 and assuming that the PES is harmonic about the MEP, the classical RPH in the reaction path coordinates has the form\(^1\)

\[
H = H_{vib} + V_0(s) + \frac{1}{2} \left( p_s - \pi_s \right)^2 \left( 1 + b_{ss} \right)^2
\]  
(2.7)

where

\[
H_{vib} = \frac{1}{2} \sum_{k=1}^{14} p_k^2(s) + \frac{1}{2} \sum_{k=1}^{14} \omega_k^2(s) Q_k^2(s)
\]  
(2.8)

\[
\pi_s = \sum_{k=1}^{14} \sum_{j=1}^{14} Q_k(s) P_j(s) B_{k,j}(s)
\]  
(2.9)

and

\[
b_{ss} = \sum_{j=1}^{14} Q_k(s) B_{k,15}(s)
\]  
(2.10)

The momenta conjugate to \(\{Q_k\}\) and \(s\) are \(\{P_k\}\) and \(p_s\), respectively. The vibrationally nonadiabatic couplings are given by

\[
B_{k,j}(s) = \sum_{i=1}^{15} \frac{dL_{i,k}(s)}{ds} L_{i,j}(s)
\]  
(2.11)

Assuming \(\vec{L}_k(s) = \{L_{i,k}(s)\}\) is the \(k\)th normal mode eigenvector at a point \(s\), as \(\vec{L}_k(s)\) and \(\vec{L}_j(s)\) vary with \(s\) during methane dissociation due to interactions with the metal, \(\vec{L}_k(s + \Delta s)\) is not in general orthogonal to \(\vec{L}_j(s)\), where \(\Delta s\) is a small distance along the reaction path. \(\vec{L}_k(s + \Delta s) \cdot \vec{L}_j(s)\) is the projection of \(\vec{L}_k(s + \Delta s)\) onto the mode \(\vec{L}_j(s)\), describing the “similarity” between \(\vec{L}_k\) at the point \(s + \Delta s\) and \(\vec{L}_j\) at the point \(s\). Given the orthonormal condition of \(\vec{L}_k(s)\) and \(\vec{L}_j(s)\), we have
Thus, a large value of $B_{k,j}(s)$ indicates that the mode $\tilde{L}_k$ at $s + \Delta s$ resembles the mode $\tilde{L}_j$ at $s$, and vice versa. In other words, the two modes $\tilde{L}_k$ and $\tilde{L}_j$ are more likely to exchange character, and the energy is more likely to flow between these two modes.

The operator $\pi_s$ in Eq. 2.7 and 2.9 describes energy flow between different vibrational modes induced by motion along the reaction path, through the so-called Coriolis couplings, $B_{k,j}(s)$. The operator $b_{ss}$ in Eq. 2.7 and 2.10 describes energy flow between motion along the reaction coordinate and the other 14 vibrational modes, due to the curvature. Note that the nonadiabatic coupling $B_{k,j}$ is only nonzero between two modes of the same symmetry.

Based on Eq. 2.7, we change the RPH to the quantum mechanical form and expand it to the first order in the $\pi_s$ and $b_{ss}$ operators:

$$H = H_{vib} + V_0(s) + \frac{1}{2} p_s^2 - \frac{1}{4} (b_{ss} p_s^2 + 2 p_s b_{ss} p_s + p_s^2 b_{ss}) - \frac{1}{2} (p_s \pi_s + \pi_s p_s)$$

(2.13)

where $H_{vib}$, $\pi_s$, $b_{ss}$ and $B_{k,j}(s)$ are given by Eq. 2.8, 2.9, 2.10 and 2.11, respectively. According to earlier studies, the terms that are higher order in $\pi_s$ and $b_{ss}$, describing transitions to multiquanta excited states, are negligible.

2.4 Close Coupled Wave Packet Approach

A closed-coupled wave packet approach is used to describe the total molecular wave function. In this approach, the molecular wave function is an expansion in vibrationally adiabatic eigenstates,
\[ \Psi(t) = \sum_n \chi_n(s; t) \Phi_n([Q_k]; s) \]  

(2.14)

where the \( \Phi_n([Q_k]; s) \) are eigenfunctions of \( H_{vlb} \), and the \( n \) is a set of the quantum numbers \( \{n_k\} \) defining a given vibrational state. These vibrationally adiabatic eigenfunctions \( \Phi_n \), with eigenvalues \( \Sigma_k \hbar \omega_k(s)(\frac{1}{2} + n_k) \), are products of one-dimensional harmonic oscillator eigenfunctions that depend parametrically on \( s \). Theoretically, we should sum over an infinite set of eigenfunctions. In practice, our basis is limited to the vibrationally adiabatic ground, single-quantum and two-quantum states. In earlier studies\(^3,5\)\(^-\)\(^8\), only the nine asymptotically bound modes, corresponding to molecular vibrations when the molecule is far from the surface, are treated in the basis set. The other five modes are unbound asymptotically in the reactant channel and become hindered types of motion when the molecule is closer to the surface. In this thesis, we also include the two asymptotically unbound modes with the highest frequencies in the curve crossing region. The frequencies for the remaining three modes are close to zero along the reaction path. Thus, the PES can be treated as flat along these coordinates.

Given the RPH of Eq. 2.13 and the molecular wave function of Eq. 2.14, the time-dependent Schrödinger equation leads to the following coupled equations of motion for the wave packets in the state \( n, \chi_n(s; t), \)

\[ i\hbar \dot{\chi}_0(s; t) = \left( \frac{1}{2} p_s^2 + V_{\text{eff},0} \right) \chi_0(s; t) + \sum_k F_k \chi_k(s; t) \]  

(2.15)
\[ i\hbar \dot{\chi}_q(s; t) \]
\[ = \left( \frac{1}{2} p_s^2 + V_{\text{eff},q} \right) \chi_q(s; t) + F_q \chi_0(s; t) + \sum_{k<q} F_k \chi_{k,q}(s; t) + \sum_{k>q} F_k \chi_{q,k}(s; t) \]
\[ + \sqrt{2} F_q \chi_{q,q}(s; t) + \sum_k G_{q,k} \chi_k(s; t) \]  
(2.16)

\[ i\hbar \dot{\chi}_{k,q}(s; t) \]
\[ = \left( \frac{1}{2} p_s^2 + V_{\text{eff},k,q} \right) \chi_{k,q}(s; t) + F_q \chi_k(s; t) + F_k \chi_q(s; t) + \sqrt{2} G_{k,q} \chi_{k,k}(s; t) \]
\[ + \sqrt{2} G_{k,q} \chi_{q,q}(s; t) + \sum_{l<k} G_{q,l} \chi_{l,k}(s; t) + \sum_{l>k} G_{q,l} \chi_{k,l}(s; t) + \sum_{l<q} G_{k,l} \chi_{l,q}(s; t) \]
\[ + \sum_{l>q} G_{k,l} \chi_{q,l}(s; t) \]
(2.17)

\[ i\hbar \dot{\chi}_{q,q}(s; t) \]
\[ = \left( \frac{1}{2} p_s^2 + V_{\text{eff},q,q} \right) \chi_{q,q}(s; t) + \sqrt{2} F_q \chi_q(s; t) + \sum_{k<q} \sqrt{2} G_{q,k} \chi_{k,q}(s; t) \]
\[ + \sum_{k>q} \sqrt{2} G_{q,k} \chi_{q,k}(s; t) \]
(2.18)

where
\[ V_{\text{eff},n}(s) = V_0(s) + \sum_{k=1}^{14} \hbar \omega_k(s) \left( \frac{1}{2} + n_k \right) \]  
(2.19)

\[ F_k = \frac{\hbar^2}{4} \left( f_k \frac{d}{ds} + 2 \frac{d}{ds} f_k \frac{d}{ds} + \frac{d^2}{ds^2} f_k \right), f_k = \sqrt{\frac{\hbar}{2\omega_k}} B_{k,15}(s) \]  
(2.20)
The subscript $n = 0$ labels the vibrationally adiabatic ground state, the subscript $n = q$ denotes the excited state with a single quantum of vibrational energy in mode $q$, and $n = q, k$ denotes the two-quanta excited state with vibrational excitations in mode $q$ and mode $k$. The coupling function $f_k$ couples two states differing by one quantum of vibrational energy, i.e., the single-quantum states to the ground state, or the two-quantum states to the single-quantum states. The function $g_{q,k}$ links states with the same number of vibrational excitations but in different modes. The parametric dependence of the $\Phi_n$ on $s$ gives rise to derivative terms of the nonadiabatic couplings with respect to $s$. Thus, the curve crossing, i.e., the transition between vibrationally adiabatic states, becomes increasingly likely at higher velocities and for larger values of the coupling functions.

For a given initial state $n_i$, the wave packets evolve on the vibrationally adiabatic PESs, and transition to other channels via the nonadiabatic couplings. The PESs and the coupling functions are fitted to a regular grid of 512 points, and the wave packets are discretized on the same grid. Initially, only the wave packet corresponding to the initial state $n_i$ is nonzero, and is of Gaussian form, centered far above the surface where the PES is flat and the couplings are zero.

We use the second order difference scheme to propagate the wave packet in time:

$$
\chi_n(s; t + \Delta t) = \chi_n(s; t - \Delta t) + 2\Delta t \dot{\chi}_n(s; t) + O(\Delta t^3)
$$

(2.22)

where the time derivatives $\dot{\chi}_n(s; t)$ are computed using Eq. 2.15 – 2.21. To evaluate the effects of the kinetic and potential operators on the $\chi_n$, the fast Fourier transform (FFT) approach\textsuperscript{48,49} is used, in which the wave packets are transformed back and forth between
the Finite Basis Representation (FBR) and the Discrete Variable Representation (DVR) via
the FFT. In the FBR, the effect of the kinetic energy and momentum operators on the $\chi_n$ is
evaluated, while the potential energy is computed at the DVR (grid) points within the DVR.
We use a small time step of 0.01 fs to ensure that the total energy is conserved for each
step. After 50 fs of propagation, two optical potentials, located at the grid edges, are turned
on. These potentials absorb the wave packets to prevent them from reaching the grid edges.
We propagate the wave packets until the total probability on the grid is less than $10^{-6}$. The
reactive flux at large positive $s$ is then Fourier transformed in time to give the vibrational-
state-resolved and energy-resolved reaction probability for different incident energies
$E_i$. The resulting probability is the rigid-lattice single-site reaction probability,
P_0(E_i, n_i), with rotational motion treated adiabatically.

2.5 Sticking Probability

To compute the sticking probability, $S_0$, we average $P_0$ over different impact sites and
reaction pathways, include the effects of lattice motion, and correct the treatment for
rotational motion.

In our wave packet calculations discussed above, the asymptotically unbound modes,
describing translation parallel to the surface and rotation of the molecule, do not strongly
couple to other modes, and follow the MEP in the entrance channel. Our calculated $P_0$ is
thus the minimum-barrier-site reaction probability with the molecular rotation treated
adiabatically. For most experiments, collision energies are near or below the dissociation
barrier for a rigid surface. At these energies, reaction is only possible for impact sites close
to the minimum-barrier sites, and over the lattice atoms that are puckered out of the surface.
The puckering of lattice atoms can significantly lower the barrier height. To compare
directly with experimental data, we include these lattice motion effects and the contributions to $S_0$ from impact sites near the minimum-barrier sites.

### 2.5.1 Averaging over Impact Sites and Reaction Pathways

We first average the single-site reaction probability $P_0$ over different impact sites. Note that if there are multiple MEPs, we break the surface unit cell into different regions, and average $P_0$ over all impact sites within the regions corresponding to different reaction paths. According to our DFT calculations, the molecular center of mass, described by the X and Y coordinates, is roughly over the minimum barrier site from the entrance channel up to the TS along the MEP. Given the relatively large molecular mass, the large collision energies, and the normal incident conditions, motion along X and Y is slow on collision time scales. We thus assume that there is no steering of the molecule along X and Y, and use a sudden model with an “energy-shifting” approximation to estimate the reaction probability for impact sites away from the minimum barrier sites,

$$P_0(E_i, \mathbf{n}_i; X, Y) \approx P_0(E_i - \Delta V(X, Y), \mathbf{n}_i; X = X_{\text{MEP}}, Y = Y_{\text{MEP}})$$  \hspace{1cm} (2.23)

where $\Delta V(X, Y)$ is the increase in barrier height at an impact site $(X, Y)$ relative to the minimum barrier site $(X_{\text{MEP}}, Y_{\text{MEP}})$. On a flat surface, we compute $\Delta V$ by translating the molecule and re-computing the total energy at the TS, or from the normal mode eigenvectors and corresponding frequencies at the TS. Let $\{r_i(s)\}, i = 1, 2, ..., 15$ be the Cartesian coordinates of the molecule at a point $s$, and $m_i$ be the atomic mass corresponding to the $i$th coordinate. From Eq. 2.6, we can write,

$$\sqrt{m_i r_i} - a_i = x_i - a_i = \sum_{q=1}^{14} L_{i,q} Q_q$$  \hspace{1cm} (2.24)
We then multiply Eq. 2.24 by \( L_{i,k} \) and sum over \( i \). Given the orthonormal condition of \( \bar{L}_k \) and \( \bar{L}_q \), i.e. \( \sum_{i=1}^{15} L_{i,k} L_{i,q} = 1 \) for \( k = q \) and 0 otherwise, we have

\[
\sum_{i=1}^{15} \left( \sqrt{m_i r_i} - a_i \right) L_{i,k} = \sum_{i=1}^{15} \left( \sum_{q=1}^{14} L_{i,q} Q_q \right) L_{i,k} = \sum_{q=1}^{14} \left( \sum_{i=1}^{15} L_{i,q} L_{i,k} \right) Q_q = Q_k \tag{2.25}
\]

If the molecule is translated along \( X \) by a small displacement \( \Delta X \) at the TS, then \( r_i - \frac{a_i}{\sqrt{m_i}} = \Delta X \) for \( i = 1, 4, 7, 10, 13 \), i.e. the \( x \) Cartesian component for each atom, and \( r_i - \frac{a_i}{\sqrt{m_i}} = 0 \) otherwise. The corresponding \( Q_k \) becomes

\[
Q_k = \sum_{i=1,4,7,10,13} \left( \sqrt{m_i r_i} - a_i \right) L_{i,k} = \sum_{i=1,4,7,10,13} \sqrt{m_i} L_{i,k} \Delta X \tag{2.26}
\]

Thus, the increase in barrier height, \( \Delta V \), is computed by replacing \( Q_k \) in Eq. 2.5,

\[
\Delta V(X, 0) = \frac{1}{2} \sum_{k=1}^{14} \omega_k^2 Q_k^2 = \frac{1}{2} \sum_{k=1}^{14} \left( \sum_{i=1,4,7,10,13} \sqrt{m_i} L_{i,k} \right)^2 \Delta X^2 \omega_k^2 = \frac{1}{2} M \Omega_X^2 \Delta X^2 \tag{2.27}
\]

Similarly, if the molecule is translated along \( Y \) by \( \Delta Y \), \( \Delta V \) is computed by

\[
\Delta V(Y, 0) = \frac{1}{2} \sum_{k=1}^{14} \omega_k^2 Q_k^2 = \frac{1}{2} \sum_{k=1}^{14} \left( \sum_{i=2,5,8,11,14} \sqrt{m_i} L_{i,k} \right)^2 \Delta Y^2 \omega_k^2 = \frac{1}{2} M \Omega_Y^2 \Delta Y^2 \tag{2.28}
\]

where \( M \) is the molecular mass, and \( \Omega_X \) and \( \Omega_Y \) are the frequencies corresponding to motion along \( X \) and \( Y \), respectively. Given Eq. 2.27 and 2.28, the total \( \Delta V \) at \( (X,Y) \) can be estimated by

\[
\Delta V(X, Y) = \frac{1}{2} M \Omega_X^2 \Delta X^2 + \frac{1}{2} M \Omega_Y^2 \Delta Y^2 \tag{2.29}
\]

This method should work well for small displacements away from the MEP. For impact sites far from the minimum barrier site, their contributions to the total sticking are very small at the energies of interest. This sudden treatment of \( X \) and \( Y \) is confirmed by
recent AIMD studies. The calculations on a stepped surface are more complicated, and will be discussed in Chapter 5.

On (111) surfaces, we estimate $P_0$ for impact sites on a regular grid within a hexagon unit region shown in Figure 2.2, and average over impact sites in this unit region.

![Figure 2.2 Unit region for averaging over impact sites on (111) surfaces. The metal bond length is $a$.](image)

### 2.5.2 Rotational Treatment

Three of the asymptotically unbound modes correspond to the rotation of the molecule. In our $P_0$ calculations, rotational motion is initially in the ground state, and follows the MEP in the entrance channel. As noted, the rotation of the non-reacting methyl group has a frequency close to zero along the reaction path. Our PES is thus treated as flat along this coordinate. On (111) surfaces, the six lowest energy TSs with different azimuthal orientation of the dissociating bond (described by the $\phi$ angle) have similar barrier heights. As there is little variation in the PES with respect to $\phi$, we treat the PES as flat in this angle. On stepped surfaces, the barrier height varies a lot for reaction paths with
different values of $\phi$. We divide this angle into sub-regions corresponding to different reaction paths, and average over all regions.

The polar orientation of the dissociating bond relative to the surface normal, $\theta$, is also treated adiabatically in the calculations for $P_0$. Given the relatively small moment of inertia, this adiabatic treatment is reasonable at lower incident energies. However, recent AIMD studies suggest that at higher energies the rotational dynamics are closer to sudden than adiabatic, as the reaction time is too short for there to be sufficient rotational steering.\(^7,\)\(^17\) We use a similar method to estimate $S_0$ in the sudden limit to our treatment of $X$ and $Y$. The increase in barrier height $\Delta V$ for small angles away from the MEP is estimated by rotating the molecule at the TS and computing the total energy. We take the rotationally adiabatic limit at lower incident energies, and the sudden limit at higher incident energies, or in most cases, define our $S_0$ as an average of these two limiting cases,

$$S_0(E_i) = [1 - f(E_i)]S_{0,ad}(E_i) + f(E_i)S_{0,sud}(E_i)$$  \(2.30\)

where

$$f(E_i) = [1 + e^{-\alpha(E_i-E_0)}]^{-1}$$  \(2.31\)

$E_0$ is the midpoint between these two limits in the switching function $f(E_i)$, and the parameter $\alpha$ is chosen so that the final $S_0$ has 90% adiabatic behavior at some incident energy $E_{i,ad}$ and 90% sudden behavior at $E_{i,sud}$. $E_{i,ad}$ and $E_{i,sud}$ are determined for different systems.

2.5.3 Effects of Lattice Motion

Finally, our methods include the effects of lattice motion, which can lead to a large variation in $S_0$ with the surface temperature $T_s$. DFT studies have shown that if the lattice
is allowed to relax at the TS, the metal atom over which the methane dissociates puckers out of the surface plane by tenths of an Å.\textsuperscript{31,34,52–54} That is, the dissociation barrier height varies with the vibration of this lattice atom. We define $Q$ as the displacement of this lattice atom perpendicular to the surface plane, with $Q = 0$ at the bare surface equilibrium position and $Q > 0$ away from the bulk.

![Figure 2.3](image)

**Figure 2.3** Total energy along the MEPs for dissociative chemisorption of methane on Ni(111) for three values of $Q$, the displacement of the lattice atom perpendicular to the surface plane.\textsuperscript{55} The curves are shifted along $s$ so that the three corresponding initial states, with the same distance of the carbon atom above the surface, have the same value of $s$.

In Figure 2.3, we plot the MEPs on Ni(111) for three fixed values of $Q$. The curves are shifted along $s$ so that the three corresponding initial states, with the same distance of the carbon atom above the surface, have the same value of $s$. This figure shows the effects of lattice motion on the PES. The vibration of the lattice atom can change both the height
of the barrier to dissociation by an amount of $-\beta Q$ and the location of the TS along $Z$, the distance of the carbon atom above the surface, by an amount of $\alpha Q$. We find that the changes in barrier height and TS location are linear in $Q$ for $Q \leq 0.2 \text{ Å}$. In Table 2.1, we list the values of $\alpha$ and $\beta$ for the dissociation of methane on several surfaces.

**Table 2.1** The molecule-lattice coupling constants $\alpha$ and $\beta$ for the dissociative chemisorption of methane on different surfaces. $\alpha$ and $\beta$ are defined by $\Delta Z^\pm_C(Q) = \alpha Q$, and $\Delta E_b(Q) = -\beta Q$, where $\Delta Z^\pm_C(Q)$ is the change in the height of the carbon atom above the surface at the TS, and $\Delta E_b(Q)$ is the change in the barrier height, as the lattice atom over which the methane dissociates is displaced by $Q$.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\alpha$</th>
<th>$\beta$ (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>0.749</td>
<td>1.099</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>0.830</td>
<td>0.952</td>
</tr>
<tr>
<td>Ni(211)</td>
<td>0.811 (P), 0.880 (Q)</td>
<td>0.621 (P), 0.833 (Q)</td>
</tr>
<tr>
<td>Pt(211)</td>
<td>0.838 (L), 0.899 (N)</td>
<td>1.241 (L), 0.998 (N)</td>
</tr>
</tbody>
</table>

Given the large mass of the metal atoms, the lattice atoms move little on collision time scales, and thus sudden models can be used to treat the effects of lattice motion.\textsuperscript{5,30,33} For the $\beta$-type coupling, we use the “energy-shifting” approximation to estimate the reaction probability on a rigid lattice where the lattice atom over which the methane dissociates is displaced by $Q$, by assuming the same shape of the PES for different values of $Q$,

$$P_0(E_i, \mathbf{n}_i; Q) \approx P_0(E_i + \beta Q, \mathbf{n}_i; Q = 0) \quad (2.32)$$

The value of $\beta$ can be estimated from the force on the lattice atom in the rigid-lattice TS calculations for $Q = 0$. Or more accurately, we can re-locate the rigid-lattice TSs with the
lattice atom displaced by several values of $Q$, and fit $\beta$ to the barrier heights. Then we use the following equation to average $P_0$ over $Q$,

$$S_0(E_i, n_i; T_s) = \int P_{\text{lat}}(Q; T_s) P_0(E_i, n_i; Q) dQ$$  \hspace{1cm} (2.33)

$P_{\text{lat}}(Q; T_s)$ is the probability that a surface atom is displaced by $Q$. We use an Einstein model or a Debye model, with surface Debye temperatures $\theta_D$ extracted from experiments, to compute $P_{\text{lat}}(Q; T_s)$. In the Einstein model, only the vibration of the single lattice atom over which the methane dissociates is considered, and the probability $P_{\text{lat}}(Q; T_s)$ is given by

$$P_{\text{lat}}(Q; T_s) = \frac{1}{\int e^{-V_M(Q')/k_B T_s} dQ'} e^{-V_M(Q)/k_B T_s}$$  \hspace{1cm} (2.34)

where $V_M(Q)$ is the Morse potential fitted to DFT calculations. In the more realistic Debye model, the lattice vibration is described by harmonic normal modes, and the probability $P_{\text{lat}}(Q; T_s)$ is written as

$$P_{\text{lat}}(Q; T_s) = \frac{1}{\int e^{-Q^2/2Q_{rms}^2} dQ'} e^{-Q^2/2Q_{rms}^2}$$  \hspace{1cm} (2.35)

where the root-mean-square displacement, $Q_{rms}$, is given by

$$Q_{rms}^2 = \frac{3 \hbar^2}{2 M k_B} \frac{T_s^2}{\theta_D^3} \left[ \frac{\theta_D}{T_s} \int_0^1 x \left( \frac{1}{e^x - 1} + \frac{1}{2} \right) dx \right]$$  \hspace{1cm} (2.36)

The effects of the $\alpha$-type coupling are treated by a modified version of the Surface Mass Model (SMM).\textsuperscript{5,29,30,33} In this approach, we change to a relative coordinate $Z' = Z - \alpha Q$, and average over the lattice atom momentum $P = M_s \frac{dQ}{dt}$, by averaging over the relative collision energy $E_{\text{rel}}$. 

37
\[ S_0(E_i, \mathbf{n}_i; T_s) = \int \frac{M'_s}{\sqrt{4\pi k_B T_s \mu_T E_{rel}}} \exp \left[ - \frac{M'_s}{2k_B T_s} \left( \frac{2E_{rel}}{\mu_T} - \frac{2E_i}{M} \right)^2 \right] P_0(E_{rel}, \mathbf{n}_i) dE_{rel} \]

(2.37)

where \( M \) and \( M_s \) are the molecular mass and the lattice atom mass, respectively, and \( M'_s = M_s/\alpha^2 \). The reduced mass corresponding to the relative collision coordinate \( Z' \) is \( \mu_T = M'_s M / (M'_s + M) \). \( P_0(E_{rel}, \mathbf{n}_i) \) is the reaction probability for the relative collision energy \( E_{rel} \), where

\[ E_{rel} = \frac{1}{2} \mu_T \left( \frac{2E_i}{M} - \alpha \frac{P}{M_s} \right)^2 \]

(2.38)

The average over momentum \( P \) amounts to an average over the relative collision velocity.
2.6 References


044706(9).


CHAPTER 3
DISSOCIATIVE CHEMISORPTION OF METHANE AND ITS ISOTOPOLOGUES ON NI(111)

3.1 Introduction

The dissociative chemisorption of methane on nickel surfaces has received considerable scientific attention, due to its important role in the steam reforming of natural gas.1 Experiments have shown that the dissociative sticking probability on a bare surface, $S_0$, increases strongly with increasing collision energy and surface temperature.1–4 Vibrational excitation of the methane can also promote the reaction. However, this behavior is nonstatistical2,3 with both mode-specificity5–14 and bond-selectivity7,8,10,14–17.

Methane’s four vibrational modes include the triply degenerate antisymmetric stretch ($\nu_3$), the symmetric stretch ($\nu_1$), the doubly degenerate bend ($\nu_2$), and the triply degenerate bend ($\nu_4$). Experiments found that exciting some vibrational modes is more effective at promoting dissociation than excitation of other modes. For example, on Ni(100), excitation of the symmetric stretch leads to a greater enhancement in reactivity than putting the same amount of energy into the incident translational mode,18 while the antisymmetric stretch excitation is less effective than the same amount of translational energy19. This mode-specific behavior is often expressed in terms of a vibrational efficacy

$$\eta = \frac{\Delta E_i}{\Delta E_v} = \frac{E_i(gs,S_0) - E_i(\nu,S_0)}{\Delta E_v}$$  \hspace{1cm} (3.1)

where $\Delta E_i$ is the increase in collision energy necessary to give the same $S_0$ as increasing the vibrational energy by $\Delta E_v$. $E_i(\nu,S_0)$ and $E_i(gs,S_0)$ are the collision energies giving a sticking probability of $S_0$ for an initial vibrational state $\nu$ and the ground state ($gs$),
respectively. On Ni(100), the efficacies are 1.4 and 0.94 for the symmetric and antisymmetric stretches, respectively. For bending states, the $3\nu_4$ overtone and $\nu_2 + \nu_4$ combination states are found to be less effective than the stretch states on Ni(111). In addition, Hundt et al. measured the state-resolved $S_0$ of CH$_4$ prepared in all three vibrational symmetry components of the $2\nu_3$ overtone vibration as well as in the $\nu_1 + \nu_3$ combination vibration, and observed strong mode specificity between different symmetry components. To predict the promotional effect of a given vibrational state on the reactivity, Guo et al. proposed a sudden vector projection (SVP) model, in which the overlap between the vibrational mode vector of the reactant and the vector corresponding to the imaginary frequency at the TS is calculated. This model works reasonably well for single-quantum states, but cannot be applied to overtone and combination states.

In addition to mode specificity, bond-selective behavior has been observed for the dissociation of methane isotopologues. Killelea et al. reported a CD$_3$:CHD$_2$ product ratio $> 30:1$ for CHD$_3$ initially in the $\nu_1$ C-H stretch state on Ni(111). Similarly, on Pt(111) excitation of the C-H stretches of CHD$_3$, CH$_2$D$_2$, and CH$_3$D preferentially breaks a C-H bond relative to a C-D bond.

In this chapter, we use our quantum approach based on the reaction path Hamiltonian (RPH) to compute the dissociative sticking probability for methane and its isotopologues on Ni(111), and investigate the origins of mode specificity and bond selectivity.

3.2 Computational Model and Electronic Structure Calculations

We use a four-layer 3×3 supercell with periodic boundary conditions to represent the metal as a series of infinite slabs, with a vacuum space of 14.3 Å between the slabs. This supercell corresponds to a methane coverage of 1/9 ML. For all the calculations, a lattice
constant of 3.522 Å is used. The Brillouin zone is sampled by an 8×8×1 Γ-centered grid of k points. Electronic structure calculations are performed with the Vienna ab initio simulation package (VASP), with the PBE functional and fully nonlocal optimized projector augmented-wave (PAW) potentials. To account for the magnetic moment of nickel, we include spin polarization in our calculations. The two topmost metal layers are relaxed before including any adsorbate. And the lattice atoms are then fixed at their bare relaxed surface positions.

We first locate the transition state (TS) on the rigid lattice using the CI-NEB method. The energies are considered converged when all forces are smaller than 0.01 eV/Å or better. Figure 3.1 shows the TS and product state configurations. From the entrance channel to the TS, the carbon atom remains roughly over the top site. At the TS, the dissociating H atom is angled toward the surface with an angle of 133° with respect to the surface normal. The dissociating bond is 1.62 Å, and the carbon atom is 2.11 Å above the surface plane. This configuration is close to the B1 transition state configuration found by Nave et al., except that they used a smaller 2×2 supercell. The barrier height for the dissociation of CH\(_4\) on Ni(111) is 1.005 eV, relative to the energy where methane is infinitely far from the surface. Our calculated barrier height is consistent with those reported in other studies.

We note that, due to the strong preference on Ni(111) for CH\(_3\) and H binding on the hollow sites, the dissociating H atom and the methyl fragment move away from the top site after the TS.
Figure 3.1 Transition state (left panel) and product state (right panel) configurations for the dissociation of CH$_4$ on Ni(111). Only the topmost lattice layer is shown. $E_b$ and $E_p$ are the energies for the transition state and the product state, respectively, relative to the energy where methane is infinitely far above the surface.

We then locate 66 images along the minimum energy path (MEP) with the NEB method$^{39}$. In Figure 3.2, we plot the total energy, $V_0(s)$, along the MEP, as a function of the distance along the path, $s$, where $(ds)^2 = \sum_{i=1}^{15} (da_i(s))^2$, with $s = 0$ at the TS, and the $\{a_i(s)\}$ are the mass-weighted Cartesian coordinates of the molecule at a point $s$. At each of these images, we also compute and diagonalize the force-projected Hessian to find the fourteen normal vibrational coordinates $Q_k$ and corresponding frequencies $\omega_k(s)$ describing displacements orthogonal to the reaction path in the harmonic approximation.

Our potential energy surface is written in the reaction path coordinate $s$ and $\{Q_k\}$, and a close-coupled wave packet approach is used to describe the molecular wave function. A detailed description of this approach and expressions for the equations of motion can be
found in Chapter 2. For a given initial vibrational state $n_t$, standard techniques are used to evolve the wave packets in time$^{40,41}$ and energy-analyze the reactive flux.$^{42,43}$ The result is the single-site rigid-lattice reaction probability $P_0$.

![Figure 3.2 Reaction path for methane dissociation on Ni(111).](image)

**Figure 3.2** Reaction path for methane dissociation on Ni(111).

### 3.3 Mode- and Bond-Selectivity in the Dissociation of CHD$_3$ on Ni(111)

In this section, we examine the dissociative chemisorption of CHD$_3$ on Ni(111), and investigate the effects of vibrational excitation on dissociative sticking and bond cleavage. As shown in Figure 3.3, there are four possible, equally probable, orientations of CHD$_3$ at the TS. Note that, for asymmetric C-D cleavage, the two configurations (configurations 3 and 4 in Figure 3.3) have mirror symmetry with respect to a plane, and thus have the same MEP and exhibit the same behavior.
Figure 3.3 Four possible orientations of CHD$_3$ at the TS on Ni(111). Carbon, deuterium, hydrogen and nickel atoms are represented by gray, blue, white and green colors, respectively.

3.3.1 Effects of Mode Softening and Nonadiabatic Couplings

In Figure 3.4, we plot $\hbar \omega_k(s)$ along the reaction path for CH$_4$ and CHD$_3$ on Ni(111). When the molecule is far from the surface, there are nine normal modes with nonzero frequency. For CHD$_3$, they are the C-H stretch ($\nu_1$), the doubly degenerate CD$_3$ antisymmetric stretch ($\nu_4$), the CD$_3$ symmetric stretch ($\nu_2$) and the bending modes ($\nu_5$, $\nu_6$ and $\nu_3$). As the molecule approaches the surface, the interaction with the surface removes all degeneracies. The remaining five modes are asymptotically unbound, with similar frequencies for all four configurations. These modes become hindered types of motion as the molecule gets closer to the surface.
Figure 3.4 Energies of the normal modes along the reaction path for \( \text{CH}_4 \) and \( \text{CHD}_3 \) dissociation on Ni(111).

For the symmetric C-H cleavage and symmetric C-D cleavage configurations, the reaction path is symmetric with respect to reflection through a plane, perpendicular to the surface plane and including the dissociating bond. Thus, the fourteen normal modes are either symmetric (A') or antisymmetric (A'') with respect to the same plane. We label the
A’ modes 1’-8’ and the A” modes 1”-6”. The vibrationally nonadiabatic coupling is only nonzero between two modes of the same symmetry. There is no symmetry in the two asymmetric C-D cleavage configurations, and the nonadiabatic coupling is thus in general nonzero. The fourteen modes are labelled as 1-14 for asymmetric C-D cleavage.

We first consider mode softening as the molecule approaches the surface. For CH₄ far from the surface, the four equivalent C-H stretches combine to form four normal modes: one symmetric stretch (3’) and three antisymmetric stretches (1’, 2’ and 1”). As CH₄ approaches the surface, the reactive C-H bond weakens. In the local mode picture, the vibration of the reactive bond has a lower frequency, while the other three C-H stretches remain unperturbed. In the normal mode picture, the 3’ mode evolves from the symmetric stretch into a lower-frequency mode comprised primarily of the reactive bond vibration. At the same time, the three relatively unperturbed stretches combine to give three approximately degenerate nonlocal modes, which correlate adiabatically with the triply degenerate antisymmetric stretch. Thus, the vibration of the softened mode becomes localized on the reactive bond, while for the three higher-frequency modes the vibration becomes localized on the nonreacting methyl group.

We see similar behavior for CHD₃ dissociation on Ni(111). For both symmetric and asymmetric C-D cleavage, the v₂ CD₃ symmetric stretch softens, and the vibration becomes localized on the reactive C-D bond. However, the doubly degenerate v₄ CD₃ antisymmetric stretch remains relatively unperturbed, and correlates with the nonreacting CD₂ group. For C-H cleavage, the v₁ C-H stretch is already localized on the dissociating C-H bond asymptotically. This mode softens as CHD₃ approaches the TS. This behavior is
also observed in studies of the gas-phase Cl + CH₃D reaction and CH₄ dissociation on the Pt and Ni surfaces.

Mode softening lowers the activation energy. For a given initial vibrational state \( n \), the activation energy, \( E_a \), is the vibrationally adiabatic potential, \( V_{\text{eff},n}(s) \), at the TS,

\[
E_a = V_{\text{eff},n}(0) = V_0(0) + \sum_{k=1}^{14} \hbar \omega_k(0) \left( n_k + \frac{1}{2} \right)
\]

where \( V_0(0) \) and \( \sum_{k=1}^{14} \hbar \omega_k(0) \left( n_k + \frac{1}{2} \right) \) are the total energy and zero-point energy (ZPE) corrections at the TS. Table 3.1 lists \( E_a \) for the three reaction configurations of CHD₃ on Ni(111). Mode softening lowers the ground state activation energy by more than 0.1 eV relative to the barrier height. We note that the activation energy is lower for C-H cleavage than for C-D cleavage by about 0.05 eV. This is roughly the difference in vibrational energy between the C-H stretch and either of the CD₃ stretches. Thus, the C-H bond is more reactive than the C-D bond in the adiabatic limit, and we expect that the C-H:C-D cleavage ratio is larger than a statistical ratio of 1:3 for ground-state CHD₃. This is consistent with the experimental observation that the cleavage ratio is larger than 1:3 for the laser-off experiments at low nozzle temperatures, where vibrationally excited molecules in the beam contribute little to \( S_0 \).

In addition, the activation energy is lowered even further for some vibrationally excited states. First, for molecules in the \( \nu_1 \) state, the decrease in activation energy relative to the ground state is 0.1 eV larger for breaking the C-H bond than the C-D bond. This is because, for the C-H cleavage configuration, the \( \nu_1 \) stretch (1’) is localized on the breaking C-H bond, thus it softens by about 0.1 eV, as the C-H bond weakens, while for both C-D cleavage configurations, mode softening in the \( \nu_1 \) mode is minimal, as the vibration is...
localized on the nonreacting C-H bond. Thus, excitation of the $\nu_1$ C-H stretch should promote C-H cleavage relative to C-D cleavage in the adiabatic limit. On the other hand, excitation of the CD$_3$ symmetric stretch enhances both C-H cleavage and C-D cleavage, but the enhancement is larger for C-D cleavage. There is little mode softening in the CD$_3$ antisymmetric stretches to lower the activation energy for these states. In general, mode softening and the decrease in activation energy are larger for the C-H stretches than the C-D stretches, due to the isotope effect that the C-H vibrational frequencies are larger than the C-D frequencies. Second, for both C-H cleavage and C-D cleavage, the activation energy for the CD$_3$ symmetric stretch state is much lower than that for the antisymmetric stretch state, for the reasons discussed.

Table 3.1 Activation energies for CHD$_3$ dissociation on Ni(111).

<table>
<thead>
<tr>
<th>Activation energy (eV)</th>
<th>ground state</th>
<th>$\nu_1$</th>
<th>$\nu_4$</th>
<th>$\nu_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetric C-H</td>
<td>0.860</td>
<td>0.762</td>
<td>0.857, 0.838</td>
<td>0.780</td>
</tr>
<tr>
<td>symmetric C-D</td>
<td>0.907</td>
<td>0.904</td>
<td>0.907, 0.891</td>
<td>0.796</td>
</tr>
<tr>
<td>asymmetric C-D</td>
<td>0.905</td>
<td>0.904</td>
<td>0.903, 0.890</td>
<td>0.793</td>
</tr>
</tbody>
</table>

In Figure 3.5, we plot the single-site rigid-lattice reaction probability, $P_0$, as a function of the incident translational energy, $E_i$, for the C-H cleavage and symmetric C-D cleavage configurations. In the vibrationally adiabatic limit, where the nonadiabatic couplings are set to be zero, $P_0$ drops rapidly for $E_i$ below the activation energies. The reaction probability curves for the excited states are shifted to lower energies relative to that for the ground state, and the shifts are consistent with the differences in activation energy.
Figure 3.5 Single-site rigid-lattice reaction probabilities for (A) the symmetric C-H cleavage configuration and (B) the symmetric C-D cleavage configuration of CHD$_3$ dissociation on Ni(111). Results are shown for the ground state (gs) and four excited states, with several levels of nonadiabatic couplings: adiabatic (solid lines), $B_{q,15}$ only (filled circles), $B_{q,k}$ only (open circles), and full coupling (xxx).
In addition to mode softening, the nonadiabatic couplings also modify the reaction probability and result in mode- and bond-selectivity. In Figure 3.6 and 3.7, we plot the curvature coupling, $B_{q,15}$, and the so-called Coriolis coupling, $B_{q,k}$, for symmetric C-H cleavage and C-D cleavage of CHD$_3$. The $B_{q,15}$ coupling couples the single-quantum and two-quantum states to the ground and single-quantum states, respectively, while the $B_{q,k}$ coupling links two vibrational states with the same number of excited vibrations. When we add $B_{q,15}$, the vibrationally excited states are coupled to the ground state, and the asymptotical vibrational energy is converted into motion along the reaction path, which corresponds to bond breaking at the TS. As shown in Figure 3.5, the effect of adding $B_{q,15}$ is to increase reactivity at low incident energies. The $B_{q,15}$ coupling also decreases $P_0$ at high $E_i$, due to nonadiabatic transitions to excited states with more quanta of vibrational energy. Note that, for symmetric C-H cleavage and C-D cleavage, the $B_{q,15}$ couplings between the A” states and the ground state are rigorously zero.

**Figure 3.6** $B_{q,15}$ couplings for symmetric C-H cleavage (left panel) and symmetric C-D cleavage (right panel) of CHD$_3$ on Ni(111).
Figure 3.7 $B_{q,k}$ couplings for symmetric C-H cleavage (left panel) and symmetric C-D cleavage (right panel) of CHD$_3$ on Ni(111).

We find the $B_{q,k}$ coupling to be more important than the $B_{q,15}$ coupling for promoting reaction at low $E_i$. As shown in Figure 3.7, the $B_{q,k}$ coupling is largest at the avoided crossings, where the two modes exchange character. At these points, amplitude is transferred from one vibrationally adiabatic state to another of lower energy. For C-H cleavage, molecules initially in the 1' state can transition to the 2' state at $s = -1.4$ amu$^{1/2}$Å. After this point, the 1' mode changes from the C-H stretch into the CD$_3$ antisymmetric stretch, while the 2' vibration resembles the C-H stretch between $s = -1.4$ and -1.0 amu$^{1/2}$Å. The molecules can then transition to the 3' state, the 4' state, and so on, and the initial vibrational energy is converted into bond breaking at the TS. Similar behavior has been found for symmetric C-D cleavage. Molecules initially in the 3' state can transition to the 4' state at $s = -0.7$ amu$^{1/2}$Å, and then transition to the 5' state, and so on. The vibrational energy in the CD$_3$ symmetric stretch can be converted into translational motion along the
reaction path. This “cascade” mechanism can significantly increase $P_0$ at low incident energies, especially for the $\nu_1$ (1’) state in C-H cleavage and the $\nu_2$ (3’) state in symmetric C-D cleavage. Note that the A” states cannot participate in this cascading mechanism for symmetric C-H and C-D cleavage, due to zero nonadiabatic couplings to the ground and A’ states. The mechanism for asymmetric C-D cleavage is similar to that for symmetric C-D cleavage, except that more states are involved.

As discussed, the vibration of the symmetric stretch becomes localized on the reactive bond, as the molecule approaches the surface. We find that, for a molecule following the cascading pathway, this localization of energy on the reactive bond is preserved as the molecule transitions between modes at the avoided crossings. For C-H cleavage, if a molecule is initially in the $\nu_1$ (1’) state, the vibration is already localized on the reactive C-H bond. And transitions from 1’ to 2’ to 3’, etc. keep the vibrational energy localized on this reactive bond, as two modes exchange character at the avoided crossings. This will significantly enhance C-H cleavage. For C-D cleavage, if a molecule is initially in the $\nu_2$ (3’) state, as we move along the reaction path, the nonlocal CD$_3$ symmetric stretch is softened, and the vibrational energy localizes on the reactive C-D bond. Transitions at the avoided crossings keep this energy localization on the reactive bond, enhancing C-D cleavage. This is vibrationally sudden behavior.

As shown in Figure 3.5(B), for C-D cleavage, the 2’ component of the doubly degenerate CD$_3$ antisymmetric stretch state is as reactive as the CD$_3$ symmetric stretch state. This is because the 2’ and 3’ modes mix in the entrance channel, due to the interaction with the metal surface. While the $B_{2', 3'}$ coupling is small in the curve crossing region right before the TS, it has a broad peak between $s = -8$ and -2 amu$^{1/2}$Å in the entrance channel.
(shown in Figure 3.8) where couplings between other modes are very weak. Similar behavior has been observed for CH₄ dissociation: the 2’ component of the antisymmetric stretch state couples strongly to the symmetric stretch state in the entrance channel around $s = -4.5 \text{ amu}^{1/2} \text{ A}$, which gives a large vibrational efficacy for the 2’ state.

![Figure 3.8](image)

**Figure 3.8** $B_{q,k}$ couplings for symmetric C-D cleavage of CHD₃ on Ni(111) in the entrance channel.

### 3.3.2 Sticking Probability

To compute the dissociative sticking probability $S_0$, we average $P_0$ over all impact sites, correct the rotational treatment, and include the effects of lattice motion, using the methods described in Chapter 2. The barrier heights for CH₄ and CHD₃ dissociation on Ni(111) are large. Thus, under most experimental conditions, reaction is only possible along or near the minimum barrier sites, and over lattice atoms that are puckered out of the surface plane. Nave *et al.* reported six TS configurations, with similar energies, for CH₄ on
They differ with respect to the azimuthal orientation of the reactive C-H bond and the rotation of the nonreacting methyl group. Thus, we treat our PES as flat along these coordinates.

Given the relatively large molecular mass and the normal incident conditions, motion along X and Y is slow on collision time scales. We thus use the “energy-shifting” approximation to estimate \( P_0 \) at other impact sites away from the top site in the sudden limit. The increase in barrier height at a site \((X, Y)\) relative to the minimum barrier site, \( \Delta V(X, Y) \), is estimated using Eq. 2.27 and 2.28. Table 3.2 lists the computed results in terms of \( \hbar \Omega_X \) and \( \hbar \Omega_Y \), where the frequencies \( \Omega_X \) and \( \Omega_Y \) satisfy \( \Delta V(X, Y) = \frac{1}{2} M \Omega_X^2 \Delta X^2 + \frac{1}{2} M \Omega_Y^2 \Delta Y^2 \).

### Table 3.2

<table>
<thead>
<tr>
<th></th>
<th>CH(_4)/Ni(111)</th>
<th>CHD(_3)/Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hbar \Omega_X ) (eV)</td>
<td>0.0184</td>
<td>0.0169</td>
</tr>
<tr>
<td>( \hbar \Omega_Y ) (eV)</td>
<td>0.0186</td>
<td>0.0171</td>
</tr>
</tbody>
</table>

The polar orientation of the reactive bond relative to the surface normal, represented by the \( \theta \) angle, is treated adiabatically as the molecule moves along the MEP. However, the rotational dynamics might be closer to sudden at high collision energies, if the interaction time is too short for the molecule to rotate.\(^{16,48-50}\) In this study, we estimate \( S_0 \)
in the rotationally sudden limit, using a method similar to our treatment of X and Y. The parameters for estimating the increase in barrier height relative to the minimum barrier orientation, $\Delta V(\theta)$, are computed by rotating the molecule at the TS and re-computing the total energy. We find that $k_\theta = 18.898 \text{ eV}$, where $\Delta V(\theta) = 0.5k_\theta \sin^2(\theta - \theta^\dagger)$, and $\theta^\dagger = 133^\circ$ is the $\theta$ angle at the TS.

Finally, we include the effects of lattice motion. When the two topmost metal layers are allowed to relax during the optimization, the Ni atom over which the methane dissociates puckers out of the surface, normal to the surface plane. We define $Q$ as the displacement of this atom normal to the surface plane, with $Q = 0$ for the equilibrium position and $Q > 0$ for motion away from the bulk. Lattice vibration modifies the barrier height by an amount of $-\beta Q$ and the location of the TS along $Z$ by an amount of $\alpha Q$. We find $\beta = 1.099 \text{ eV/Å}$ and $\alpha = 0.749$ for CH$_4$ and its isotopologues on Ni(111).

In this study, we only consider the vibration of the lattice atom over which the methane dissociates, and describe this atom as a Morse oscillator, with the Morse potential

$$V_M = D \cdot (e^{-\alpha Q} - 1)^2$$

(3.3)

where $D = 2.829 \text{ eV}$ and $\alpha = 1.052 \text{ Å}^{-1}$ are obtained from DFT calculations. We then average $P_0$ over all displacements and momenta conjugate to $Q$, using Eq. 2.33, 2.34, 2.37 and 2.38.

Figure 3.9 and 3.10 show the dissociative sticking probability $S_0$ for three TS configurations shown in Figure 3.3 at 90 K. For the ground state, the sticking curve for C-H cleavage is shifted to lower $E_i$ by about 0.05 eV relative to that for C-D cleavage, which is consistent with the difference in activation energy, while the two C-D cleavage configurations have similar $S_0$. At high collision energies, the probabilities for C-H and C-
D cleavage become similar, if the geometry factor is not considered, as most molecules can react, following the over-the-barrier pathways.

Figure 3.9 Dissociative sticking probabilities for CHD$_3$ initially in the ground state (gs) and the 1’ excited state at 90 K. Results are shown for symmetric C-H cleavage (sym C-H cleavage), symmetric C-D cleavage (sym C-D cleavage) and asymmetric C-D cleavage (asym C-D cleavage).

As shown in Figure 3.9, excitation of the $\nu_1$ C-H stretch (1’) significantly enhances C-H cleavage, due to mode softening and nonadiabatic transitions discussed above. The vibrational efficacy for $\nu_1$ promoting C-H cleavage is 0.85 at $S_0 = 10^{-4}$. In Figure 3.10, excitation of the $\nu_2$ CD$_3$ symmetric stretch (3’) leads to a large enhancement of symmetric C-D cleavage, with a vibrational efficacy $\eta = 0.81$ at $S_0 = 10^{-4}$, similar to the efficacy for $\nu_1$ promoting C-H cleavage. The 2’ component of the CD$_3$ antisymmetric stretch state also
has a large efficacy for promoting C-D cleavage, due to the strong $B_{2',3'}$ coupling in the entrance channel. However, there is little enhancement of C-D cleavage with excitation of the 1” component at most energies, because of minimal mode softening and zero nonadiabatic coupling to any symmetric mode. We do observe some enhancement in $S_0$ at very low energies, due to nonadiabatic transitions to other lower-energy antisymmetric states.

Figure 3.10 Dissociative sticking probabilities for CHD$_3$ initially in the ground state (gs), the 2’, 3’ and 1” excited states at 90 K. Results are shown for symmetric C-H cleavage (sym C-H cleavage) and symmetric C-D cleavage (sym C-D cleavage).

We also observe surface-induced intramolecular vibrational energy redistribution (IVR) for this reaction. For example, in Figure 3.9, we see a small enhancement of C-D cleavage with excitation of the C-H stretch at low incident energies. This arises from the small nonadiabatic transition from the $\nu_1$ state to the CD$_3$ stretch states. In Figure 3.10,
excitation of either the 2’ or 3’ mode promotes C-H cleavage. This effect is stronger than
the C-H stretch promoting C-D cleavage, because the $B_{2',3'}$ and $B_{3',4'}$ couplings in the C-
H cleavage configuration are stronger than the $B_{1',2'}$ and $B_{2',3'}$ couplings for C-D
 cleavage. As shown in Figure 3.4, molecules in the 2’ or 3’ state can follow the cascading
pathways for C-H cleavage, while the 1’ state is not on the pathway for C-D cleavage. The
minor IVR effect becomes important only at very low energies, where the over-the-barrier
adiabatic pathways are not available, and the lower-energy nonadiabatic pathways
dominate the total $S_0$.

In Figure 3.11, we plot the dissociative sticking probability for C-H and C-D cleavage,
assuming that the CHD$_3$ molecules are randomly oriented: for C-H cleavage, the C-H
cleavage results in Figure 3.9 and 3.10 are divided by 4; and for C-D cleavage, the results
are averaged over the three C-D cleavage configurations. For the doubly degenerate $\nu_4$
state, $S_0$ is an average of the 2’ and 1” components. For molecules initially in the ground
state, C-H cleavage is slightly favored over C-D cleavage at low incident energies, because
of the lower activation energy for C-H cleavage. At higher energies, the C-D:C-H cleavage
ratio is close to the statistical ratio of 3:1. Excitation of the $\nu_1$ stretch leads to a significant
enhancement of C-H cleavage, and preferentially breaks the C-H bond over a C-D bond,
except at very high energies. Excitation of the $\nu_2$ and $\nu_4$ stretches promotes C-D cleavage
over C-H cleavage, and the vibrational efficacy is larger for the $\nu_2$ state than the $\nu_4$ state.
The $\nu_2$ symmetric stretch state has a large vibrational efficacy, for the reasons discussed.
For the $\nu_4$ antisymmetric stretch state, only the 2’ component is very reactive, due to the
2’ and 3’ modes mixing in the entrance channel. The increase in $S_0$ with excitation of the
1” component is negligible. After we average over two components, the CD$_3$ antisymmetric
stretch state is less reactive than the symmetric stretch state. For CH₄, the antisymmetric stretch is triply degenerate, including the reactive 2’ component, which coupled strongly to the 3’ symmetric stretch state, and the A’’ component. The third component (1’) is only weakly coupled to the 2’ or 3’ state. Thus, the antisymmetric stretch has a smaller efficacy. The same trend is observed in experiments for CH₄ dissociation on Ni(100)¹⁸,¹⁹ and for gas-phase reactions of Cl with CH₄⁵¹ and CH₃D⁴⁵. The SVP model²²,²³ also predicts a larger vibrational efficacy for the symmetric stretch over the antisymmetric stretch for methane dissociation on different metal surfaces.

Figure 3.11 Dissociative sticking probability for either C-H or C-D cleavage. Results are shown for molecules initially in the ground state (gs) or one of the vibrationally excited states.
In Figure 3.12, we plot the C-H:C-D cleavage ratio for molecules initially in the ground and three excited states. Our results are compared with recent quasi-classical trajectory (QCT) studies by Guo et al. (circles in Figure 3.12). Their calculations were based on a 12-dimensional PES, computed using the PW91 functional. For the ground state, our results suggest that C-H cleavage is slightly favored for $E_l < 0.9$ eV, while at higher energies C-D cleavage is preferred, and the cleavage ratio approaches the statistical value as $E_l$ increases. Without laser excitation, Utz et al. reported a preference for C-D cleavage, with a cleavage ratio of 1:3 at 0.83 eV. However, their experiments were performed at high nozzle temperatures from 550 to 900 K. At these high temperatures, the molecular beam contains a fraction of thermally excited molecules, and there are more molecules populated in the lower-energy CD$_3$ stretch states than the C-H stretch states. Utz et al. found that the fraction of C-H cleavage increases as the nozzle temperature drops. Our ground-state results correspond to laser-off experiments with $T_{nozzle} = 0$ K, and Utz’ results show that the C-H bond is more reactive in this limit, consistent with our calculations. However, the QCT study by Guo et al. reports a C-H:C-D cleavage ratio below 1:3 at all energies, which contrasts with the lower activation energy for C-H cleavage.

For the $\nu_1$ excited state, our calculations show 100% C-H selectivity at low energies. This is consistent with Utz’ experimental results that the C-H:C-D cleavage ratio is at least 30:1 with excitation of the $\nu_1$ stretch. Similar results were found in the QCT study. For the $\nu_2$ and $\nu_4$ states, we find that they both promote C-D cleavage relative to C-H cleavage, but this effect is larger for the $\nu_2$ symmetric stretch. The QCT study also shows C-D cleavage selectivity for two states, but the cleavage ratios are similar for $\nu_2$ and $\nu_4$. 
Figure 3.12 C-H:C-D cleavage ratio for molecules initially in the ground state (gs) or one of the vibrationally excited states. The lines are from our calculations, and the circles are from the QCT studies by Guo et al.\textsuperscript{14}

In Figure 3.13, we compare our total $S_0$ with experimental data\textsuperscript{17} for CHD$_3$ dissociation on Ni(111) at $T_s = 90$ K. The laser-off results are calculated by averaging $S_0$ over different vibrational states, assuming a Boltzmann distribution of states at a given nozzle temperature. The sticking probabilities for thermally excited molecules in the laser-off molecular beam are estimated by shifting the ground-state sticking curve to lower energies and assuming the same vibrational efficacy $\eta = 0.7$ for all excited states. The overall agreement with experiment is reasonable. We overestimate the laser-off $S_0$ at high $E_i$. This could be due to the use of the PBE functional, which tends to underestimate the barrier height. Table 3.3 lists the vibrational efficacies for three vibrational states at $S_0 = 10^{-4}$. 

65
Figure 3.13 Total dissociative sticking probability for CHD$_3$ dissociation on Ni(111) at 90 K. Results are shown for molecules initially in the ground state (gs), three excited states and the laser-off state. Circles are experimental data (exp) from Utz et al.$^{17}$

Table 3.3 Vibrational efficacies, $\eta$, for the $\nu_1$, $\nu_2$ and $\nu_4$ states at $S_0 = 10^{-4}$.

<table>
<thead>
<tr>
<th></th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>0.82</td>
<td>0.67</td>
<td>0.51</td>
</tr>
</tbody>
</table>

3.3.3 Summary

In this section, we have examined mode- and bond-selectivity in the dissociation of CHD$_3$ on Ni(111). We find that these behaviors can be explained in terms of mode softening, nonadiabatic transitions and symmetry. As vibrational time scales and reaction
time scales are very close for this reaction, the overall dynamics exhibit both adiabatic and sudden behavior.

As the molecule approaches the surface, the symmetric stretch softens, and the vibration becomes localized on the reactive bond, while the antisymmetric stretch correlates with the relatively unperturbed CD$_2$ group. This mode softening lowers the activation energy in the adiabatic limit, especially for the C-H stretch state in C-H cleavage and the CD$_3$ symmetric stretch state in C-D cleavage.

The $B_{q,k}$ coupling couples one vibrationally adiabatic state to another. At energies below the adiabatic barrier heights, molecules follow a cascading pathway via nonadiabatic transitions to lower-energy vibrational states at the avoided crossings, converting asymptotic vibrational energy into bond breaking at the TS. These nonadiabatic transitions keep the energy localized on the reactive bond, and significantly increase the vibrational efficacies for the C-H stretch promoting C-H cleavage and the CD$_3$ symmetric stretch promoting C-D cleavage.

For the doubly degenerate CD$_3$ antisymmetric stretch state, the 2’ component couples strongly to the symmetric stretch state in the entrance channel, and is thus very reactive. The other component (1”) cannot couple to any A’ state, and given minimal mode softening, the 1” state is not reactive. Thus, the antisymmetric stretch state is less reactive than the symmetric stretch state.

For bond selectivity, excitation of the $\nu_1$ state can give 100% C-H cleavage selectivity, while both the $\nu_2$ and $\nu_4$ excitations lead to C-D cleavage selectivity. In addition, there is minor IVR at low incident energies, due to nonadiabatic transitions. The
IVR effect is larger for the CD₃ stretch promoting C-H cleavage than the C-H stretch promoting C-D cleavage.

3.4 Mode- and Bond-Selectivity in the Dissociation of CH₂D₂ on Ni(111)

In this section, we examine mode specificity and bond selectivity in the dissociative chemisorption of CH₂D₂ on Ni(111). Unlike CH₄ and CHD₃, for CH₂D₂ dissociation the symmetric and antisymmetric stretches have similar reactivity.⁷ As shown in Figure 3.14, there are six possible, equally probable, orientations of CH₂D₂ at the TS. For asymmetric C-H or C-D cleavage, the two configurations have mirror symmetry with respect to reflection through a plane, and thus have the same MEP and behaviors.

**Figure 3.14** Six possible orientations of CH₂D₂ at the TS on Ni(111). Carbon, deuterium, hydrogen and nickel atoms are represented by gray, blue, white and green colors, respectively.
In Figure 3.15, we plot $\hbar \omega_k (s)$ along the reaction path for CH$_2$D$_2$ dissociation on Ni(111). When the molecule is far from the surface, there are nine normal modes with nonzero frequency: the CH$_2$ antisymmetric stretch ($\nu_6$), the CH$_2$ symmetric stretch ($\nu_1$), the CD$_2$ antisymmetric stretch ($\nu_9$), the CD$_2$ symmetric stretch ($\nu_2$) and the bending modes ($\nu_3$, $\nu_5$, $\nu_9$, $\nu_7$ and $\nu_4$). The remaining five modes are asymptotically unbound. For symmetric C-H and C-D cleavage, the reaction path is symmetric with respect to reflection through a plane, which is perpendicular to the surface plane and including the reactive bond. Thus, the fourteen normal modes are either symmetric (A’) or antisymmetric (A’’) with respect to the same plane. And the A’’ modes cannot couple to the A’ modes. For asymmetric cleavage, the reaction path has no symmetry.

Like CHD$_3$ and CH$_4$ reactions, there is mode softening in the dissociation of CH$_2$D$_2$ on Ni(111). For C-H cleavage, as the molecule approaches the TS, the reactive C-H bond weakens, while the other C-H bond remains unperturbed. The nonlocal CH$_2$ symmetric stretch ($\nu_1$) evolves into vibration entirely localized on the reactive C-H bond, and its frequency drops. The CH$_2$ antisymmetric stretch ($\nu_6$) correlates with the unperturbed C-H bond, and its frequency remains unchanged. For C-D cleavage, we see similar behavior. The CD$_2$ symmetric stretch ($\nu_2$) softens, and the vibration increasingly localizes on the reactive C-D bond, while the CD$_2$ antisymmetric stretch ($\nu_8$) becomes localized on the nonreacting C-D bond.
This mode softening lowers the activation energies for the ground and excited states in the adiabatic limit. Table 3.4 lists $E_a$ for CH$_2$D$_2$ dissociation on Ni(111). The ground state activation energy for C-H cleavage is about 0.04 eV lower than that for C-D cleavage. For the excited states, the vibrationally adiabatic barriers are lower for the symmetric
stretch states than the antisymmetric stretch states. Thus, in the adiabatic limit, we expect the symmetric stretch states to be more reactive.

Table 3.4 Activation energies for CH$_2$D$_2$ dissociation on Ni(111).

<table>
<thead>
<tr>
<th></th>
<th>ground state</th>
<th>$\nu_6$</th>
<th>$\nu_1$</th>
<th>$\nu_8$</th>
<th>$\nu_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetric C-H</td>
<td>0.873</td>
<td>0.866</td>
<td>0.763</td>
<td>0.872</td>
<td>0.791</td>
</tr>
<tr>
<td>asymmetric C-H</td>
<td>0.870</td>
<td>0.864</td>
<td>0.774</td>
<td>0.855</td>
<td>0.785</td>
</tr>
<tr>
<td>symmetric C-D</td>
<td>0.913</td>
<td>0.912</td>
<td>0.908</td>
<td>0.904</td>
<td>0.809</td>
</tr>
<tr>
<td>asymmetric C-D</td>
<td>0.916</td>
<td>0.913</td>
<td>0.912</td>
<td>0.907</td>
<td>0.815</td>
</tr>
</tbody>
</table>

At energies below the vibrationally adiabatic barrier heights, reaction can occur via nonadiabatic transitions to lower-energy states at the avoided crossings. Figure 3.16 shows the $B_{q,k}$ couplings for C-H cleavage and C-D cleavage. For example, for symmetric C-H cleavage, molecules initially in the $\nu_1$ state can transition to the $\nu_2$ state at $s = -1$ amu$^{1/2}$ Å, where the $\nu_2$ mode changes into the vibration of the reactive C-H bond. Then they can transition to the $\nu_3$ state, then to the $\nu_7$ state, eventually converting the asymptotic vibrational energy into translational motion along the reaction path. These nonadiabatic transitions preserve the vibrational energy localization on the reactive C-H bond. This mechanism increases the efficacy for $\nu_1$ promoting C-H cleavage. A similar mechanism is found for molecules in the $\nu_2$ state, which enhances the sticking probability for C-D cleavage.
Figure 3.16 $B_{q,k}$ couplings for symmetric C-H cleavage (top left), asymmetric C-H cleavage (top right), symmetric C-D cleavage (bottom left) and asymmetric C-D cleavage (bottom right) of CH$_2$D$_2$ on Ni(111).

More importantly, we find that the symmetric stretch states mix with the antisymmetric stretch states in the entrance channel, where $\nu_1$ and $\nu_6$ (or $\nu_2$ and $\nu_8$) are nearly degenerate. For C-H cleavage, the $B_{\nu_6, \nu_1}$ coupling, which mixes the $\nu_1$ and $\nu_6$ states,
has a broad peak in the entrance channel between \( s = -8 \) and -3 \text{amu}^{1/2} \text{Å} \) (shown in the left panel of Figure 3.17), due to the molecule-surface interaction. Because of this coupling, the sticking probability for the CH\(_2\) antisymmetric stretch state is similar to that for the CH\(_2\) symmetric stretch state.

\[ \text{Figure 3.17} \text{ Effects of the } B_{v_6,v_1} \text{ coupling on } P_0 \text{ for symmetric C-H cleavage. (A) } B_{q,k} \text{ couplings in the entrance channel. (B) Single-site rigid-lattice reaction probability for symmetric C-H cleavage of CH}_2\text{D}_2 \text{ on Ni(111). The dotted lines represent } P_0 \text{ computed with } B_{v_6,v_1} = 0 \text{ for } s < -2.5 \text{ amu}^{1/2} \text{Å.} \]

To illustrate the effects of this coupling in the entrance channel, we set \( B_{v_6,v_1} = 0 \) for \( s < -2.5 \text{ amu}^{1/2} \text{Å} \), and repeat the calculations of \( P_0 \). The results are shown in the right panel of Figure 3.17. Removing the \( B_{v_6,v_1} \) coupling in the entrance channel decreases the reaction probability for the \( v_6 \) state by at least one order of magnitude. On the other hand, when we include the full \( B_{v_6,v_1} \) coupling, the reaction probability for the \( v_1 \) state is slightly
decreased, due to the transition to the unreactive state. Thus, we can conclude that \( \nu_1 \) and \( \nu_6 \) state mixing early in the entrance channel via the \( B_{\nu_6,\nu_1} \) coupling is responsible for the similar \( P_0 \) for these two states. Similarly, the \( B_{\nu_6,\nu_2} \) coupling mixes the \( \nu_6 \) and \( \nu_2 \) states in the entrance channel, and results in similar reactivity for the CD\(_2\) symmetric and antisymmetric stretch states, shown in Figure 3.18.

![Figure 3.18](image.png)

**Figure 3.18** Single-site rigid-lattice reaction probability for symmetric C-D cleavage of CH\(_2\)D\(_2\) on Ni(111).

We then average \( P_0 \) over surface impact sites, correct the rotational treatment, and include the effects of lattice motion to compute the dissociative sticking probability \( S_0 \), using approaches similar to those described in Chapter 2 and Section 3.3.2.

We use the “energy-shifting” approximation to estimate \( P_0 \) for impact sites away from the minimum barrier site, and then average \( P_0 \) over different impact sites. The increase in barrier height at a site \((X,Y)\) relative to the minimum barrier site, \( \Delta V(X,Y) \), is computed.
And we find $\hbar \Omega_x = 0.173$ eV and $\hbar \Omega_y = 0.175$ eV for CH$_2$D$_2$ dissociation on Ni(111), where the frequencies $\Omega_x$ and $\Omega_y$ satisfy $\Delta V(X, Y) = \frac{1}{2} M \Omega_x^2 \Delta X^2 + \frac{1}{2} M \Omega_y^2 \Delta Y^2$.

For the rotational motion, we estimate $S_0$ in the sudden limit, and use Eq 2.26 and 2.27 to compute our final $S_0$ as an average of the sudden and adiabatic limiting cases. The final $S_0$ has 90% adiabatic behavior at $E_i = 0.2$ eV and 90% sudden behavior at $E_i = 1.2$ eV.

Finally, to treat the effects of lattice motion, we define $Q$ as the displacement of the Ni atom over which the methane dissociates, with $Q = 0$ for the equilibrium position and $Q > 0$ for motion away from the bulk. The vibration of this atom modifies the height of the barrier to dissociation by an amount of $-\beta Q$ and the location of the TS along $Z$ by an amount of $\alpha Q$. We find $\beta = 1.099$ eV/Å and $\alpha = 0.749$ for CH$_2$D$_2$ on Ni(111). The Debye model is used to compute the probability for $Q$, and the root-mean-square displacement is determined by the surface Debye temperature $\theta_D$. We use $\theta_D = 280$ K for Ni(111), extracted from a low energy electron diffraction (LEED) study. We use Eq. 2.33, 2.37 and 2.38 to average $P_0$ over all displacements and momenta normal to the surface of the Ni atom over which the methane dissociates.

Figure 3.19 shows the dissociative sticking probability for C-H cleavage and C-D cleavage of CH$_2$D$_2$ on Ni(111) at 95 K. The result is the sum over the three C-H cleavage or C-D cleavage configurations divided by six. We observe a weak C-H bond selectivity for molecules initially in the ground state, due to the lower ZPE-corrected barrier height. For C-H cleavage, as expected, both the $\nu_1$ state and the $\nu_6$ state are very reactive, with a slightly larger vibrational efficacy for the CH$_2$ symmetric stretch state, for the reasons discussed. On the other hand, the $\nu_2$ and $\nu_8$ states are very reactive for C-D cleavage.
We observe minor IVR for excitation of the CH$_2$ stretches promoting C-D bond cleavage and excitation of the CD$_2$ stretches promoting C-H bond cleavage at low incident energies, due to nonadiabatic transitions from the CH$_2$ stretch states to the CD$_2$ stretch states, and vice versa. These IVR effects are larger for the $v_2$ and $v_8$ states, because the corresponding nonadiabatic couplings are stronger.

![Figure 3.19](image)

**Figure 3.19** Dissociative sticking probability for either C-H or C-D cleavage of CH$_2$D$_2$ on Ni(111) at 95 K. Results are shown for molecules initially in the ground state (gs) or one of the vibrationally excited states.

We plot the C-H:C-D cleavage ratio in Figure 3.20. The ground state has a small preference for C-H cleavage at low incident energies. As expected, both CH$_2$ stretch states give C-H cleavage selectivity, and this bond selectivity is slightly larger for the symmetric stretch over the antisymmetric stretch. The two CD$_2$ stretch states promote C-D cleavage
over C-H cleavage. However, at high energies, near saturation, the C-H:C-D cleavage ratio approaches the statistical value of 1:1 for all states.

Figure 3.20 C-H:C-D cleavage ratio for CH$_2$D$_2$ initially in the ground state (gs) or one of the vibrationally excited states on Ni(111).

In Figure 3.21, we plot the total dissociative sticking probability for CH$_2$D$_2$ dissociation on Ni(111). While molecules in the CH$_2$ stretch states have a larger $S_0$ than those in the CD$_2$ stretch states, there is more vibrational energy in the CH$_2$ stretch states. The vibrational efficacies for these states at $S_0 = 10^{-4}$ are listed in Table 3.5. The $v_1$ state has the largest vibrational efficacy, and is as effective as the same amount of translational energy.
Figure 3.21 Total dissociative sticking probability for CH$_2$D$_2$ dissociation on Ni(111) at 95 K. Results are shown for molecules initially in the ground state and four excited states.

Table 3.5 Vibrational efficacies, $\eta$, for the $\nu_6$, $\nu_1$, $\nu_8$ and $\nu_2$ states at $S_0 = 10^{-4}$.

<table>
<thead>
<tr>
<th></th>
<th>$\nu_6$</th>
<th>$\nu_1$</th>
<th>$\nu_8$</th>
<th>$\nu_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>0.84</td>
<td>0.99</td>
<td>0.75</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Finally, Figure 3.22 shows the comparison of the computed sticking probabilities with experimental data measured by the Utz group (unpublished data). The agreement between theory and experiment is very good, except that the theoretical results predict a slight preference for the symmetric CH$_2$ stretch, while the experimental data suggest identical $S_0$ for the symmetric and antisymmetric stretch states at all energies measured. The “laser-off” results plotted in Figure 3.22 include the contributions from vibrationally excited molecules in the beam.
Figure 3.22 Total sticking probabilities for CH$_2$D$_2$ on Ni(111) at 95 K. Lines are theoretical results for molecules in the ground, $\nu_1$ or $\nu_6$ state, and open black circles represent vibrational-state-average theoretical $S_0$ under “laser-off” conditions. Triangles are experimental measurements from the Utz group (unpublished data).

### 3.5 Reactivity of Overtone Excited CH$_4$ on Ni(111)

In this section, we examine the dissociation of CH$_4$ prepared in overtone and combination vibrations, including three different vibrational symmetry components of the $2\nu_3$ state and the $\nu_1 + \nu_3$ state, on Ni(111). Hundt et al. used IR-IR double resonance excitation in a molecular beam to prepare CH$_4$ in the A$_1$, E and F$_2$ symmetry components of the $2\nu_3$ state as well as in the $\nu_1 + \nu_3$ state.$^{5,9}$ Figure 3.23 shows a simplified level-diagram of the excitation path. In their experiments, strong mode specificity is observed:

$S_0 (\nu_1 + \nu_3) > S_0 (2\nu_3 - A_1) > S_0 (2\nu_3 - F_2) > S_0 (2\nu_3 - E)$, inversely correlated with the vibrational energy of these states.
Figure 3.23 Level diagram of the C-H stretch overtone states $\nu_1 + \nu_3 - F_2$, $2\nu_3 - F_2$, $2\nu_3 - A_1$ and $2\nu_3 - E$ prepared by double resonance excitation. The excitation path for all four overtone states starts from $\nu = 0, J = 1$ using the $\nu_3 = 1, J = 0$ level as intermediate state. This diagram is from Ref. 5. The symmetric C-H stretch overtone state $2\nu_1 - A_1$ is included in the diagram but could not be prepared in the study of Ref. 5.

In the harmonic approximation, the $2\nu_3$ state is sixfold degenerate, but the true vibrational eigenstate splits into three symmetry components, $A_1$, $E$ and $F_2$, with slightly different energies, due to anharmonicity. We find that the difference in localization of the C-H stretch amplitude in a single C-H bond is responsible for the variation in reactivity for different states. This is consistent with a study by Abram et al., using the anharmonic
symmetrized internal coordinates (SIC).\textsuperscript{53} In their study, the vibrational overtone states are described in terms of the SIC states, |2000; A\textsubscript{1}>, |2000; F\textsubscript{2}>, |1100; A\textsubscript{1}>, |1100; E>, and |1100; F\textsubscript{2}>, where the |2000> states have two quanta of energy in a single C-H bond, while the |1100> states have two quanta each in one of two different C-H bonds. Based on the provided coefficients,\textsuperscript{53} we find that the $\nu_1 + \nu_3$ combination state contains a higher percentage of |2000> local mode character than other states, and thus has the strongest localization of the C-H vibration in a single C-H bond. This is followed by the 2$\nu_3$-A\textsubscript{1} and 2$\nu_3$-F\textsubscript{2} symmetry states, while the 2$\nu_3$-E state contains 100% |1100> character.

Similar behavior is found for CH$_2$D$_2$ dissociation on Ni(100).\textsuperscript{13} Beck et al. reported that the local mode state with two quanta of excitation in one C-H bond is more reactive than the delocalized state with one quantum in each of the two C-H bonds.\textsuperscript{13} This is because localizing the C-H stretch in a single C-H bond makes the reactant state resemble the TS more than distributing the C-H stretch amplitude over two bonds. This idea can be quantified by the SVP model, proposed by Guo et al.,\textsuperscript{22,23} in which the vibrational efficacy is proportional to the overlap between the vibrational mode vector of the reactant and the vector corresponding to the imaginary frequency at the TS. However, the SVP model cannot be applied to the overtone and combination states. In addition, even if the vibration is not localized for the reactant molecules, the surface-molecule interaction may lead to energy localization on the reactive bond as the molecules approach the surface. For example, the $\nu_1$ normal mode can evolve from a nonlocal mode into vibration entirely localized in a single C-H bond, while the $\nu_3$ normal mode becomes localized on the nonreacting group. Thus, the $\nu_1$ state is more reactive than the $\nu_3$ state.
The SIC representation has some limitations. It cannot explain the difference in reactivity between the $\nu_1$ and $\nu_3$ states, as well as the difference between the $2\nu_3$-A$_1$ and $2\nu_3$-F$_2$ states, because of complexity in the true vibrational eigenstates. The eigenstates are mixing of the normal mode states, including some high-quanta bending normal mode states, as the frequencies of the stretch modes are about twice those of the bending modes. Wang et al. performed fourth order perturbative calculations to compute the vibrational eigenstates of CH$_4$, using a normal mode basis set\textsuperscript{54}. Table 3.6 lists the results of their calculations. To distinguish between the normal mode states and the true vibrational eigenstates, we label the eigenstates with the symmetry labels. As shown in Table 3.6, the bending normal mode states, like $\nu_1 + 2\nu_2$, $\nu_2 + \nu_3 + \nu_4$ and $\nu_3 + 2\nu_2$, contribute to the C-H stretch eigenstates in the experiment.

**Table 3.6** Composition, as a percent, of the C-H stretch overtone and combination eigenstates of CH$_4$, in terms of the normal mode basis set of Ref. 54.

<table>
<thead>
<tr>
<th></th>
<th>$2\nu_3$</th>
<th>$\nu_1 + \nu_3$</th>
<th>$2\nu_1$</th>
<th>$\nu_1 + 2\nu_2$</th>
<th>$\nu_2 + \nu_3 + \nu_4$</th>
<th>$\nu_3 + 2\nu_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\nu_3$-E</td>
<td>94</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>$2\nu_3$-F$_2$</td>
<td>73</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>$2\nu_3$-A$_1$</td>
<td>48</td>
<td>-</td>
<td>12</td>
<td>29</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>$\nu_1 + \nu_3$-F$_2$</td>
<td>6</td>
<td>48</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>$2\nu_1$-A$_1$</td>
<td>13</td>
<td>-</td>
<td>74</td>
<td>3</td>
<td>3</td>
<td>-</td>
</tr>
</tbody>
</table>

Based on the study by Wang et al.,\textsuperscript{54} we can use our RPH approach to compute $S_0$ for the vibrational eigenstates from the sticking probabilities of the normal mode states. To compute $S_0$ for the normal mode states, we first compute the single-site rigid-lattice...
reaction probability, $P_0$, by evolving the wave packets in time, and energy-analyzing the reactive flux for a given initial state. Then the reaction probability $P_0$ is averaged over all impact sites, using the “energy-shifting” approximation and the parameters in Table 3.2. For the rotational treatment, we define the final $S_0$ as an average of the adiabatic and sudden limiting cases, with 90% adiabatic behavior at $E_l = 0.2$ eV and 90% sudden behavior at $E_l = 1.2$ eV. Finally, the Debye model is used to include the effects of lattice motion, with the Debye temperature $\theta_D = 280$ K from a LEED experiment.$^{52}$ And we find $\beta = 1.099$ eV/Å and $\alpha = 0.749$ for the $\beta$-type coupling and $\alpha$-type coupling, respectively. More computational details can be found in Section 3.3, 3.4 and Chapter 2.

In Figure 3.24, we plot the computed $S_0$ for the normal mode states at 475 K. As noted, the $\nu_1$ state is more reactive than the $\nu_3$ state. As the molecule approaches the TS, the $\nu_1$ symmetric stretch softens, and the vibration becomes localized on the reactive C-H bond, which weakens, as we move along the reaction path, while the $\nu_3$ antisymmetric stretch becomes localized on the nonreacting CH$_3$ group. Due to this mode softening, the adiabatic barrier height for the $\nu_1$ state is lower than that for the $\nu_3$ state. In addition, as discussed before, nonadiabatic transitions to vibrational states of lower energy at the avoided crossings preserve the energy localization on the reactive bond, and convert the excess energy into translational motion along the reaction path. For the $\nu_3$ state, only one component (2’ component) is strongly coupled to the $\nu_1$ state in the entrance channel, and is thus very reactive, while the other two components (1’ and 1” components) are about as reactive as the ground state.
Figure 3.24 Dissociative sticking probability for CH$_4$ dissociation on Ni(111) at 475 K. Results are shown for the ground, single-quantum and two-quanta normal mode states.

Similar ideas can be applied to the two-quanta normal mode states. As shown in Figure 3.24, the overtone and combination states with more $\nu_1$ character are more reactive. Due to mode softening in the $\nu_1$ mode, the vibrationally adiabatic barrier heights are 0.52, 0.69 and 0.86 eV for the $2\nu_1$, $\nu_1+\nu_3$ and $2\nu_3$ states, respectively. In addition, nonadiabatic transitions significantly increase the reactivity for the $2\nu_1$ state at energies below the barrier height. For the $\nu_1+\nu_3$ state, only the $3'+2'$ component is about as reactive as the $2\nu_1$ state, thus the $\nu_1+\nu_3$ state is less reactive than the $2\nu_1$ state, but more reactive than the sixfold degenerate $2\nu_3$ state, which contains more contributions from unreactive components.

To compute $S_0$ for the true vibrational eigenstates, we can use an initial state of the form $\sum c_i|\nu_i>$, where $|\nu_i>$ are the normal mode states, and $c_i$ are the coefficients derived
from the data in Table 3.6, and propagate the wave packets in time. However, we find that this approach gives the same results as averaging the normal mode sticking probabilities, using \( \sum c_i^2 S_0(\nu_i) \), where the coefficients are from the Wang et al. study.\(^{54} \) We choose the second approach in this study.

Another problem is that our normal mode basis set includes only the ground, single-quantum and two-quanta states, so we are not able to directly compute \( S_0 \) for the three- and four-quanta states listed in Table 3.6. In this study, we estimate \( S_0 \) for these high-quanta states by shifting the sticking curves for the two-quanta and single-quantum states along the energy axis. As shown in Figure 3.25, the computed sticking curve for the \( \nu_2 \) state is shifted about 0.11 eV from the ground state curve, while the shift is about 0.10 eV from the \( \nu_2 \) state to the \( 2\nu_2 \) state. And we find that the shift between the higher energy \( \nu_3 \) state and the \( \nu_3 + \nu_2 \) state is even smaller, only about 0.07 eV. Thus, we expect that adding a quantum of \( \nu_2 \) bend to the \( \nu_3 + \nu_2 \) state should lead to an even smaller shift. We estimate this shift to be 0.05 eV. This approach is used to estimate \( S_0 \) for other high-quanta states. Figure 3.26 shows the computed \( S_0 \) (solid lines) and the estimated \( S_0 \) (dotted lines) for several normal mode states. Although this approach is arbitrary, the errors in the estimated \( S_0 \) are likely to be small, because the contributions from the high-quanta states to the total \( S_0 \) are smaller than those from the \( 2\nu_1, \nu_3 + \nu_2 \) and \( 2\nu_3 \) states.
Figure 3.25 The dissociative sticking probability for the $v_3 + 2v_2$ normal mode state estimated from single-quantum and two-quanta states by shifting the curves.

Figure 3.26 Dissociative sticking probabilities for the computed $S_0$ (solid lines) and the estimated $S_0$ (dotted lines) for several normal mode states.
In Figure 3.27, we plot the computed sticking probabilities for molecules in the three symmetry components of the $2\nu_3$ eigenstate and the $\nu_1 + \nu_3$-$\text{F}_2$ state. The results are compared with experimental data. Our calculations reproduce the experimental trends, but not the magnitude of the difference in $S_0$. As noted, the overtone and combination states with more $2\nu_1$ and $\nu_1 + \nu_3$ character are more reactive. Among these four eigenstates, the $\nu_1 + \nu_3$-$\text{F}_2$ state, with the largest contribution (48%) from the $\nu_1 + \nu_3$ normal mode state, is the most reactive. The $2\nu_3$-$\text{A}_1$ and $2\nu_3$-$\text{F}_2$ states contain 12% $2\nu_1$ character and 15% $\nu_1 + \nu_3$ character, respectively, and are more reactive than the $2\nu_3$-$\text{E}$ state, which is comprised primarily (94%) of the $2\nu_3$ normal mode state. At high energies, the differences in reactivity are small, and our calculations reproduce the magnitude of $S_0$. At lower energies, we underestimate $S_0$ for the $\nu_1 + \nu_3$-$\text{F}_2$, $2\nu_3$-$\text{A}_1$ and $2\nu_3$-$\text{F}_2$ states.

**Figure 3.27** Sticking probabilities for the three symmetry components of the $2\nu_3$ eigenstate and the $\nu_1 + \nu_3$-$\text{F}_2$ state. The lines represent the theoretical results, and the circles are the experimental data.
Finally, as shown in Figure 3.26, the bend plus stretch combination states are as reactive as the $2\nu_3$ normal mode state, and are less reactive than the $2\nu_1$ and $\nu_1 + \nu_3$ states. Thus, the contributions from the $2\nu_1$, $\nu_1 + \nu_3$ and $2\nu_3$ states dominate the total $S_0$. The eigenstates of the $A_1$ and $F_2$ symmetry can have contributions from the $2\nu_1$ and $\nu_1 + \nu_3$ normal mode states respectively, due to symmetry, and are thus more reactive.

3.6 Conclusion

In this Chapter, we have examined the dissociative chemisorption of methane and its isotopologues on Ni(111). We observe mode-specificity and bond-selectivity in these reactions, which can be explained in terms of mode softening, nonadiabatic transitions and symmetry.

The symmetric stretch states are usually very reactive. As the molecule approaches the TS, the dissociating bond weakens, and decouples from the nonreacting stretches. The symmetric stretch evolves from a nonlocal mode into vibration entirely localized on this weakened bond, while for the antisymmetric stretch, the vibration is localized on the nonreacting group. This mode softening lowers the vibrationally adiabatic barrier heights for the symmetric stretch states. In addition, nonadiabatic transitions to lower energy states at the avoided crossings preserve energy localization on the reactive bond, and convert the excess energy into translational motion along the reaction path. This cascade mechanism significantly increases the reactivity for the symmetric stretch state. For the N-fold degenerate antisymmetric stretch state, only one component is very reactive, due to the relatively strong $B_{q,k}$ coupling to the symmetric stretch state in the entrance channel.
We also observe strong bond selectivity in the dissociative chemisorption of methane isotopologues on Ni(111), due to mode softening and nonadiabatic transitions, with minor IVR at very low incident energies.

In addition, we have examined mode specificity in the dissociation of CH₄ prepared in different symmetry components of the 2ν₃ stretch overtone state and the ν₁ + ν₃ combination state. These eigenstates can be written as linear combinations of the normal mode states, and the eigenstates with more ν₁ normal mode character are more reactive.
3.7 References


CHAPTER 4

DISSOCIATIVE CHEMISORPTION OF METHANE ON Pt(111)

4.1 Introduction

The reaction path Hamiltonian (RPH) approach is used to examine the dissociative chemisorption of methane on Pt(111). In recent years, many experimental and theoretical studies have been performed on Pt(111), because of the relatively high reactivity of the Pt catalyst for the steam reforming of natural gas. For methane dissociation, the zero-coverage dissociative sticking probability on a bare surface, \( S_0 \), is shown to increase strongly with increasing incident translational energy and vibrational excitation of the methane.\(^1\)\(^-\)\(^4\) This behavior is nonstatistical, with mode specificity.\(^5\)\(^-\)\(^10\) In addition, theoretical studies find that lattice vibration can modify the height of the barrier to dissociation,\(^11\)\(^-\)\(^14\) which leads to a strong variation in \( S_0 \) with surface temperature.\(^1\)\(^-\)\(^4\)

In this chapter, we first examine the mode-selective behavior for methane dissociation on Pt(111). The results are compared with those on Ni(111). While most studies focus on the effects of exciting the stretching modes in the incident molecules, we also look at the vibrational efficacies for the bending states. Second, we study the effects of lattice motion on the sticking probability.

Finally, our scattering calculations are performed based on a potential energy surface (PES) computed using the Density Functional Theory (DFT) method. Thus, the accuracy of the PES is very important to achieve quantitative agreement with experiment. In Section 4.5, we perform calculations using the specific reaction parameter (SRP) functional, which is able to reproduce \( S_0 \) obtained experimentally for several systems.\(^15\)\(^-\)\(^17\)
4.2 Computational Model and Electronic Structure Calculations

For the Pt(111) surface, a five-layer $3\times3$ supercell with periodic boundary conditions, corresponding to a methane coverage of 1/9 ML, is used to represent the metal as a series of infinite slabs, with a large vacuum space of 16.1 Å between the slabs. The Brillouin zone is sampled by an $8\times8\times1\Gamma$-centered grid of $k$ points. Electronic structure calculations are performed with the Vienna \textit{ab initio} simulation package (VASP), developed at the Institut für Materialphysik of the Universität Wien.\textsuperscript{18–22} We use fully nonlocal optimized projector augmented-wave (PAW) potentials\textsuperscript{22,23} to describe the interactions between the ionic cores and the electrons. The Perdew-Burke-Ernzerhof (PBE) functional,\textsuperscript{24,25} with a lattice constant of 3.978 Å, is used to treat exchange-correlation effects, unless otherwise specified. We first relax the top two substrate layers before including any adsorbate, and then keep the lattice atoms fixed at their bare relaxed surface positions.

We use the CI-NEB and NEB methods\textsuperscript{26,27} to locate the transition state (TS) and another 60 images along the minimum energy path (MEP). The calculations are considered converged when all forces are smaller than 0.01 eV/Å or better. Figure 4.1 shows the TS and product state configurations. The TS geometry on Pt(111) is very similar to that on Ni(111). The carbon atom is roughly over the top site from the entrance channel to the TS. At the TS, the distance between the carbon atom and the surface plane is 2.24 Å, larger than that on Ni(111). This is consistent with the larger atomic radius for Pt (1.83 Å) over Ni (1.62 Å). The reactive C-H bond is about 0.1 Å more stretched on Ni(111) than on Pt(111), suggesting a “later” barrier on Ni(111). The dissociating H atom is oriented toward the surface, with an angle of 131.5° with respect to the surface normal.
The barrier height, relative to the energy of the molecule and the metal surface at infinite separation, is 0.815 eV on Pt(111), about 0.2 eV lower than that on Ni(111). Thus, we expect that the sticking probability for molecules initially in the ground state is larger on Pt(111) than on Ni(111). Our Pt(111) transition state configuration is very similar to the F1 configuration reported in ref. 28 and 13, but our barrier height is 0.134 eV lower, due to their use of a smaller 2×2 supercell.

Finally, on Pt(111) the methyl group remains above the top site during the reaction, because of the strong preference for CH₃ binding on the top site,¹³,²⁸ while on Ni(111) the most stable site is the hollow site,¹³,²⁸ thus CH₃ moves toward the hollow site after the TS. This should decrease the tunneling probability for reactions on Ni(111), relative to those on Pt(111).

**Figure 4.1** Transition state (left panel) and product state (right panel) configurations for the dissociation of CH₄ on Pt(111). Only the topmost Pt layer is shown. \( E_b \) and \( E_p \) are the energies for the transition state and the product state, respectively, relative to the energy where methane is infinitely far above the surface.

\[
\begin{align*}
\text{Transition state} & \quad E_b = 0.815 \text{ eV} \\
\text{Product state} & \quad E_p = 0.104 \text{ eV}
\end{align*}
\]
Figure 4.2 shows the total energy, $V_0(s)$, along the MEP, as a function of the distance along the path, $s$, where $(ds)^2 = \sum_{i=1}^{15}(d\alpha_i(s))^2$, and $s = 0$ at the TS. The $\{\alpha_i(s)\}$ are the mass-weighted Cartesian coordinates of the molecule at a point $s$. At each of these images, we compute and diagonalize the force-projected Hessian to get the fourteen normal vibrational coordinates $Q_k$ and corresponding frequencies, $\omega_k(s)$, that describe motion orthogonal to the reaction path at $s$ in the harmonic approximation. Ignoring anharmonic terms, we write our PES in the reaction path coordinate $s$ and $\{Q_k\}$. The molecular wave function is described as close-coupled wave packets. For a given initial vibrational state $n_i$, standard techniques are used to propagate the wave packets in time$^{29,30}$ and energy-analyze the reactive flux$^{31,32}$. The result is the single-site rigid-lattice reaction probability, $P_0$. A detailed description of this approach can be found in Chapter 2.

Figure 4.2 Reaction path for methane dissociation on Pt(111).
In our $P_0$ calculation, the location of the molecular center of mass parallel to the surface, $X$ and $Y$, follows the MEP, and changes little in the entrance channel. Thus, $P_0$ corresponds to reaction at the minimum barrier site. The rotation of the molecule also follows the MEP, and is treated adiabatically. To compute the dissociative sticking probability $S_0$, we average $P_0$ over different impact sites, correct the rotational treatment, and include the effects of lattice vibration. Previous DFT studies found that there are six lowest energy TSs on Pt(111), differing with respect to the azimuthal orientation of the reactive C-H bond and the rotation of the nonreacting methyl group.\textsuperscript{13,28} These TSs have similar barrier heights and MEPs. Thus, we treat the PES as flat along these coordinates.

The lateral translation of the molecule along $X$ and $Y$ is slow on collision time scales, given the relatively large molecular mass and the normal incident conditions. We thus use the sudden model, described in Section 2.5.1, to estimate the reaction probability at an impact site $(X,Y)$ away from the minimum barrier site. The increase in barrier height relative to the minimum barrier site, $\Delta V(X,Y)$, is computed using Eq. 2.27 and 2.28. We find $\hbar \Omega_X = 0.0152$ eV and $\hbar \Omega_Y = 0.0157$ eV for CH$_4$ dissociation on Pt(111), where the frequencies $\Omega_X$ and $\Omega_Y$ satisfy $\Delta V(X,Y) = \frac{1}{2} M \Omega^2_x \Delta X^2 + \frac{1}{2} M \Omega^2_y \Delta Y^2$.

As noted, the polar orientation of the reactive bond relative to the surface normal, $\theta$, is treated adiabatically for $P_0$ calculation. This treatment is reasonable at low incident energies, given the relatively small moment of inertia. However, recent AIMD studies suggest that this rotational motion might be closer to sudden at high energies,\textsuperscript{29,33} because the reaction time is too short for a significant amount of rotational steering.\textsuperscript{34,35} Thus, we use an approach similar to the treatment of $X$ and $Y$ to estimate the reaction probability in the sudden limit. The increase in barrier height relative to the MEP value $\theta^\dagger = 131.5^\circ$, 

98
\(\Delta V(\theta)\), is computed by rotating the molecule at the TS, and re-computing the total energy. We find \(k_\theta = 22.2919\) eV, where \(\Delta V(\theta) = 0.5k_\theta \sin^2(\theta - \theta^\circ)\). The final \(S_0\) is an average of the sudden and adiabatic limiting cases, assuming 90% adiabatic behavior at \(E_i = 0.2\) eV and 90% sudden behavior at \(E_i = 1.2\) eV.

Finally, we introduce the effects of lattice motion. As discussed in Chapter 2 and 3, both the barrier height and the location of the TS vary with the vibrational displacement of the Pt atom over which the methane dissociates. We define \(Q\) as the displacement of this atom normal to the surface plane, with \(Q = 0\) for the equilibrium position and \(Q > 0\) for motion away from the bulk. Lattice vibration changes the height of the barrier to dissociation by an amount of \(-\beta Q\) and the location of the TS along \(Z\) by an amount of \(\alpha Q\). We find \(\beta = 0.952\) eV/Å and \(\alpha = 0.830\) for CH\(_4\) dissociation on Pt(111).

In earlier studies, we only considered the vibration of the single metal atom over which the methane dissociates, thus underestimating the root-mean-square displacement, \(Q_{rms}\). In this study, we use the more realistic Debye model, in which lattice motion is described in terms of harmonic normal modes. In this model, the displacement \(Q\) has a Gaussian distribution, where \(Q_{rms}(T_s)\) can be related to the surface Debye temperature \(\theta_D\) using Eq. 2.36. The Debye temperature \(\theta_D = 140\) K for Pt (111) is extracted from experiments.\(^{36-38}\) This treatment is supported by a recent AIMD study of CH\(_4\) dissociation on Pt(111).\(^{16}\) In Figure 4.3, we compare the root-mean-square displacements \(Q_{rms}\) computed using the Debye model and the old model with those reported in the AIMD study.\(^{16}\) Clearly, the new \(Q_{rms}\) are in good agreement with the AIMD results, while the old model underestimates the value of \(Q_{rms}\). The use of the Debye model increases the computed sticking probability at low incident energies, and improves the agreement with
experiment. Finally, we use Eq. 2.33, 2.37 and 2.38 to average $P_0$ over all displacements and momenta of the Pt atom over which the methane dissociates.

Figure 4.3 The root-mean-square displacement $Q_{rms}$ as a function of the surface temperature $T_s$, using the Debye model with $\theta_D = 140$ K\textsuperscript{36,38} (solid lines) and the old model (dotted lines). Results are compared with the AIMD results reported in Ref. 16.

4.3 Normal Mode Analysis

Figure 4.4 shows $\hbar \omega_k (s)$ along the reaction path for CH\textsubscript{4} dissociation on Pt(111). When CH\textsubscript{4} is far above the surface, nine of the normal modes have nonzero frequencies: the triply degenerate antisymmetric stretch ($\nu_3$), the symmetric stretch ($\nu_1$), the doubly degenerate bend ($\nu_2$), and the triply degenerate bend ($\nu_4$). The remaining five modes are asymptotically unbound, corresponding to translation parallel to the surface and rotation of the molecule. They become hindered types of motion near the TS. The reaction path is symmetric with respect to reflection through a plane, which is perpendicular to the surface.
plane and includes the reactive C-H bond. Thus, the fourteen normal modes are either symmetric (A’) or antisymmetric (A”) with respect to reflection through this plane. We label the A’ modes 1’-8’ and the A” modes 1”-6”. This symmetry is important, as the nonadiabatic coupling is only nonzero between two modes of the same symmetry.

As was found in studies on Ni(111), excitation of the symmetric stretch is more effective at promoting the dissociation of CH$_4$ than excitation of the antisymmetric stretch. This mode selectivity and the difference in reactivity between Ni(111) and Pt(111) can be explained in terms of mode softening, the nonadiabatic couplings and the barrier heights.

![Figure 4.4](image)

**Figure 4.4** Energies of the normal modes along the reaction path for CH$_4$ dissociation on Pt(111).

As shown in Figure 4.4, the frequencies are very similar for methane dissociation on Pt(111) and Ni(111), except that mode softening is slightly weaker on Pt(111). Table 4.1
lists the activation energies $E_a$, i.e. the zero-point energy corrected barrier heights, for the vibrationally adiabatic ground state and some excited states on Pt(111) and Ni(111). Mode softening in the $3'$ mode and some bending modes lowers $E_a$ for the ground state by about 0.1 eV. The activation energy is lowered even further for the $\nu_1$ symmetric stretch state, while the three components of the $\nu_3$ antisymmetric stretch state have an $E_a$ similar to that of the ground state. Thus, in the vibrationally adiabatic limit, the $\nu_1$ state is more reactive than the $\nu_3$ state, while the $\nu_3$ state and the ground state should have similar reactivity.

Mode softening is a bit stronger on Ni(111) than on Pt(111), consistent with the reactive C-H bond being more stretched at the TS on Ni(111). But the activation energies are still lower on Pt(111), with the difference in $E_a$ being slightly smaller than the difference in barrier height. Thus, we expect the sticking probabilities to be larger on Pt(111).

Table 4.1 Activation energies for CH$_4$ dissociation on Pt(111) and Ni(111).

<table>
<thead>
<tr>
<th>$E_a$ (eV)</th>
<th>Pt(111)</th>
<th>Ni(111)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ground state</td>
<td>0.698</td>
<td>0.876</td>
<td>0.178</td>
</tr>
<tr>
<td>$\nu_3$ ($1', 2', 1''$)</td>
<td>0.695, 0.684, 0.703</td>
<td>0.872, 0.860, 0.874</td>
<td>0.177, 0.176, 0.171</td>
</tr>
<tr>
<td>$\nu_1$ ($3'$)</td>
<td>0.542</td>
<td>0.698</td>
<td>0.156</td>
</tr>
<tr>
<td>$\nu_2$ ($4', 2''$)</td>
<td>0.680, 0.683</td>
<td>0.854, 0.861</td>
<td>0.174, 0.178</td>
</tr>
<tr>
<td>$\nu_4$ ($5', 6', 3''$)</td>
<td>0.685, 0.641, 0.639</td>
<td>0.857, 0.812, 0.800</td>
<td>0.172, 0.171, 0.161</td>
</tr>
</tbody>
</table>

As discussed in Chapter 3, mode softening is associated with vibrational energy localization on the reactive C-H bond.$^{39,40}$ As the molecule approaches the TS, the reactive
bond weakens, and decouples from the three nonreacting C-H stretches. In the normal mode picture, the symmetric stretch evolves from a nonlocal mode into vibration entirely localized on this weakened bond, while the antisymmetric stretches become localized on the nonreacting CH₃ group.

In addition to mode softening, the nonadiabatic couplings are also very important. In Figure 4.5 and 4.6, we plot the curvature couplings, $B_{q,15}$, and the so-called Coriolis couplings, $B_{q,k}$, respectively. The Ni(111) results are included for comparison. The magnitude of the curvature coupling, which couples the single-quantum states to the ground state and the two-quanta states, is similar for the two metal surfaces. The effect of this coupling is to slightly increase $S_0$ at low energies and slightly decrease $S_0$ at high energies.

![Figure 4.5](image.png)

**Figure 4.5** Curvature couplings for CH₄ dissociation on Pt(111) (solid lines) and Ni(111) (dotted lines).
Figure 4.6 $B_{q,k}$ couplings for CH$_4$ dissociation on Pt(111) (solid lines) and Ni(111) (dotted lines).

We find that the $B_{q,15}$ coupling is less important than the $B_{q,k}$ coupling, which couples one vibrationally adiabatic state to another of lower energy. At energies below the adiabatic activation energies listed in Table 4.1, reaction can occur via nonadiabatic transitions to lower-energy states at the avoided crossings. Molecules initially in the 3’ state, i.e., the symmetric stretch state, can transition to the 4’ state at about $s = -0.6$ amu$^{1/2}$Å, where the $B_{3',4'}$ coupling has a peak. At this point, the 3’ and 4’ modes exchange character, and the vibration of the 4’ mode localizes on the reactive bond between $s = -0.6$ and -0.4 amu$^{1/2}$Å. Thus, this nonadiabatic transition preserves the energy localization on the reactive C-H bond. The molecules can then have transitions from 4’ to 5’, 5’ to 6’, and so on, and the excess vibrational energy is converted into translational motion along the
reaction path. This “cascading” mechanism corresponds to vibrationally sudden behavior, and increases the reactivity for molecules initially in the symmetric stretch state.

The nonadiabatic transition amplitudes are proportional to the $B_{q,k}$ couplings. It is clear in Figure 4.6 that $B_{q,k}$ are stronger for CH$_4$ dissociation on Ni(111). Thus, the enhancement in $S_0$ with vibrational excitation should be larger on Ni(111) than on Pt(111).

![Figure 4.7](image)

**Figure 4.7** Single-site rigid-lattice reaction probabilities for CH$_4$ on Pt(111) and Ni(111). Results are shown for molecules in the ground state (gs) or four excited stretch states.

In Figure 4.7, we plot the single-site rigid-lattice reaction probability, $P_0$, for CH$_4$ dissociation on Pt(111) and Ni(111). The $P_0$ curve for ground-state CH$_4$ on Pt(111) is shifted to lower $E_i$ by about 0.2 eV relative to that for Ni(111), consistent with the difference in activation energy. As expected, the symmetric stretch state is one of the most
reactive states on two surfaces. The shift between the $P_0$ curves for the 3’ state and the ground state is larger than the difference in adiabatic activation energy.

![Figure 4.8](image)

**Figure 4.8** $B_{q,k}$ couplings for CH$_4$ dissociation on Pt(111) in the entrance channel.

We note that the 2’ component of the antisymmetric stretch state is as reactive as the 3’ state, due to the relatively strong $B_{2’,3’}$ coupling in the entrance channel between $s = -9.0$ and $-2.0$ amu$^{1/2} \text{Å}$, where the 2’ and 3’ modes are nearly degenerate (shown in Figure 4.8). This coupling mixes the 2’ and 3’ states when methane is far above the surface, and leads to similar behaviors for molecules in these two states. The 1’ state does not strongly couple to the 2’ or 3’ state. Thus, molecules in the 1’ state mostly stay on the 1’ adiabatic PES, and have a reactivity similar to that of the ground-state molecules, except at very low energies. The coupling between the 1” state and any A’ state is rigorously zero, so molecules in the 1” state cannot follow the cascading mechanism. Molecules excited to the
1” state can transition to the 2” state, but this transition is weak. When the degeneracy is averaged over, the antisymmetric stretch state is less reactive than the symmetric stretch state, but more reactive than the ground state.

Finally, the vibrational efficacies for promoting reaction are larger on Ni(111) than on Pt(111), because of the stronger $B_{q,k}$ couplings on Ni(111).

### 4.4 Dissociative Sticking Probability

In Figure 4.9, we plot the zero-coverage dissociative sticking probabilities, $S_0$, for CH$_4$ dissociation on Pt(111) at 600 K. Our computed results are compared with molecular beam experiments by Bisson $et$ $al.$

For comparison, in Figure 4.10, we also plot $S_0$ for CH$_4$ dissociation on Ni(111) at 475 K, along with available experimental results from the Utz group and the Beck group. To compute $S_0$ on Ni(111), we use the same approaches and parameters as those in Section 3.4. Note that the laser-off experiments were performed at low nozzle temperatures, where nearly all of the laser-off molecules are in the ground state. We plot two results for the $2\nu_3$ overtone state. The curve labeled by “$2\nu_3$” corresponds to the $2\nu_3$ normal mode state, which is a sixfold-degenerate state with two quanta of excitation in the 1’, 2’ and 1” modes in the harmonic approximation. As discussed in Section 3.5, the true vibrational eigenstate is split into three symmetry components, A, F2 and E, due to anharmonicity, and each component can be written as a linear combination of the (harmonic) normal mode states, using the results of a study by Wang $et$ $al.$

Here, we plot $S_0$ for the F2 symmetry component, which is the one excited in the experiment.
Figure 4.9 Computed dissociative sticking probabilities (lines) for CH$_4$ dissociation on Pt(111) at 600 K. Results are compared with the experimental data (circles) from Ref. 9.

Figure 4.10 Computed dissociative sticking probabilities (lines) for CH$_4$ dissociation on Ni(111) at 475 K. Results are compared with the experimental data (circles) from Ref. 9 and 42.
Overall, our results are in good agreement with experiment. We reproduce the vibration in reactivity with collision energy and the experimental trends in vibrational efficacy. For CH$_4$ on Pt(111), the calculations slightly overestimate the experimental laser-off sticking probabilities at all energies. The shift between the theoretical and experimental sticking curves along the energy axis is less than 0.1 eV. One source of error is the PBE-based PES. The PBE functional is known to underestimate the height of the barrier to dissociation.\textsuperscript{33} In addition, the PBE functional neglects the van der Waals (vdW) interaction. Recent AIMD studies, using the SRP functional, suggest that including the vdW interaction leads to a deeper attractive well in the entrance channel,\textsuperscript{15–17} which may increase the molecular velocity in the curve-crossing region and thus the vibrational efficacies for promoting reaction. For CH$_4$ on Ni(111), the agreement with experiment is improved compared with previous studies,\textsuperscript{29,44,45} as we have improved the treatments of rotational motion and lattice vibration. The new treatments enhance the reactivity at low incident energies. Like on Pt(111), our calculations overestimate the ground state $S_0$ on Ni(111), consistent the PBE functional underestimating the barrier height. As expected, for both theory and experiment, the ground state sticking probabilities are larger on Pt(111) than on Ni(111), due to the lower activation energy on Pt(111).

For the vibrationally excited states, excitation of either the $\nu_1$ or $\nu_3$ stretch significantly increases the sticking probabilities, with the $\nu_1$ state being roughly three times more reactive than the $\nu_3$ state. The enhancement in $S_0$ with vibrational excitation can be expressed in terms of the vibrational efficacy,

$$\eta = \frac{\Delta E_i}{\Delta E_v} = \frac{E_i(gs, S_0) - E_i(\nu, S_0)}{\Delta E_v}$$  \hspace{1cm} (4.1)
where $\Delta E_i$ is the increase in collision energy necessary to give the same $S_0$ as increasing the vibrational energy by $\Delta E_v$. $E_i(\nu, S_0)$ and $E_i(gs, S_0)$ are the collision energies giving a sticking probability of $S_0$ for an initial vibrational state $\nu$ and the ground state (gs), respectively. The computed vibrational efficacy can vary with the choice of $S_0$. Table 4.2 lists the theoretical vibrational efficacy, computed as an average of the $\eta$ values at $S_0 = 10^{-3}$, $10^{-4}$ and $10^{-5}$, as well as the experimental results for comparison. For the $\nu_3$ state, the efficacies for the individual 1’, 2’ and 1” components are also listed. As shown in Table 4.2, the efficacies for the 1’ and 1” components are close to zero, because the 1” state cannot couple to any A’ state due to symmetry, and the 1’ state couples only weakly to the 2’ state, and given minimal mode softening, these two states have $S_0$ similar to that of the ground state. The vibrational efficacies for the 2’ component of the antisymmetric stretch state and the symmetric stretch state (3’) are very similar, because the two states mix in the entrance channel due the surface-molecule interaction. Thus, for CH$_4$ on both Pt(111) and Ni(111), the $\nu_1$ state has a larger vibrational efficacy than the $\nu_3$ state. Similar behavior has been observed both experimentally$^{46,47}$ and theoretically$^{30}$ for CH$_4$ dissociation on Ni(100).

For the 2$\nu_3$ overtone state, our computed $\eta(2\nu_3)$ on Pt(111) is in excellent agreement with the experimental value, while on Ni(111) the theoretical value is smaller than the experimental result. Similarly, the computed efficacy for the $\nu_3$ state is too low on Ni(111) when compared with experiment. This is because on Ni(111) we overestimate the ground-state $S_0$, while the vibrationally excited sticking curves are consistent with experimental data. However, given the tendency for the PBE functional to underestimate the barrier height, we might have expected all of the theoretical sticking probabilities to be larger than the experimental data.
The vibrational efficacies are consistently larger on Ni(111) than on Pt(111), due to the stronger nonadiabatic couplings on Ni(111), which lead to stronger transitions from one vibrationally adiabatic state to lower-energy states at the avoided crossings. This reflects the extent to which the vibrational states are mixed due to the surface-molecule interaction.

To predict mode selective behavior, the Guo group proposed the Sudden Vector Projection (SVP) model, which assumes that the collision is much faster than the intramolecular vibrational energy redistribution (IVR). In this sudden limit, the efficacy of a vibrational mode \( \nu \) for promoting reaction is approximately proportional to the overlap between the mode vector at large negative \( s \) (\( s = s_0 \), \( \bar{L}_\nu(s_0) \)), and the vector corresponding to the imaginary frequency at the TS (\( s = 0 \), \( \bar{L}_{15}(0) \)),

\[
\gamma = \sum_{i=1}^{15} L_{i,\nu}(s_0)L_{i,15}(0)
\]  

(4.2)
We maximize the overlap $\gamma$ between the vectors by aligning the molecule at $s_0$ similar to that at the TS. This overlap reflects how much the vibrational mode $\nu$ resembles the motion of the molecule as it dissociates at the TS.

In Table 4.2, we also list the overlap $\gamma$ for the stretch states on two surfaces. For both surfaces, the SVP overlap is larger for the $\nu_1$ symmetric stretch state than the $\nu_3$ antisymmetric stretch state, consistent with the observed vibrational efficacies for these states. The overlap for the $\nu_3$ state is an average of the $\gamma$ values for the three components. We note that the 2’ component of the $\nu_3$ mode has a larger $\gamma$ value than the 3’ mode, suggesting that the 2’ mode more closely resembles the imaginary-frequency mode at the TS. However, the SVP overlap for the 1’ mode is smaller than that for the 3’ mode, and the 1” mode has zero overlap due to symmetry. Thus, the overall $\gamma$ for the $\nu_3$ mode is smaller than that for the $\nu_1$ mode. Note that, in our RPH model, even if the symmetric stretch does not mostly resemble the imaginary-frequency mode when CH$_4$ is far above the surface, it evolves into a mode with vibration localized on the reactive bond.

In Figure 4.11 and 4.12, we plot the dissociative sticking probabilities for molecules in the $\nu_2$ and $\nu_4$ bending states on Pt(111) and Ni(111), respectively, as well as the $\nu_1$ and $\nu_3$ results for comparison. We also plot the sticking curves for the 4’ and 2” components of the $\nu_2$ state and the 5’, 6’ and 3” components of the $\nu_4$ state. While the $\nu_2$ and $\nu_4$ states have much lower $S_0$ than the stretch states, the vibrational energies for the bending states are only half of the energies for the stretch states. Thus, the vibrational efficacies are similar for the stretch and bending states.
Figure 4.11 Dissociative sticking probabilities for CH$_4$ dissociation on Pt(111) at 600 K. Results are shown for the ground state (gs), the $\nu_3$, $\nu_1$, $\nu_2$ and $\nu_4$ excited states and the components of the $\nu_2$ and $\nu_4$ bending states.

Figure 4.12 Dissociative sticking probabilities for CH$_4$ dissociation on Ni(111) at 475 K. Results are shown for the ground state (gs), the $\nu_3$, $\nu_1$, $\nu_2$ and $\nu_4$ excited states and the components of the $\nu_2$ and $\nu_4$ bending states.
Table 4.3 shows the vibrational efficacies $\eta$, computed as an average of the values at $S_0 = 10^{-3}, 10^{-4}$ and $10^{-5}$, as well as the SVP overlaps $\gamma$ for the bending states. Again, the vibrational efficacies are larger on Ni(111) than on Pt(111), for the reasons discussed. On Pt(111), the $\nu_2$ and $\nu_4$ states have similar $\eta$, slightly smaller than that for the $\nu_3$ state. On Ni(111), the efficacies for the bending states are close to or even larger than the $\nu_3$ efficacy.

Unlike the $1''$ component of the antisymmetric stretch, the $3''$ mode softens in the curve-crossing region, which leads to the lower activation energy for the $3''$ state listed in Table 4.1. On the other hand, the $1''$ mode is only weakly coupled to the $2''$ mode, due to the large energy gap between these two modes, while the $2''$ and $3''$ modes can couple to other lower-energy $A''$ modes. As a result, molecules excited to either the $2''$ or $3''$ state can transition to lower-energy PESs, and have relatively large reactivity. For the $4', 5'$ and $6'$ states, the nonadiabatic couplings between the bending modes are large, and as shown in Figure 4.4 these modes are on the “cascading” pathway for CH$_4$ dissociation. Thus, our model suggests reasonable vibrational efficacies for the bending states.

The SVP model gives slightly different results. The SVP overlaps for the bending modes are about half as big as the overlaps for the stretch modes. For the bending states, the $A''$ modes have zero overlap, and none of the $A'$ modes has a particularly large $\gamma$ value comparable to that for the $2'$ mode. In fact, Guo et al. found similar behavior for H$_2$O dissociation on Cu(111). They found that the SVP overlaps for the bending modes are much smaller than those for the stretch modes, while the computed efficacies are similar for the stretch and bending states.
Table 4.3 Vibrational efficacies $\eta$ from theory and experiment (expt.) and Sudden Vector Projection overlaps $\gamma$ for CH$_4$ dissociation on Pt(111) and Ni(111). Results are shown for the bending states.

<table>
<thead>
<tr>
<th></th>
<th>$v_2$ ($4', 2''$)</th>
<th>$v_3$ ($5', 6', 3''$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111), $\eta$</td>
<td>0.38 (0.43, 0.32)</td>
<td>0.36 (0.23, 0.40, 0.38)</td>
</tr>
<tr>
<td>Pt(111), $\gamma$</td>
<td>0.15 (0.29, 0.00)</td>
<td>0.13 (0.15, 0.22, 0.01)</td>
</tr>
<tr>
<td>Ni(111), $\eta$</td>
<td>0.57 (0.66, 0.45)</td>
<td>0.71 (0.69, 0.86, 0.54)</td>
</tr>
<tr>
<td>Ni(111), $\gamma$</td>
<td>0.15 (0.31, 0.00)</td>
<td>0.15 (0.19, 0.24, 0.00)</td>
</tr>
</tbody>
</table>

Figure 4.13 shows the sticking probability for CHD$_3$ dissociation on Pt(111) at 120 K and 500 K. To benchmark our RPH model, we compare our results with recent AIMD studies by Nattino et al.,$^{33}$ who used the PBE functional with a moving five-layer $3 \times 3$ supercell to perform calculations at energies well above the barrier heights, where quantum effects should be small. The agreement between our RPH results and the AIMD calculations is excellent, suggesting that the approximations in our model are reasonable. At low energies, the AIMD data are a bit above the RPH sticking curves, because the zero-point energy may flow into other degrees of freedom in the classical calculations.$^{54}$ Our model assumes that most of the reactive trajectories correspond to CH$_4$ dissociation at or near the minimum barrier sites. This assumption is reasonable at energies close to or below the barrier heights, where most of the experiments are performed. However, at higher energies, other impact sites may start to contribute. This AIMD study shows that the majority of the reactive trajectories are close to the MEP at 120K.$^{33}$
Figure 4.13 Dissociative sticking probabilities for CHD₃ dissociation on Pt(111) at 120 K and 500 K. Our calculations (lines) are compared with the AIMD results (circles) from Ref. 33.

Finally, in Figure 4.14, we plot the ground-state sticking probability, \( S_0 \), as a function of the surface temperature, \( T_s \), for CH₄ dissociation on Pt(111) at four incident energies \( E_i \) = 0.42, 0.48, 0.62 and 1.27 eV. Our results are compared with some older experimental molecular beam studies.⁵⁵,⁵⁶ The agreement between theory and experiment is good. The sticking probability increases with increasing surface temperature at all temperatures and incident energies considered. At energies below the static surface barrier height, the increase in \( S_0 \) with \( T_s \) is large. At these energies, reaction is only possible over metal atoms that are puckered out of the surface plane, as this puckering can significantly lower the height of the barrier to dissociation by an amount of \( \beta Q \), where \( Q \) is the vibrational displacement of the metal atom over which the methane dissociates. As shown in Figure 4.3, the root-mean-square displacement \( Q_{rms} \) increases with \( T_s \). As a result, raising \( T_s \)
increases the probabilities for large values of $Q$, and thus greatly increases the sticking probability. On the other hand, at high energies, where the reactivity is large, the variation in $S_0$ with $T_s$ is small, because most of the molecules can overcome the static surface barrier. In addition, lattice recoil, due to molecular impact, can convert energy from the molecule to the metal lattice and decrease the sticking probability at high incident energies. Note that our model only approximates this effect by including relative velocities smaller than the incident velocity, which may be a problem at high energies.

Figure 4.14 Computed ground-state sticking probability (lines) as a function of the surface temperature, $T_s$, for CH$_4$ dissociation on Pt(111) at four incident energies $E_i = 0.42, 0.48, 0.62$ and 1.27 eV. The experimental data (symbols) are from Ref. 55 and 56.
4.5 Sticking Probability Using the Specific Reaction Parameter (SRP) Functional

As noted, the PBE functional tends to underestimate the barrier to dissociation, and neglects the van der Waals interaction. Recently, the Kroes group, using the Specific Reaction Parameter (SRP) functional, was able to reproduce $S_0$ obtained experimentally for CHD$_3$ dissociation on several surfaces within chemical accuracy.$^{15-17}$ In this section, we use the SRP functional$^{15,17}$, combined with our quantum approach, to describe the dissociation of CHD$_3$ on Pt(111), and compare the results with those using the PBE functional.

The SRP functional is a linear combination of the PBE$^{24,25}$ and RPBE$^{57}$ functionals,$^{15-17}$

$$E_{XC} = xE_{X}^{RPBE} + (1 - x)E_{X}^{PBE} + E_{C}^{vdW} \quad (4.3)$$

where $E_{X}^{RPBE}$ and $E_{X}^{PBE}$ are the exchange parts of the RPBE and PBE functionals, and $E_{C}^{vdW}$ is the correlation part that provides an approximation of the attractive van der Waals interaction. The Kroes group fitted a candidate SRP functional to the measured “laser-off” $S_0$ for CHD$_3$ dissociation on Ni(111) using AIMD calculations, and found $x = 0.32.$$^{15,17}$

4.5.1 Transition State and Minimum Energy Path Using the SRP Functional

We first re-locate the MEP for CH$_4$ dissociation on Pt(111), using the SRP functional$^{15,17}$ with a lattice constant of 4.0202 Å. A five-layer 3×3 supercell with periodic boundary conditions is used to model the metal as a series of infinite slabs, with a large vacuum space between the slabs. Details on the TS geometry and energy are compared with the PBE results in Table 4.4.
Table 4.4 Transition state data for CH$_4$ on Pt(111) using the SRP and PBE functionals. $Z_C^\ddagger$ is the distance from the carbon atom to the Pt atom directly below it. $r^\ddagger$ and $\theta^\ddagger$ are the length of the dissociating bond and its angle relative to the surface normal, respectively. $E_{ads}$ is the molecular adsorption energy. $E_b$ is the barrier height relative to the methane molecule infinitely far above the surface, and the activation energy $E_a$ is $E_b$ with ZPE corrections.

<table>
<thead>
<tr>
<th></th>
<th>$Z_C^\ddagger$ (Å)</th>
<th>$r^\ddagger$ (Å)</th>
<th>$\theta^\ddagger$ (°)</th>
<th>$E_{ads}$ (eV)</th>
<th>$E_b$ (eV)</th>
<th>ZPE (eV)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRP</td>
<td>2.283</td>
<td>1.562</td>
<td>133.0</td>
<td>-0.214</td>
<td>0.819</td>
<td>-0.115</td>
<td>0.704</td>
</tr>
<tr>
<td>PBE</td>
<td>2.241</td>
<td>1.521</td>
<td>131.7</td>
<td>-0.032</td>
<td>0.815</td>
<td>-0.117</td>
<td>0.698</td>
</tr>
</tbody>
</table>

The TS geometries for the two functionals are very similar, except the reactive C-H bond being slightly more stretched for the SRP functional. The inclusion of the vdW interaction in the SRP function gives a deeper attractive well in the entrance channel with $E_{ads} = -0.214$ eV, which will increase molecular velocities in the curve-crossing region. The barrier heights are similar for the two functionals. In Figure 4.15, we plot the total energy, $V_0$, as a function of the distance along the reaction path, $s$, and the distance of the carbon atom above the surface, $Z_C$, using both the PBE and SRP functionals.
4.5.2 Normal Mode Analysis

Similar to CHD$_3$ dissociation on Ni(111) discussed in Section 3.3, there are four possible, equally probable, orientations of CHD$_3$ at the TS. For molecules initially in either the ground or $v_1$ state, the C-H cleavage configuration contributes most to the total sticking, except at very high energies. In Figure 4.16, we plot some of the normal mode energies $\hbar \omega_k(s)$ along the reaction path for C-H cleavage. This MEP is symmetric with respect to reflection through a plane that is perpendicular to the surface plane and include the dissociating bond. The fourteen normal modes are thus either symmetric (A') or antisymmetric (A'') with respect to this reflection. This symmetry is important, as the nonadiabatic coupling is rigorously zero between two modes of different symmetry. Figure
4.16 includes only the eight symmetric modes, as they dominate the reaction dynamics. The normal modes computed using the SRP and PBE functionals are very similar, as are the ZPE-corrected barrier heights.

![Figure 4.16](image)

**Figure 4.16** Energies of the eight symmetric normal modes along the reaction path for CHD₃ dissociation on Pt(111), using the SRP (solid lines) and PBE (dotted lines) functionals.

In Figure 4.17, we plot the nonadiabatic coupling, $B_{q,k}$, for C-H cleavage in the curve-crossing region. These couplings are responsible for the large enhancement in $S_0$ with vibrational excitation. As discussed, vibrationally excited molecules can transition to vibrationally adiabatic states of lower energy at the avoided crossings, where the nonadiabatic couplings are largest, and convert the excess vibrational energy into translational motion along the reaction path. The magnitude of this effect is proportional to the nonadiabatic couplings.
Figure 4.17 $B_{q,k}$ couplings for symmetric C-H cleavage of CHD$_3$ on Pt(111) in the curve-crossing region, using the SRP (solid lines) and PBE (dotted lines) functionals.

Figure 4.18 $B_{q,k}$ couplings for symmetric C-H cleavage of CHD$_3$ on Pt(111) in the entrance channel, using the SRP (solid lines) and PBE (dotted lines) functionals.
In the curve-crossing region right before the TS, the $B_{q,k}$ couplings are similar for the SRP and PBE functionals, except that the $B_{v_1,v_4}$ and $B_{v_4,v_2}$ couplings are slightly larger for the SRP functional. However, in the entrance channel (Figure 4.18), the SRP couplings are twice as big as the PBE results, due to the inclusion of the vdW interaction in the SRP function. These couplings can mix vibrationally adiabatic states that are nearly degenerate in the entrance channel.

Similar behavior has been found for the $B_{q,15}$ couplings in Figure 4.19 and 4.20. While $B_{q,15}$ are similar for the two functionals near the TS, the SRP functional gives much larger couplings in the entrance channel, due to the stronger molecule-surface interaction. The $B_{q,15}$ couplings can transition ground-state molecules to excited states, thus decrease $S_0$ for the ground state at high incident energies.

![Figure 4.19](Image)

**Figure 4.19** $B_{q,15}$ couplings for symmetric C-H cleavage of CHD$_3$ on Pt(111) in the curve-crossing region, using the SRP (solid lines) and PBE (dotted lines) functionals.
4.5.3 Reaction Probabilities Using the SRP and PBE Functionals

As discussed, the SRP functional gives a deeper van der Waals attractive well as well as slightly larger nonadiabatic couplings relative to the PBE functional. In Figure 4.21, we plot the single-site rigid-lattice reaction probability, $P_0$, for molecules initially in either the ground or $\nu_1$ excited state. For the $\nu_1$ state, the reaction probabilities computed using the SRP functional, labelled by “SRP $V_0 +$ SRP couplings”, are much larger than those using the PBE functional, labelled by “PBE $V_0 +$ PBE couplings”, at low incident energies. This may result from the slightly larger nonadiabatic couplings and/or the deeper attractive well, which leads to larger molecular velocities and transition probabilities.

To disentangle these two effects, we consider two other cases in Figure 4.21: one with $V_0$ computed from the SRP functional but the couplings from the PBE functional (“SRP $V_0$
+ PBE couplings”), the other with $V_0$ from the PBE functional combined the SRP couplings ("PBE $V_0$ + SRP couplings"). For the $\nu_1$ state, the inclusion of the van der Waals well has a larger effect, as the reaction probability curves are similar for the “SRP $V_0$ + PBE couplings” and “SRP $V_0$ + SRP couplings” cases. For the ground state, both the deeper attractive well and the stronger couplings are important, and they increase $P_0$ at low incident energies but decrease the reactivity at high energies.

![Figure 4.21](image)

**Figure 4.21** Single-site rigid-lattice reaction probability, $P_0$, for C-H cleavage of CHD$_3$. The molecules are initially in the ground state or the $1\nu_1$ excited state. Results are shown for four combinations of couplings and MEPs.

In Figure 4.22, we plot $P_0$ for the two components of the CD$_3$ antisymmetric stretch state ($\nu_4$) and the CD$_3$ symmetric stretch state ($\nu_2$). Again, the reaction probabilities are computed for the four combinations of couplings and MEPs. We see similar behavior for
these states: both the increased molecular velocities due to the inclusion of the van der Waals interaction and the stronger nonadiabatic couplings boost the reactivity for the SRP results. The enhancement in $P_0$ with the SRP functional is larger for the CD$_3$ stretch states than the C-H stretch state and the ground state.

Figure 4.22 Single-site rigid-lattice reaction probability, $P_0$, for C-H cleavage of CHD$_3$. The molecules are initially in one component of the $\nu_4$ state or the $\nu_2$ state. Results are shown for four combinations of couplings and MEPs.

Finally, to compute the dissociative sticking probability, $S_0$, we average $P_0$ over all impact sites, correct the rotational treatment, and include the effects of lattice motion, using approaches described in Section 4.2. In Figure 4.23, we plot $S_0$ for CHD$_3$ dissociation on Pt(111) at 500 K. The total sticking probability is the sum over the four configurations, divided by four. We find that using the SPR functional leads to an increase in reactivity for
excited states and a slightly smaller $S_0$ for the ground state at high energies. Thus, the overall effect is to increase the vibrational efficacies for promoting reaction. This improves the agreement with experiment.

\[ \text{Figure 4.23} \] Dissociative sticking probabilities, $S_0$, for CHD$_3$ dissociation on Pt(111) at 500 K, computed using the SRP (solid lines) and PBE (dotted lines) functionals. The molecules are initially in the ground state or one of the single-quantum excited states.

In Figure 4.24, we compare our SRP-based RPH results with available experimental data and AIMD calculations using the SRP functional.$^{17}$ The “laser-off” $S_0$, labelled by “LO” in Figure 4.24, includes the contributions from vibrationally excited molecules. The agreement between experiment and the two theoretical models is very good, though our RPH $S_0$ for the $v_1$ state is about three times smaller than the experimental data at $E_i = 0.6$ eV.
Figure 4.24 Dissociative sticking probabilities, $S_0$, for CHD$_3$ dissociation on Pt(111) at 500 K. The RPH calculations are compared with the AIMD calculations and the experimental data from Ref. 17.

4.6 Conclusion

In this chapter, we examined the dissociative chemisorption of CH$_4$ on Pt(111). As we have observed in similar studies on Ni(111) in Chapter 3, excitation of the symmetric stretch has a larger vibrational efficacy for promoting reaction than exciting the antisymmetric stretch for the reasons discussed. The vibrational efficacies for the bending states are smaller than that for the symmetric stretch state, but similar to the antisymmetric stretch state.

The results for CH$_4$ dissociation on Pt(111) are compared with those on Ni(111). We find that the dissociative sticking probabilities at a given energy are larger on Pt(111) than on Ni(111), due to the smaller activation energies on Pt(111), while the vibrational
Efficacies are larger for reaction on Ni(111), because of the stronger nonadiabatic couplings on Ni(111) that mix the different vibrationally adiabatic states.

Our calculations show that the sticking probability increases strongly with increasing surface temperature at low incident energies, due to lattice motion that modifies the barrier for dissociation. On the other hand, at higher energies, the variation in $S_0$ with $T_s$ is small.

Finally, we compare the results computed using the SRP and PBE functionals. The SRP functional gives a deeper attractive well in the entrance channel, due to the inclusion of van der Waals interactions, and slightly larger nonadiabatic couplings, both of which increase the vibrational efficacies for promoting reaction.
4.7 References


CHAPTER 5
DISSOCIATIVE CHEMISORPTION OF METHANE ON STEPPED SURFACES

5.1 Introduction

While the dissociative chemisorption of methane on flat or low Miller index surfaces has been intensively studied both experimentally and theoretically, practical catalysts are likely to be atomically rough and have defect sites, such as steps and kinks, on the surface. Figure 5.1 shows the structures of various defect sites on a corrugated surface, described by the “terrace-ledge-kink” (TLK) model: the terraces are low index faces terminated by atomic steps (edges), while these steps consist of densely packed rows of atoms separated by monatomic kinks.

![Figure 5.1 Schematic representation of the terrace, step and kink sites on a vicinal surface.](image)

As the metal-metal coordination numbers of the step and kink atoms are different from that of the terrace atoms, reactions at these defect sites are expected to have different reactivity and dynamics. It is known that stepped surfaces are generally more reactive for
methane dissociation compared to flat surfaces.\textsuperscript{1–10} Abild-Pedersen \textit{et al.} reported an experimental and theoretical investigation of methane dissociation on the steps and terraces of a stepped Ni surface. They found the intrinsic sticking probability of methane on the steps to be two orders of magnitude higher than that on the terraces at 500 K, which is in good agreement with their calculated difference in activation energy of 17 kJ/mol.\textsuperscript{8} For Pt surfaces, Gee \textit{et al.} performed molecular beam experiments on a stepped Pt(533) surface, and found that the activation barrier to dissociation is about 0.3 eV lower on the steps than on the planar Pt(111) surface.\textsuperscript{9} The difficult part, when experimentally exploring the effect of step sites, is to distinguish between dissociation on steps and terraces. Recently, Chadwick \textit{et al.} used the reflection absorption infrared spectroscopy (RAIRS) technique to determine the site-resolved sticking probability on Pt(211), and found a difference in activation barrier of at least 30 kJ/mol between the step and terrace sites.\textsuperscript{1}

In addition to the activation energy, the details of the dissociation dynamics at steps can differ from that on terraces. In this chapter, we study the dissociative chemisorption of methane on the stepped Pt(211) and Ni(211) surfaces. We first locate the MEPs on these stepped surfaces, and then perform scattering calculations to examine the dynamics on the two surfaces.

\textbf{5.2 Computational Model and Electronic Structure Calculations}

The stepped (211) surface contains a three-atom wide (111) terrace and a (100) step. In our calculations, a four-layer 3×2 supercell with periodic boundary conditions is used to represent the Pt(211) surface as a series of infinite slabs (shown in Figure 5.2(A)). The Brillouin zone is sampled by an 8×6×1 Γ-centered grid of k points. However, we find that using a smaller 3×1 unit cell increases the barrier height by only 0.01 eV. To save
computational time, we use a four-layer $3 \times 1$ supercell and an $8 \times 8 \times 1$ k-point grid to model the Ni(211) surface (shown in Figure 5.2(B)). The vacuum spaces between the slabs are 18.2 Å and 16.1 Å for Pt(211) and Ni(211), respectively. For Pt(211), we use the PBE functional\textsuperscript{11,12} to locate the MEPs and the SRP functional\textsuperscript{2,13,14} to rescale the barrier heights. The two functionals give similar geometries but slightly different barrier heights. For Ni(211), electronic structure calculations are performed using the SRP functional. To account for the magnetic moment of nickel, we perform spin polarized calculations for Ni(211).

Before locating MEPs, we relax the two topmost metal layers. After surface relaxation, the step atoms move inward by 2.8 % and 4.3 %, while the corner atoms move outward by 1.2 % and 3.3 % for Ni(211) and Pt(211), respectively.

**Figure 5.2** Schematic presentation of the bare relaxed surfaces: (A) Pt(211), (B) Ni(211).
5.3 Adsorption of H and CH₃

We first examine the binding of the H and CH₃ product fragments on these two surfaces. The adsorption sites on the (211) surface are more complex than those on the high-symmetry (111) surface. We consider 14 sites on the surface (shown in Figure 5.3), including several unique top (t), bridge (b), fcc threefold hollow (fcc), and hcp threefold hollow (hcp) sites, and the fourfold hollow (h) site.

![Figure 5.3 Adsorption sites on the (211) surface. Only the topmost layer of the 3×2 unit cell is shown.]

For H adsorption, the adsorption energies $E_{ads}$, relative to the energy where the H atom is infinitely far from the surface, are summarized in Table 5.1. For Pt(211), binding is preferred on the bridge site along the step edge (b1), with an adsorption energy of -2.914 eV, 0.075 eV larger than the second most stable state (t1). We find that on Pt(211) adsorption at the step edge is strongly favored, and the PES for adsorption is more energetically corrugated for Pt(211) and Pt(100) compared to Pt(111). Our calculated adsorption energy for H on Pt(211) is consistent with that reported by Chen et al.
For H on Ni(211), the four threefold hollow sites (fcc1, fcc2, hcp1 and hcp2) have similar $E_{ads}$, with the hcp site near the step edge (hcp1) being slightly more stable, while binding on the bridge and top sites is much less favorable or even unstable, except for the bridge site along the step edge (b1). Similar behavior was found for Ni(111) and Ni(100): the hollow site is slightly preferred over the bridge site, with binding on the top site unstable by about 0.6 eV.\textsuperscript{15,16} Our results are in good agreement with other studies,\textsuperscript{17–20} including a theoretical study by Wang et al.,\textsuperscript{17} who found an adsorption energy of -2.84 eV for the most stable site (i.e., the hcp site) with the PBE functional.

According to previous studies,\textsuperscript{6,15,16,21} the methyl group binds preferentially on the top site of Pt surfaces, so we only examine the three top sites of the Pt(211) surface. At these top sites, the adsorption energy changes little for different orientations of the methyl group. The adsorption energies for the three Pt(211) top sites are listed in Table 5.2. Similar to H on Pt(211), the binding of CH$_3$ at the step edge is the most stable, with an adsorption energy of -2.174 eV, close to the energy reported by Chen et al.\textsuperscript{6}. Methyl adsorption on the terrace top site (t2) of Pt(211) is very similar to that on Pt(111). The binding strength of CH$_3$ on the top sites tends to decrease with the increase in coordination number of the Pt atom over which CH$_3$ adsorbs.

For methyl adsorption on Ni(211), we consider the same 14 adsorption sites as for H. The methyl group has a strong preference for the step bridge site, which is at least 0.2 eV more stable than other sites. The most stable site on the terrace of Ni(211) is the fcc site near the step edge, which is consistent with the binding of CH$_3$ on Ni(111). We find that the adsorption energy for the most stable site on Ni(211) is 0.33 eV larger than that on Ni(111). These results are in good agreement with other theoretical studies.\textsuperscript{17,18,20}
We find that the binding strength of H and CH₃ decreases with increasing coordination number of the metal atom over which the adsorbate adsorbs. This can be explained by the \( d \)-band model proposed by Hammer and Nørskov.\textsuperscript{22-24} According to their studies, the adsorbate-metal interaction includes two parts. First, the adsorbate \( s \) orbital interacts with the metal \( s \) band, forming a filled low-energy bonding orbital and an empty high-energy antibonding orbital. Second, the \( \sigma \) bonding orbital will further interact with the metal \( d \) band, which results in \( \sigma-d \) bonding and \( (\sigma-d)^* \) antibonding states, shown in Figure 5.4. The \( \sigma-d \) state is filled, while the degree of filling of the \( (\sigma-d)^* \) antibonding state depends on the electronic structure of the metal atom, and an increased filling of the \( (\sigma-d)^* \) state will destabilize the binding of H and CH₃. For a transition metal atom, a higher \( d \)-band center with respect to the Fermi level corresponds to a decrease in filling of the \( (\sigma-d)^* \) state and the stronger binding of H and CH₃. On the other hand, the \( d \)-band center increases with the decrease in coordination number of the metal atom.\textsuperscript{8,25} Thus, H and CH₃ binding on a step atom is more stable than that on a terrace atom.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_4.png}
\caption{Schematic illustration of the interaction between the \( \sigma \) bonding orbital and the metal \( d \) band.\textsuperscript{23}}
\end{figure}
Table 5.1 The adsorption energy $E_{ads}$, relative to the energy where the H atom is infinitely far from the surface, for H on Pt(211) and Ni(211). The lattice atoms are fixed at their bare relaxed surface positions. The results for H on Pt(111) and Ni(111) are also listed for comparison.

<table>
<thead>
<tr>
<th>$E_{ads}$ (eV)</th>
<th>Site</th>
<th>Pt(211)</th>
<th>Pt(111)</th>
<th>Ni(211)</th>
<th>Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SRP</td>
<td>PBE</td>
<td>SRP</td>
<td>PBE</td>
</tr>
<tr>
<td>t1</td>
<td></td>
<td>-2.839</td>
<td>-2.717</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t2</td>
<td></td>
<td>-2.789</td>
<td>-2.640</td>
<td>-2.832</td>
<td>-2.709</td>
</tr>
<tr>
<td>t3</td>
<td></td>
<td>-2.590</td>
<td>-2.481</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b2</td>
<td></td>
<td>-2.649</td>
<td>-2.591</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b4</td>
<td></td>
<td>-2.496</td>
<td>-2.459</td>
<td>-2.707</td>
<td>-2.666</td>
</tr>
<tr>
<td>b5</td>
<td></td>
<td>-2.632</td>
<td>-2.562</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b6</td>
<td></td>
<td>-2.612</td>
<td>-2.549</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc2</td>
<td></td>
<td>-2.563</td>
<td>-2.531</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hcp1</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-2.673</td>
<td>-2.663</td>
</tr>
<tr>
<td>hcp2</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-2.549</td>
<td></td>
</tr>
<tr>
<td>h1</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

*As these adsorption sites are metastable, we restrict the horizontal coordinates for H.*
Table 5.2 The adsorption energy $E_{ads}$, relative to the energy where CH$_3$ is infinitely far from the surface, for CH$_3$ on Pt(211) and Ni(211). The lattice atoms are fixed at their bare relaxed surface positions. The results for CH$_3$ on Pt(111) and Ni(111) are also listed for comparison.

<table>
<thead>
<tr>
<th>$E_{ads}$ (eV)</th>
<th>Pt(211)</th>
<th>Pt(111)</th>
<th>Ni(211)</th>
<th>Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>SRP</td>
<td>PBE</td>
<td>SRP</td>
<td>PBE</td>
</tr>
<tr>
<td>t1</td>
<td>-2.174</td>
<td>-2.113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t2</td>
<td>-2.014</td>
<td>-1.842</td>
<td>-2.073</td>
<td>-1.944</td>
</tr>
<tr>
<td>t3</td>
<td>-1.277</td>
<td>-1.160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b1</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b4</td>
<td>-</td>
<td>-</td>
<td>-1.329 $^a$</td>
<td>-1.329 $^a$</td>
</tr>
<tr>
<td>b5</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fcc1</td>
<td>-</td>
<td>-</td>
<td>-1.225</td>
<td>-1.278</td>
</tr>
<tr>
<td>hcp1</td>
<td>-</td>
<td>-</td>
<td>-1.162</td>
<td>-1.188</td>
</tr>
</tbody>
</table>

$^a$ As these adsorption sites are metastable, we restrict the horizontal coordinates for the carbon atom.

5.4 Reaction Paths and Transition States on Pt(211) and Ni(211)

We use the CI-NEB$^{26}$ and NEB$^{27}$ methods to locate MEPs and TSs on Pt(211) and Ni(211). The lattice atoms are fixed at their bare relaxed surface positions, and the energies are considered converged when all forces are smaller than 0.01 eV/Å. Our zero of energy corresponds to the gas phase molecule far above the bare relaxed surface. For a given
surface, the reactant state is the same for all reaction paths, with the methane molecule far above the surface.

We have located four MEPs on Pt(211): dissociation along the step edge (path N), dissociation across the step edge (paths M and L), and dissociation over a terrace atom. The corresponding TS configurations are shown in Figure 5.5. At these TSs, the carbon atom is roughly over the top site with the dissociating H atom angled toward the surface. For the N transition state, the carbon atom is over an edge atom and the dissociating C-H bond is oriented parallel to the step edge. The M and L transition states have similar geometries, except that the dissociating bond is oriented perpendicular to the edge with the reactive H atom toward the (111) terrace for the M path and toward the (100) step for the L path. These two geometries allow the molecule to get closer to the surface and the reactive C-H bond to be more stretched. The terrace TS geometry is very similar to that on Pt(111), taking into account the angle between the (211) surface and the (111) terrace, with the dissociating bond being more stretched than the N transition state but less stretched than the M and L transition states.

Details on the TS geometries and energies are reported in Table 5.3. Among these four MEPs, the lowest barrier is along the N path, consistent with the strong binding of CH$_3$ on the step top site and H on the step bridge site. As shown in Table 5.3, the activation energy for this path is only 0.435 eV. The activation energy for dissociation on the terrace sites is 0.872 eV, 0.437 eV higher than that of the N path on the step sites. This is consistent with the experimental observation that the difference in the activation barrier is at least 30 kJ/mol (0.31 eV) between the step and terrace sites.$^1$ For the corner sites, the CH$_3$ binding energy is only -1.28 eV, and we estimate the barrier height to be 1.92 eV, with the carbon
atom restricted over a Pt(211) corner atom. Thus, dissociation is not likely to occur at the corner sites under most experimental conditions, and we expect that the N path will dominate the total sticking on Pt(211) except at the highest energies.

The barrier to dissociation decreases with the increase in binding strength of the product fragments. Again, this can be explained in terms of the $d$-band theory.\textsuperscript{22–24} As CH$_4$ approaches the surface, the interaction with the metal $s$ and $p$ states gives rise to a shift in the CH$_4$ bonding and antibonding orbitals, and the new orbitals further interact with the metal $d$ band, forming the $\sigma$-$d$ and $(\sigma$-$d)^*$ states. The step atom has a higher $d$-band center with respect to the Fermi level, corresponding to a decrease in filling of the $(\sigma$-$d)^*$ antibonding state and a lower barrier height.\textsuperscript{8,25}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{transition_state_configurations.png}
\caption{Transition state configurations for the dissociation of CH$_4$ on Pt(211). Only three rows of the topmost metal layer are shown. The geometries are optimized with the PBE functional. The barrier height $E_b$ is given for each configuration.}
\end{figure}
Table 5.3 Transition state data for methane dissociation on Pt(211) and Pt(111). For TSs on the step sites of Pt(211), $Z_C^\ddagger$ is the distance from the carbon atom to the (211) surface through the step edge; for Pt(111) and the terrace sites of Pt(211), it is the distance from the carbon atom to the Pt atom directly below it. $r^\ddagger$ and $\theta^\ddagger$ are the length of the dissociating bond and its angle relative to the surface normal, respectively. $E_b$ is the barrier height relative to the methane molecule infinitely far above the surface, and the activation energy $E_a$ is $E_b$ with zero point energy (ZPE) corrections. All calculations are for the PBE functional, except for $E_a^{SRP}$, the activation energy using the SRP functional.

<table>
<thead>
<tr>
<th></th>
<th>$Z_C^\ddagger$ (Å)</th>
<th>$r^\ddagger$ (Å)</th>
<th>$\theta^\ddagger$ (°)</th>
<th>$E_b$ (eV)</th>
<th>ZPE (eV)</th>
<th>$E_a$ (eV)</th>
<th>$E_a^{SRP}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(211), N</td>
<td>2.242</td>
<td>1.480</td>
<td>133.6</td>
<td>0.477</td>
<td>-0.103</td>
<td>0.374</td>
<td>0.435</td>
</tr>
<tr>
<td>Pt(211), M</td>
<td>2.157</td>
<td>1.608</td>
<td>122.0</td>
<td>0.557</td>
<td>-0.076</td>
<td>0.481</td>
<td>0.484</td>
</tr>
<tr>
<td>Pt(211), L</td>
<td>2.175</td>
<td>1.654</td>
<td>124.3</td>
<td>0.643</td>
<td>-0.089</td>
<td>0.554</td>
<td>0.567</td>
</tr>
<tr>
<td>Pt(211), terr</td>
<td>2.254</td>
<td>1.525</td>
<td>129.4</td>
<td>1.044</td>
<td>-0.109</td>
<td>0.935</td>
<td>0.872</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>2.241</td>
<td>1.521</td>
<td>131.7</td>
<td>0.815</td>
<td>-0.117</td>
<td>0.698</td>
<td>0.705</td>
</tr>
</tbody>
</table>

* For the terrace TS, $\theta^\ddagger$ is the angle of the dissociating bond relative to the (111) surface normal.

For methane dissociation on Ni(211), we have characterized three MEPs: dissociation along the step edge (path Q), dissociation across the edge (path P), and dissociation over a terrace atom. Figure 5.6 shows the corresponding TS configurations. The results for the TS geometries and energies are summarized in Table 5.4. The lowest energy TS on Ni(211) (along the Q path) is very similar to that on Pt(211), with the carbon atom roughly over an edge atom and the dissociating bond parallel to the edge, but the activation energy is larger on Ni(211) by about 0.26 eV, due to the stronger attractive forces on the top site for the Pt surfaces relative to the Ni surfaces. For the Q path, as the bond breaks, both H and CH$_3$ move to their most stable sites, i.e., the hcp1 site and the step bridge site. This TS geometry is very similar to that reported by Abild-Pedersen et al., in which a 2×1 unit cell is used,
and the topmost layer and the adsorbates are allowed to relax during geometry optimization. However, our barrier height is about 0.3 eV lower than their results. This discrepancy is due to their use of a smaller supercell, which leads to higher repulsion between two neighboring adsorbates at the TS. Other DFT studies by Xu et al.,\textsuperscript{18} using a 3×1 unit cell, and by Wang et al.,\textsuperscript{17} using a 4×1 unit cell, found the barrier heights to be 0.62 and 0.61 eV, respectively, when the two topmost substrate layers are allowed to relax. These results are consistent with our relaxed-surface barrier height of 0.62 eV for the Q path (not shown). In addition, different functionals can also contribute to the variation in energy.

Figure 5.6 Transition state configurations for the dissociation of CH\textsubscript{4} on Ni(211). Only the topmost metal layer is shown. The geometries are optimized with the SRP functional. The barrier height $E_b$ is given for each configuration.
Table 5.4 Transition state data for methane dissociation on Ni(211) and Ni(111). For TSs on the step sites of Ni(211), $Z_C^\ddagger$ is the distance from the carbon atom to the (211) surface through the step edge; for Ni(111) and the terrace sites of Ni(211), it is the distance from the carbon atom to the Ni atom directly below it. $r^\ddagger$ and $\theta^\ddagger$ are the length of the dissociating bond and its angle relative to the surface normal, respectively. $E_b$ is the barrier height relative to the methane molecule infinitely far above the surface, and the activation energy $E_a$ is $E_b$ with zero point energy (ZPE) corrections. All calculations are for the SRP functional.

<table>
<thead>
<tr>
<th></th>
<th>$Z_C^\ddagger$ (Å)</th>
<th>$r^\ddagger$ (Å)</th>
<th>$\theta^\ddagger$ (°)</th>
<th>$E_b$ (eV)</th>
<th>ZPE (eV)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(211), P</td>
<td>2.048</td>
<td>1.652</td>
<td>133.1</td>
<td>0.835</td>
<td>-0.144</td>
<td>0.691</td>
</tr>
<tr>
<td>Ni(211), Q</td>
<td>2.033</td>
<td>1.632</td>
<td>126.0</td>
<td>0.699</td>
<td>-0.127</td>
<td>0.572</td>
</tr>
<tr>
<td>Ni(211), terr</td>
<td>2.199</td>
<td>1.651</td>
<td>135.3$^a$</td>
<td>1.129</td>
<td>-0.135</td>
<td>0.994</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>2.168</td>
<td>1.634</td>
<td>134.7</td>
<td>1.022</td>
<td>-0.134</td>
<td>0.888</td>
</tr>
</tbody>
</table>

$^a$ For the terrace TS, $\theta^\ddagger$ is the angle of the dissociating bond relative to the (111) surface normal.

For the P path, the reactive H atom dissociates toward the (111) terrace, with an activation energy of 0.69 eV, 0.12 eV higher than that of the lowest barrier path. On Ni(211), we are not able to locate the TS for dissociation on the step sites with the reactive H toward the (100) step, similar to the L transition state on Pt(211). The corresponding product state has a high energy of 0.48 eV, consistent with the weak binding of H on the bridge site (b3).

For methane dissociation on the terrace sites, the activation energy is 0.44 eV larger than that for the lowest barrier path on the step edge. Thus, reactivity on Ni(211) is dominated by dissociation on the step sites.
Finally, we note that the reactive C-H bond lengths at the TS are similar for all paths on Ni(211), except a slightly smaller value for the Q path, and all of them are larger than those on Pt(211), if the same functional is used.

5.5 Scattering Dynamics for Methane Dissociation on Pt(211)

We use our RPH-based approach, described in Chapter 2, to perform scattering calculations for the dissociative chemisorption of methane on Pt(211). In Figure 5.7, we plot the total energy, $V_0(s)$, along the L and N paths on Pt(211) and along the MEP on Pt(111), as a function of the distance along the path, $s$, where $(ds)^2 = \sum_{i=1}^{15} (d\alpha_i(s))^2$, with $s = 0$ at the TS, and the $\{\alpha_i(s)\}$ are the mass-weighted Cartesian coordinates of the molecule at a point $s$. The MEP on the Pt(211) terrace is very similar to that on Pt(111), except for a higher barrier height, while the M path has a similar PES to the L path.

![Figure 5.7](image)

**Figure 5.7** Reaction paths for CH$_4$ dissociation on Pt(211) and Pt(111), using the PBE functional.
5.5.1 Normal Mode Analysis

We diagonalize the force-projected Hessian to find the fourteen normal modes and corresponding frequencies $\omega_k(s)$ that describe motion orthogonal to the reaction path in the harmonic approximation. In Figure 5.8, we plot $\hbar \omega_k(s)$ along the L (left panel) and N (right panel) paths on Pt(211). Note that the L path is symmetric with respect to reflection through a plane perpendicular to the step edge and including the reactive bond. Thus, the fourteen normal modes are either symmetric (A') or antisymmetric (A'') with respect to this reflection. We label the A’ modes 1’-8’ and the A’’ modes 1’’-6’’. The nonadiabatic coupling is only nonzero between two modes of the same symmetry. There is no symmetry in the N path, and the nonadiabatic coupling is in general nonzero. We label the fourteen modes 1-14 for the N path.

![Figure 5.8](image)

Figure 5.8 Energies of the normal modes for the L (left panel) and N (right panel) paths on Pt(211). Results are computed using the PBE functional.

As discussed in previous chapters, the vibrational efficacy is affected by mode-softening and nonadiabatic couplings. Mode softening lowers the adiabatic barrier for dissociation. As shown in Table 5.3, mode softening is slightly larger for reaction on the
terraces than on the steps. For nonadiabatic couplings, the so-called Coriolis couplings, $B_{q,k}$, which are responsible for transitions between vibrationally adiabatic states, are more important than the curvature couplings, $B_{q,15}$. In Figure 5.9, we plot the $B_{q,k}$ couplings for the L (left panel) and N (right panel) paths on Pt(211), as well as for the MEP on Pt(111) for comparison. The magnitude of the $B_{q,k}$ couplings is similar for dissociation on the step sites of Pt(211) and on Pt(111), which leads to similar nonadiabatic transition amplitudes. Considering these two factors, we expect to see slightly larger vibrational efficacies on the terrace sites.

![Figure 5.9](image)

**Figure 5.9** $B_{q,k}$ couplings for the L (left panel) and N (right panel) paths on Pt(211). Results are computed using the PBE functional.

### 5.5.2 Rotational Treatment and Impact Site Averaging

To compute the dissociative sticking probability $S_0$, we average the single-site reaction probability $P_0$ over all reaction pathways and impact sites, and correct the
rotational treatment. We first divide the Pt(211) surface into three regions: the step region, the terrace region and the corner region. For each region, we average $P_0$ over impact sites within a unit region shown in Figure 5.10. Motion along X and Y is slow on collision time scales, given the relatively large molecular mass and the normal incident conditions. Assuming no translational steering, we use the sudden model with the “energy-shifting” approximation, given by Eq. 2.23, to approximate $P_0$ at other impact sites close to the minimum barrier sites. The increase in barrier height relative to the minimum barrier sites, $\Delta V(X,Y)$, is computed by re-locating the TS with the x and y coordinates of the carbon atom fixed at several impact sites (X, Y). Table 5.5 lists the calculated results in terms of $\hbar \Omega_x$ and $\hbar \Omega_y$ for impact sites near the minimum barrier sites on Pt(211), where the frequencies $\Omega_x$ and $\Omega_y$ satisfy $\Delta V(X,Y) = \frac{1}{2}M\Omega_x^2\Delta X^2 + \frac{1}{2}M\Omega_y^2\Delta Y^2$, and the molecule is translated by $(\Delta X, \Delta Y)$ at the TS.

**Figure 5.10** Unit regions for averaging over impact sites near the step, terrace, and corner atoms on Pt(211).
Table 5.5 The increase in barrier height relative to the minimum barrier sites on Pt(211). Results are reported in terms of $\hbar\Omega_{X}$ and $\hbar\Omega_{Y}$, where the frequencies $\Omega_{X}$ and $\Omega_{Y}$ satisfy

$$
\Delta V(X,Y) = \frac{1}{2} M \Omega_{X}^2 \Delta X^2 + \frac{1}{2} M \Omega_{Y}^2 \Delta Y^2,
$$

and the molecule is translated by $(\Delta X, \Delta Y)$ at the TS.

<table>
<thead>
<tr>
<th></th>
<th>Pt(211), L</th>
<th>Pt(211), M$^a$</th>
<th>Pt(211), N</th>
<th>Pt(211), Terrace/Pt(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hbar\Omega_{X}$ (eV)</td>
<td>0.0144</td>
<td>0.0144</td>
<td>0.0158</td>
<td>0.0121</td>
</tr>
<tr>
<td>$\hbar\Omega_{Y}$ (eV)</td>
<td>0.0108</td>
<td>0.0108</td>
<td>0.0081</td>
<td>0.0159</td>
</tr>
</tbody>
</table>

$^a$ For the M path, we use the L path results.

This approach is used to average $P_0$ over impact sites within the terrace region. For the step region, we need to consider different reaction pathways. The three lowest energy TSs differ with respect to the azimuthal orientation of the reactive C-H bond, described by the $\phi$ angle. We break up the step region into sub-regions by dividing $\phi$ into sub-regions corresponding to the L, M, and N paths, and a similar approach is used to average $P_0$ over impact sites and $\phi$ within each sub-region. For the corner region, given the high barrier height, we assume that it contributes nothing to the total $S_0$. This is consistent with the experimental observation that only two peaks, rather than three, in the C-H stretch region of the RAIRS spectrum are detected.$^1$

The polar orientation of the reactive bond relative to the surface normal, described by the $\theta$ angle, is treated adiabatically in our $P_0$ calculations. This adiabatic treatment is reasonable at lower incident energies, given the relatively small moment of inertia. However, at higher energies the rotational dynamics might be closer to sudden.$^{28}$ We thus estimate $S_0$ in the sudden limit using the approach described in Chapter 2, and define our $S_0$ as an average of these two limiting cases. The parameters for averaging are chosen so
that the total sticking probability has 90% adiabatic behavior at 0.2 eV and 90% sudden behavior at 0.9 eV.

5.5.3 Effects of Lattice Motion

As noted in Chapter 2, we use the sudden model to treat the effects of lattice motion, given the large mass of the metal atoms and the short collision time. Lattice vibration can change the height of the barrier to dissociation. On the Pt(211) terrace, like the (111) and (100) surfaces,29,30 this effect is mostly confined to the motion of the lattice atom over which the methane dissociates, and this motion is normal to the (111) terrace. On the step edge, the motion of the metal atom right below the methane also most strongly modifies the barrier, but the direction is away from the surface normal. The motion of other atoms can also change the barrier height, but their contributions are small. For both step and terrace atoms, we define \( Q \) as the displacement of the metal atom over which the methane dissociates, in the direction of the motion that most strongly changes the barrier height, and \( Q > 0 \) for motion away from the bulk. As the lattice atom vibrates, the height of the barrier to dissociation changes by an amount of \( -\beta Q \). Note that for step atoms this \( \beta \)-type coupling arises from lattice motion with components both perpendicular to and lateral to the (211) surface. Figure 5.11 shows the directions and magnitudes of the largest of the \( \beta \)-type couplings for the TSs on the step sites. For the terrace atoms, we use the same \( \beta \) value of 0.95 eV/Å obtained for Pt(111).31
Figure 5.11 Transition states for the dissociation of methane on the Pt(211) step sites. Only three rows of the topmost metal layer are shown. The arrows indicate the directions and magnitudes of the largest of the $\beta$-type couplings, in units of eV/Å.

For a given surface temperature $T_s$, we average $S_0$ over the displacement $Q$, using the Debye model described in Chapter 2. To do this, we need to know the root-mean-square displacement $Q_{rms}$. For the Pt(111) surface, this value is obtained from surface scattering experiments, but such data is not available for Pt(211). We thus perform AIMD calculations to compute $Q_{rms}$ at 300 K, and find $Q_{rms} = 0.109$ Å for the motion of the terrace atom in the direction normal to the (111) terrace. For the step atom, we find a value of 0.099 Å in the direction normal to the (211) surface. Our total energy calculations suggest that this value is very similar to those in the directions of the largest $\beta$-couplings. As the $Q_{rms}$ values for the step and terrace atoms on Pt(211) are close to the value of 0.104 Å on Pt(111) at 300 K, we use the Pt(111) Debye temperature of 140 K$^{32,33}$, extracted from experiments, to compute $Q_{rms}$ on Pt(211) at a given $T_s$.

Lattice vibration also modifies the location of the TS along $Z$ by an amount of $\alpha Q_Z$. We find $\alpha = 0.8379$ and 0.8993 for the L and N paths, respectively. The modified Surface Mass Model (SMM)$^{29,30,34,35}$ is used to include this effect.
5.5.4 Dissociative Sticking Probability for CH$_4$ on Pt(211)

Figure 5.12 shows the contributions to the total sticking from the four reaction pathways on Pt(211) at $T_s = 120$ K. For molecules initially in the ground state, the dissociative sticking probability for the N path is an order of magnitude larger than that for any other path, except at the highest energies. The enhancement in reactivity by excitation of the antisymmetric stretch ($1\nu_3$) is largest for the L and M paths and for dissociation on the terrace sites, consistent with the reactive C-H bond being more stretched at the TS.

![Graph showing computed contributions to the total dissociative sticking probability of methane from the L, M, N and terrace (T) paths. Results are shown for methane initially in the ground state (gs) or the $1\nu_3$ excited state at $T_s = 120$ K, using the PBE functional.]

The dissociative sticking probability computed using the PBE functional is in good agreement with experiment. To further improve the agreement, we rescale the barrier heights to the SRP values. The SRP functional gives larger activation energies for all paths on the step edge, but a smaller value on the terrace site (shown in Table 5.3). The inclusion of van der Waals forces in the SRP functional also leads to a deeper physisorption well and
slightly larger nonadiabatic couplings in the entrance channel, which might affect $S_0$ for both ground-state and excited molecules. However, we do not include this effect in this study. In addition, we find that on Pt(111) the SRP functional gives stronger nonadiabatic couplings in the entrance channel, and thus enhances the reactivity for excited states. Similarly, the computed couplings on Pt(211) might also be larger from the SRP functional.

In Figure 5.13, the computed $S_0$ for molecules initially in the ground state (gs) and the $1\nu_3$ excited state are compared with experimental results. The agreement between theory and experiment for dissociation on the step sites is very good. Our calculations reproduce the ground state $S_0$ and the vibrational efficacy for the $1\nu_3$ state measured in experiments. The vibrational efficacy for the $1\nu_3$ state is defined by

$$\eta_{\nu_3} = \frac{E_k(\text{laser-off}, S_0) - E_k(\nu_3, S_0)}{\Delta E_{\nu_3}}$$

where the numerator is the increase in collision energy necessary to give the same $S_0$ as increasing the vibrational energy by $\Delta E_{\nu_3}$. The computed efficacies typically vary with $S_0$. We find $\eta_{\nu_3}(\text{step}) = 0.50$ at $S_0 = 3 \times 10^{-3}$ and $\eta_{\nu_3}(\text{step}) = 0.37$ at $S_0 = 10^{-1}$ for the step sites, consistent with the experimental value $\eta_{\nu_3}(\text{step}) = 0.45$.

For the terrace sites, the agreement is less good. However, the experimental $S_0(\text{terr})$ is estimated using the same RAIRS conversion factor obtained for Pt(111), because it is not possible to calibrate $S_0$ on the terrace sites. It is possible that the transition dipole moment is different for the symmetric stretch of CH$_3$ on these two sites. If the experimental $S_0(\text{terr})$ is rescaled by a factor of 0.3, the agreement improves significantly. The computed vibrational efficacies for the terrace sites are $\eta_{\nu_3}(\text{terr}) = 0.53$ at $S_0 = 10^{-4}$ and $\eta_{\nu_3}(\text{terr}) = 0.55$ at $S_0 = 7 \times 10^{-5}$, in good agreement with the experimental value of 0.59.
5.6 Scattering Dynamics for Methane Dissociation on Ni(211)

We use a similar approach with the SRP functional to compute the dissociative sticking probability for CH$_4$ on Ni(211). Figure 5.14 shows the total energy $V_0(s)$, along the two MEPs on the step sites, as a function of $s$, the distance along the path. The Q path is both thermodynamically and kinetically favored. However, the motion of the methyl group during the reaction, due to the strong preference for CH$_3$ binding on the step bridge site, decreases the tunneling probability for this path relative to the P path, where the methyl group binds on the step top site. For both paths, the inclusion of van der Waals forces in the SRP functional gives a physisorption well depth of about 0.2 eV in the entrance channel. As noted, the activation energy for the lowest energy path is 0.26 eV larger on Ni(211) than on Pt(211), using the SRP functional.
Figure 5.14 Reaction paths for methane dissociation on Ni(211) using the SRP functional.

5.6.1 Normal Mode Analysis

We compute and diagonalize the force-projected Hessian to find the fourteen normal coordinates $Q_k$ and corresponding frequencies $\omega_k(s)$ describing displacements orthogonal to the reaction path in the harmonic approximation. In Figure 5.15, we plot $\hbar \omega_k(s)$ along the P (left panel) and Q (right panel) paths on Ni(211). The P path, with CH$_4$ dissociating across the step edge, is symmetric with respect to reflection through a plane perpendicular to the edge and including the reactive bond. We label the symmetric modes 1’-8’ and the antisymmetric modes 1”-6”. The Q path has no symmetry, and the nonadiabatic coupling is in general nonzero. We label the fourteen modes 1-14.
Figure 5.15 Energies of the normal modes for the P (left panel) and Q (right panel) paths on Ni (211). Results are computed using the SRP functional.

Due to mode softening of the $v_1$ symmetric stretch mode and some of the bending modes, ZPE corrections lower the activation energy in the adiabatic limit. This softening is slightly larger for the P path than the Q path, but the difference is only 0.017 eV. Like the Pt(111) and Ni(111) surfaces, mode softening is stronger on Ni(211) than on Pt(211), consistent with the reactive C-H bond being more stretched at the TS on Ni(211). For the P path, we find that the 3’ mode, correlated adiabatically with the symmetric stretch, evolves from a nonlocal mode into vibration entirely localized on the reactive bond. Similar behavior has been observed for the Q path on Ni(211) and the MEPs on Pt(211). Thus, stronger reactive bond softening on the Ni surfaces leads to a stronger softening of the 3’ mode before $s = -0.7$ amu$^{1/2}$/Å, compared to the Pt surfaces. At $s = -0.7$ amu$^{1/2}$/Å, the 3’ mode exchanges character with the 4’ mode, and the 4’ mode becomes the softened C-H stretch between $s = -0.7$ to -0.5 amu$^{1/2}$/Å. This character-exchange behavior occurs at the avoided crossings. Thus, reactive C-H bond softening also results in mode softening of the lower-frequency modes correlated adiabatically with the bending modes.
On the other hand, as shown in Figure 5.16, the $B_{q,k}$ coupling is a bit stronger for the Q path than the P path in the curve-crossing region. This coupling leads to nonadiabatic transitions from one vibrationally adiabatic state to another of lower energy, and can explain the relatively large vibrational efficacy for the $\nu_1$ symmetric stretch.

![Figure 5.16](image)

**Figure 5.16** $B_{q,k}$ couplings for the P (left panel) and Q (right panel) paths in curve-crossing region on Ni(211). Results are computed using the SRP functional.

In addition, we find that the $B_{q,k}$ coupling in the entrance channel is responsible for the large vibrational efficacy observed for the triply degenerate antisymmetric stretch ($\nu_3$) state on the step sites of Ni(211). In our previous studies of methane dissociation on the Ni(111) and Pt(111) surfaces,$^{31,37}$ only the $B_{q,k}$ coupling between the $\nu_1$ state and one component of the $\nu_3$ state (i.e., the 2' state for symmetric MEPs or the state 3 for asymmetric MEPs) is relatively strong in the entrance channel. Thus, only this component is very reactive, comparable to the $\nu_1$ state. On the step sites of Pt(211), there are nonzero
couplings between different $\nu_3$ components, but they have little effect on the vibrational efficacy.

For the Q path on Ni(211), as shown in the right panel of Figure 5.17, we find strong couplings between some components of the $\nu_3$ state, and the components are mixed by these couplings as the molecule approaches the surface. Similar behavior has been observed for the P path, except that the 1” mode does not couple to any symmetric mode. As shown in Figure 5.18, these strong couplings result in large reaction probabilities for the antisymmetric stretch states, with the state 2, instead of the state 3 observed for other surfaces, being the most reactive state. In the left panel of Figure 5.17, we illustrate how these couplings affect the reaction probabilities for the $\nu_3$ components by plotting the state-resolved reaction probabilities along the Q MEP in the entrance channel. Results are shown for molecules initially in the state 2 with a collision energy of 0.9 eV. To remove the scattered wave from the total wave (incident wave + scattered wave), we set an optical potential at $s = -3.0$ amu$^{1/2}$/Å to absorb the scattered wave. We find that most of the molecules in the state 2 can transition to the state 3 through the strong nonadiabatic coupling $B_{2,3}$ around $s = -7.0$ amu$^{1/2}$/Å, then transition to the state 4, and so on, following the reactive channel. However, only a small amount of molecules transition to the state 1, because the coupling $B_{1,2}$ is small before $B_{2,3}$ reaches the largest value. Thus, only about 1% molecules stay on the less reactive trajectory along the adiabatic PES for the state 1.
Figure 5.17 Left panel: state-resolved reaction probabilities along the Q MEP in the entrance channel. Results are shown for molecules initially in the state 2 with a collision energy of 0.9 eV. Right panel: $B_{q,k}$ couplings for the Q path in the entrance channel on Ni(211). All the results are computed using the SRP functional.

Figure 5.18 Single-site rigid-lattice reaction probabilities for the P (left panel) and Q (right panel) paths on Ni(211). Results are shown for molecules initially in the ground state (gs), and the $v_1$ and $v_3$ excited states, using the SRP functional.
5.6.2 Dissociative Sticking Probability for CH$_4$ on Ni(211)

We use similar approaches to those for Pt(211) to average the single-site rigid-lattice reaction probability $P_0$ over all reaction pathways and impact sites, correct the rotational treatment, and include the effects of lattice motion. To average over impact sites close to each minimum barrier site, we compute the increase in barrier height relative to the minimum barrier site, $\Delta V(X,Y)$. Table 5.6 lists the results in terms of $\hbar \Omega_X$ and $\hbar \Omega_Y$ on Ni(211). For the step region, we average over two MEPs, assuming that the dissociation of methane with H moving toward the (100) step contributes nothing to the total $S_0$. For the rotational treatment, we define $S_0$ as an average of two limiting cases: the adiabatic limit and the sudden limit. For Ni(211), the total sticking probability has 90% adiabatic behavior at 0.2 eV and 90% sudden behavior at 1.1 eV.

Table 5.6 The increase in barrier height relative to the minimum barrier sites on Ni(211). Results are reported in terms of $\hbar \Omega_X$ and $\hbar \Omega_Y$, where the frequencies $\Omega_X$ and $\Omega_Y$ satisfy $\Delta V(X,Y) = \frac{1}{2} M \Omega_X^2 \Delta X^2 + \frac{1}{2} M \Omega_Y^2 \Delta Y^2$, and the molecule is translated by $(\Delta X, \Delta Y)$ at the TS.

<table>
<thead>
<tr>
<th></th>
<th>Ni(211), P</th>
<th>Ni(211), Q</th>
<th>Ni(211), Terrace/Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hbar \Omega_X$ (eV)</td>
<td>0.0096</td>
<td>0.0175</td>
<td>0.0184</td>
</tr>
<tr>
<td>$\hbar \Omega_Y$ (eV)</td>
<td>0.0087</td>
<td>0.0049</td>
<td>0.0186</td>
</tr>
</tbody>
</table>

Finally, we introduce the effects of lattice motion, using the Debye model with a Debye temperature of 280 K$^{38}$. Lattice vibration modifies the barrier height by an amount $\beta Q$ and the location of the TS along $Z$ by an amount $\alpha Q_Z$. We find $\beta = 0.621$ and 0.833 eV/Å for the P and Q paths, respectively. The modified SMM is used to treat the $\alpha$-type
coupling, with $\alpha = 0.811$ and 0.880 for the P and Q paths. For dissociation on the terrace sites, we estimate $S_0$ (terr) by shifting the Ni(111) sticking curves to higher $E_i$ by the differences in activation energy.

Figure 5.19 shows the contributions to the dissociative sticking probability from the three reaction pathways on Ni(211) at $T_s = 500$ K. The total $S_0$ for the ground state is dominated by dissociation on the step sites except at the highest energies, due to the lower activation energy compared to the terrace sites. Excitation of either the symmetric or antisymmetric stretch promotes reaction at all energies. We find that the $v_3$ state has a high vibrational efficacy on Ni(211), similar to that for the $v_1$ state, due to the strong nonadiabatic couplings. The ground state reactivity is higher on Pt(211) than on Ni(211), while the vibrational efficacies are larger on Ni(211).

**Figure 5.19** Computed contributions to the total dissociative sticking probability of methane from the P, Q and terrace (T) paths. Results are shown for the ground state (gs), and two excited states at $T_s = 500$ K.
As noted, Abild-Pedersen et al. performed molecular beam experiments at 500 K for methane dissociation on a stepped Ni(14 13 13) surface, using ultra high vacuum (UHV) techniques.\(^8\) To distinguish between sticking on the step and terrace atoms, they blocked the step sites with sulfur, and measured \(S_0\) for the terrace sites. The sticking probability for the steps is obtained by subtracting \(S_0\) (terrace) from the total sticking probability. Their measurements correspond to both incident-energy-averaged and vibrational-state-averaged sticking probabilities.

To compare with their experiments, we average our energy-resolved and state-resolved sticking probability, \(S_0(E_i, \nu_k)\), over incident energies and vibrational states, assuming a thermal distribution of molecules in different initial vibrational states, to compute the averaged sticking probability, \(<S_0>\),

\[
<S_0> = \frac{1}{kT} \int_0^\infty \left( \sum_{\nu_k} P_{\nu_k} S_0(E_i, \nu_k) \right) e^{-\frac{E_i}{kT}} dE_i \tag{5.2}
\]

where \(P_{\nu_k}\) is the fraction of beam molecules in the \(\nu_k\) state at a nozzle temperature \(T_{\text{nozzle}}\). In this case, we assume \(T_{\text{nozzle}} = T = 500\) K. The fraction \(P_{\nu_k}\) is given by

\[
P_{\nu_k} = \frac{e^{-\frac{\epsilon_k}{kT_{\text{nozzle}}}}}{\sum_{\nu_j} e^{-\frac{\epsilon_j}{kT_{\text{nozzle}}}}} \tag{5.3}
\]

where \(\epsilon_k\) is the vibrational energy for the \(\nu_k\) state.

The computed \(<S_0>\) for CH\(_4\) dissociation at the step site is \(1.04 \times 10^{-6}\), about four times larger than the experimental value of \(2.8 \times 10^{-7}\), reported by Abild-Pedersen et al.\(^8\) For the terrace site, the computed \(<S_0>\) on the (211) terrace is \(1.04 \times 10^{-9}\), less than the experimental value of \(2.1 \times 10^{-9}\) for the Ni(14 13 13) terrace.\(^8\) This is because the Ni(14 13 13) surface has a wider terrace compared with Ni(211). Thus, the activation energy on
the Ni(14 13 13) terrace is lower than that on the Ni(211) terrace, but higher than the Ni(111) surface. As expected, the computed $< S_0 >$ on Ni(111) is $1.3 \times 10^{-8}$, larger than the experimental $< S_0 >$ for the Ni(14 13 13) terrace.

5.7 Conclusion

In this Chapter, we have examined the dissociative chemisorption of CH$_4$ on the stepped Pt(211) and Ni(211) surfaces. We have located four and three MEPs on Pt(211) and Ni(211), respectively, including dissociation along the step edge, dissociation across the step edge, and dissociation over a terrace atom. For both step and terrace sites, methane dissociates over a top site, producing chemisorbed H and CH$_3$ fragments. On both surfaces, dissociation along the step edge dominates the total sticking at all but the highest energies. The ZPE-corrected barrier heights corresponding to this MEP are 0.435 and 0.691 eV on Pt(211) and Ni(211), respectively, about 0.3 - 0.4 eV lower than those for the terrace sites, consistent with the binding of CH$_3$ and H being more stable at the step edge. This is because the $d$-band center of a step atom is closer to the Fermi level. Thus, the degree of filling of the antibonding state, arising from the interaction between the CH$_4$ $\sigma$ bonding orbital and the metal $d$ band, and the barrier to dissociation is lower for the step sites than the terrace sites. Dissociation is not likely to occur at the corner sites, due to the high barrier height. The computed sticking probabilities are in good agreement with experiment.$^{1,8}$
5.8 References


BIBLIOGRAPHY


2015, 119 (50), 12434–12441.


(131) Zhao, Z.; Chiu, C.-C.; Gong, J. Chem. Sci. 2015, 6 (8), 4403–4425.

(132) Kleis, J.; Jones, G.; Abild-Pedersen, F.; Tripkovic, V.; Bligaard, T.; Rossmeisl, J.


